Beer

ULLMANN'S

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1. Introduction

Beer is a beverage containing alcohol, extract, and carbon dioxide. Beer is prepared from barley malt, raw hops or other hop products, brewing water, and top- or bottom-fermenting yeast. The alcohol must be produced exclusively from these ingredients, which are converted to fermentable products during the brewing process. Barley malt may be combined with wheat malt, unmalted

cereal adjuncts (raw grain), and other extractcontaining materials. Legal regulations concerning raw materials and additives as well as rules for listing these vary from one country to another.

To obtain barley malt, the grain is germinated under controlled conditions of moisture content, germination temperature, ratio of oxygen to carbon dioxide in the germinating grain, and germinating time. *Green malt* is formed once a certain increase in enzyme activity and partial

degradation of the starchy endosperm have taken place; this latter process is called *modification*. Green malt is then processed into kiln or brewing malt by drying. This malt is subsequently milled (ground) and mixed with brewing water. During the subsequent procedure, called *mashing*, high molecular mass components of malt are degraded by enzymes at specific well-defined temperatures (rest periods). The suspension is filtered to separate the liquid, called *wort*, from the spent grains. This process is called *lautering*. The wort is subsequently boiled with the addition of hops; this causes a coagulation of constituents, which are then called hot trub or break. They are separated together with the solids from the hops (hot trub removal). The clarified wort is subsequently cooled to the pitching temperature required by the fermentation method and the yeast strain used. The fermentation process is initiated by *pitching*: this consists of saturating the cold wort with air and adding cultured yeast. The fermentable low molecular mass components of the wort are converted to ethanol and numerous aroma compounds (fermentation byproducts) according to the metabolism of the yeast strain. After maturing to taste and enriching with carbon dioxide produced by fermentation, the beer is filtered to clearness and bottled.

The extract of original wort (original extract; original gravity) is defined as the mass fraction of nonvolatile, dissolved extract substances in the unfermented, cold pitching wort. During fermentation most of these substances are metabolized by the yeast, and the content of extract continually decreases. The extract of original wort can, however, be determined in samples taken during fermentation and in the finished beer, provided that the alcohol concentration and the real extract (extract contained in the de-alcoholized beer) are both known.

The *degree of attenuation* is defined as the ratio of fermented extract to original extract, expressed as a percentage. The *attenuation limit* indicates the maximum amount of extract that the yeast will ferment.

Furthermore, a distinction is made between top- and bottom-fermenting types of beer. *Top-fermenting yeast* rises to the surface at the end of the main fermentation process, whereas *bottom-fermenting yeast* settles at the bottom. The two yeast types differ morphologically, in their enzyme composition, and in their physiological

behavior. The nomenclature of beer types is determined by their general production method (see Chap. Production Technology). Typical beer designations have developed from the natural chemical composition of the water in various regions, e.g., Pilsener, Munich, Dortmunder.

In Germany, teaching and research in the area of brewing is concentrated at the technical universities of Berlin and Munich-Weihenstephan. The universities of other European countries and of Japan also have formidable research capacities. Furthermore, in numerous countries research facilities are operated jointly with the brewing industry. In addition, the laboratories of the large brewing companies have contributed greatly to current knowledge. Research results are discussed at scientific meetings in Europe (European Brewery Convention, EBC) and at international meetings in the United States, South America, Australia, and Japan.

History. The word beer comes from the Latin word "bibere" (to drink), which is the origin of the Old English word "beor" (the brewed), akin to the Old High German word "bior", from which also the French word "bière", the Italian "birra", the East European "pivo", and the Spanish "cerveza" developed.

The roots of beer production, however, go back much farther to the first agrarian societies, the Sumerers. They used a variety of grain called emmer (*Triticum dicoccum*), which was dehusked and baked to give flat bread. The flat breads were soaked in water and then allowed to ferment spontaneously through the action of wild yeasts. The Babylonians developed the art of brewing further and distinguished between twenty different types of beer, in which the emmer and barley content as well as the strength of the beer were closely regulated. The "Codex Hammurabi" contained regulations regarding the quality of beer and described strict punishment for beer adulterators.

The Egyptians further refined the art of beer brewing and the legal requirements. They made the grain germinate and eliminated the soaked pieces of bread by sieving.

The Jews, Greeks, Romans, and Germanic peoples all knew beer, but partly preferred wine as a drink. From the seventh century, malting and brewing processes were researched with great experimental zeal, mainly in German

monasteries. In the following centuries, brewing and dispensing rights were loaned out to several monasteries. It was also the monks who first used hops as a flavoring agent. From the fourteenth century, hops were generally accepted as an additive; earlier, tree bark, bitter herbs, and berries were added to the brew.

Until the sixteenth century, only the spontaneous top fermentation, which occurs at higher temperature, was known; later, bottom fermentation was discovered.

War changed drinking habits because of the destruction of cultural values. Bavaria, for instance, became a beer country only after the Thirty Years' War, when its vineyards were destroyed.

Beer as it is known today was only made possible through numerous inventions in technology. Hot-air kilns, steam engines, refrigerating machines, and filtration equipment enabled brewers to work throughout the year. Increasingly, more precise control of the brewing process also became possible. The most significant improvement in quality was finally accomplished after the invention of the microscope: yeasts were found to cause the alcoholic fermentation. At the end of the nineteenth century, yeasts were cultivated and introduced into the brewery as pure strains.

Reinheitsgebot. Laws that regulate the production of beer have always been regarded as consumer-protecting regulations. One of these statutory regulations was laid down by the Bavarian dukes Wilhelm IV and Ludwig X at the State Parliament at Ingolstadt on April 23, 1516; the law was accepted and is known today as the *Reinheitsgebot* (Purity Law). It requires that only barley (barley malt), hops, and water are to be used for the production of beer; yeast, as the organism responsible for fermentation, was mentioned for the first time in 1551. Germany, Greece, and Switzerland brew according to this very strict law, the oldest in the world that pertains to food processing.

Other sources of extract and numerous additives and brewing aids are permitted in countries elsewhere. Because brewing technology does not require additives and chemicals for the production of beer of a consistently high quality, the Reinheitsgebot brewers insist on the maintenance of the Reinheitsgebot.

2. Raw Materials

2.1. Starch-Containing Raw Materials

For further information, see also (\rightarrow Cereals and \rightarrow Starch).

2.1.1. Malting Barley

The main production areas of barley are the mild climate zones in the northern hemisphere with centers in Europe and Fore Asia [21, 22].

Barley belongs to the family of grasses (Gramineae) and is found in various forms. First, a distinction is made between spring barley (spring sowing) and winter barley (late fall sowing), and second, between two-row and multiple-row barleys, according to the number of blossoms on the stalk. Multiple-row barleys produce malts richer in husks, protein, and enzymes, which may prove advantageous when using unmalted grain adjuncts. Two-row barley is divided into two main groups: straight barley, and "nodding" barley, whose ear hangs down during maturation. Tworow spring barley (Hordeum distichum nutans) has the best malting and brewing properties; the most important varieties of spring barley are Prestige, Scarlett, Barke, and Vanessa in Europe; Metcalfe, Harrington, and Robust in North America; Alfa, Musa, and Embrapa in South America; and Schooner, Gairdner, Arapiles, and Grimmet in Australia. The advantages of barley over other grains that could be used for malting are the easier regulation and control of the germination process, the superior taste of beer made with barley, and the brewing technology available. Barley grows best in a humid climate and on soils with moderate contents of nutrients. The husks produce a filter bed for lautering, and the enzyme complement is advantageous for bringing about the desired modification. A similar uniform development of kernels as in two-row spring barley can only be achieved in the newly bred two-row winter barley varieties. Mixtures of spring and winter barleys cause technological difficulties in the malting process. Because the developmental rhythms of the two types of barley are different, the germination process occurs unevenly when processing mixed charges. These problems may be overcome by using separate malting processes, but processing difficulties can

be expected in the brewery in connection with lautering, fermentation, and the filterability of the beer; impaired beer stability can also be expected.

Quality Requirements. Minimum specifications are laid down in the EC quality standard. Moreover, maltsters place further requirements on their raw material:

Germinative ability	> 96 %
Screening:	> 90 % > 2.5 mm
Raw protein content	< 11.5 %
Extract	> 80 %
Attenuation limit	> 80 %

Smell, color, gloss, and husk fineness are checked by manual appraisal. Further mechanical, chemical, and physiological inspection methods are listed in [19, 20].

The most important malting attribute of barley lies in its *germinative vitality*, which is defined as the percentage of kernels that initiate germination in the very beginning of the malting process. Freshly harvested barley must pass through a post-maturation period. This dormancy may be shortened by physical or chemical methods.

The germinative energy is a measure of germination maturity: it indicates how many grains have actually germinated after three days under conditions that are similar to those used in practice. A further indicator of maltability is the sensitivity of the barley to an overexposure to water during steeping (water sensitivity); the importance of this criterion has declined following the application of extended air rest periods during steeping.

The standardization of pilot-scale malting methods has become an indispensable aid for the assessment of barley and optimization of malting technology parameters; furthermore these methods provide reliable criteria in the selection of newly bred barley varieties for planting. Directions for the cultivation, storage, and physiological preservation of brewing barley, as well as detailed descriptions of its morphology and breeding, may be found in the literature [1, 2, 8].

Chemical Composition. The chemical composition of brewing barley versus a pale malt is shown in Table 1. The moisture content, which is especially relevant to the storage quality of freshly harvested barley, may range from 12 to

Table 1. The chemical composition of brewing barley and malt (mass fractions in %)

Malting barley		Malt	
As is	Dry matter	As is	Dry matter
12 – 14		4 – 5	
55 - 57	64 - 66	56 - 58	58 - 60
12 - 14	14 - 16	16 - 18	17 – 19
9 - 10.5	10 - 12	8.5 - 10	9 – 11
4	4.5	5	5.2
2.5	2.8	2.4	2.5
2	2.3	2	2.1
	As is 12 - 14 55 - 57 12 - 14 9 - 10.5 4 2.5	As is Dry matter 12 - 14 55 - 57 64 - 66 12 - 14 14 - 16 9 - 10.5 10 - 12 4 4.5 2.5 2.8	As is Dry matter 12 - 14

20 %; 14 to 16 % is normal. The α -glucans (amylose and amylopectin of the starch) are the most important carbohydrates in barley. Other carbohydrate components include \(\beta\)-glucans (cellulose, hemicellulose, gums), pentosans, as well as minute portions of low molecular mass sugars. Proteins are especially important for maltability, yeast nutrition, foam, taste, and the stability of the beer. Lipids are only partially used up during malting, the remainder staying mainly in the spent grains. Other important components are phosphates (ca. 0.3 %), minerals (2.5 – 3.5 %), vitamins (ca. 0.5×10^{-3} %), and phenolic substances (ca. 0.2 %). The enzymes of barley and of malt, as well as their effects during mashing, are shown in Table 3.

2.1.2. Malting Wheat

For some top-fermenting beers (see Section 3.4) wheat malt is added in order to achieve a special flavor quality. Brewing wheat should contain 11 % protein. Its extract yield is in the range of 83 to 87 %.

2.1.3. Unmalted Grains

Economic reasons or insufficient supplies of brewing barley or brewing malt have resulted in obtaining part of the starch by the addition of other, unmalted grain types. These *adjuncts* may account for up to 30 % of the grist in Europe, and up to 50 % in the USA. The processing of adjuncts requires the use of protein-rich barley

malts with very high enzyme contents. In many countries these adjuncts are defined as replacement material for brewing malt, which add mostly carbohydrates to the wort; their use must be legally permitted.

Unmalted barley gives lower yields and sometimes insufficient conversion in the brewery. Beers produced in this manner contain less nitrogen, have a lover attenuation limit, and display better head retention, but filtration is more difficult.

Partially unmalted wheat is added to the mash. Its composition is similar to that of barley. With a moisture content of 15 %, wheat contains 65 % starch and other carbohydrates, 12 - 14 % protein, and 1.7 % fat.

Rice is processed as broken rice. This byproduct of table rice production must be pure white. The moisture content is 12 - 13 %; other concentrations (expressed on a dry basis) are: extract 93 - 95 %, fat 0.5 - 0.7 %, protein 8 - 9 %. Rice starch gelatinizes at 65 - 70 °C, sometimes only at about 80 °C. Co-processing of rice generally results in very light and dry beers.

Corn (maize) is processed as corn starch, flakes, or larger corn grits, and is popular because extract yields range from 87 to 91 % after removal of the oil-rich embryo. Moisture content should not exceed 12 – 13 %; protein content (dry basis) is in the range of 8.5 – 9 %; a residual fat content of less than 1 % in the grits is not harmful to head retention. Addition of corn results in sweetish, full-bodied beers. Commercial corn starch is practically free from protein and fat. The final yield is about 103 %, because of the addition of water during enzymatic hydrolysis.

Sorghum, as a malt additive, has only regional importance in Africa.

2.1.4. Other Sources of Extract

Other sources of extract are processed *starch preparations* and *carbohydrates* in fermentable low molecular mass form. Besides starch flour itself, syrups frequently are used, which are manufactured from grain or starch flour by enzymatic or acidic hydrolysis. All syrups have an extract content of about 80 %, while their fermentability is in the range of 40 - 78 %. They are added to the wort kettle. The concentration of the wort may be increased in this manner to

15 - 18 % without affecting the further process development adversely (see Section 3.5.4).

Sugar is added to the wort kettle shortly before the end of boiling in order to raise the proportion of fermentable extract. Amounts up to 15 % yield very soft beers with a wine-like flavor. For malt beers and nutrient beers, sugar is added to the filtered beer in order to achieve the sweetness character and extract of original wort. Sugar is added as sucrose, as invert sugar, or as glucose. For nutrient beers, caramelized brewing sugar may be added. The extract content of the sugar solution is between 65 and 85 %, depending on consistency and quality.

2.2. Hops and Hop Products

Hops added to the wort are an indispensable ingredient for many reasons. They impart a bitter taste to the beer, a specific aroma, and promote clarification. Furthermore, they are considered to have foam-improving qualities. Hops also are believed to act as an antiseptic in beer. The hop plant, Humulus lupulus, is a hardy, dioecious, climbing plant, and belongs to the hemp family. Only female vines are planted in hop farms; propagation is carried out by perpetuating vegetative clones. Hop cultivation requires special climatic conditions (hops grow between the 35th and 55th degree of latitude) and a soil varying in texture from sandy to muddy. The hop cones are of primary interest to the brewer. They are clusters of blossoms on the female plant that grow despite the lack of pollination. Hops are picked in August or September. Yellowishgreen, sticky, cup-like glands (lupulin glands) are located on the inner sides of the inner and outer bracteoles; they contain the aromatic and bitter substances. Hops are classified according to their origin and type; for similar varieties, the influence of origin dominates. The cultivated types have been obtained by separation according to shape [7].

- Hops in Europe:
 - Aroma hops: Hallertauer Tradition, Hersbrucker, Perle, Saazer, Spalter, Select, Tardif de Bourgogne, Tettnanger, Saphir, Smaragd and Opal
 - Bitter hops: Brewer's Gold, Northern Brewer, Merkur

Table 2. Chemical composition of hops (wt %)

	As is	Dry matter
Water	9 – 12	
α-Acids	2 - 15	2.2 - 11.5
β-Acids	2 - 10	2.2 - 11.2
Hop oils	0.5 - 2.5	0.6 - 2.8
Non-nitrogen extract compounds	4 - 9	4.5 - 10
Protein	15 - 21	13 - 22
Fiber	10 - 17	11 - 19
Polyphenols	3 – 8	4.5 - 16
Minerals	7 - 11	8 - 12
Lipids and waxes	up to 3	up to 3.4
Fatty acids	0.05 - 0.2	0.06 - 0.22

- High-α varieties: Magnum, Taurus, Herkules, Nugget, Wye Target, Yeoman
- Hops in America:
 - Traditional varieties: Fuggle, Cluster
 - Aroma hops: Perle, Willamette, Cascade
 - Bitter hops: Galena, Nugget, Chinook

According to the certification policy within the EC hop market law, since 1978 producers of hops are required to designate varieties and to indicate origin. The most important hop-producing countries, together with their quantities harvested, are listed in Chapter 6. Hops can be judged on the basis of manual classification (appearance, color, pest infestation), whereas brewing values can only be determined by chemical analysis. Table 2 lists the most important components found in hops. The bitter acids (α - and β -acids) and the aroma substances (hop oils) are of great importance both from the viewpoint of brewing technology and for the taste of the beer.

2.2.1. Bitter Acids

The bitter constituents of hops consist of α -acids (humulones), β -acids (lupulones) and the oxidation products of bitter acids, namely, the soft und hard resins. The brewing value of the individual fractions varies and depends on their solubility in beer and wort and on their bitterness potential. The α -acids are the most important of these bitter components because of their high bitterness potential.

The soft resins, which result from the oxidation and polymerization of α -acids and β -acids,

produce a lower bitterness level, roughly 33 % of the intensity produced by humulones. Hard resins are even less bitter, accounting for only 12 % of the level produced by humulones. The β -acids are not bitter at all. The solubility of the α -acids is very dependent on the pH value. At the pH of the wort, these substances will dissolve to only a limited degree. In beer itself, α -acids are found only in very limited quantities, because they are isomerized during the boiling process, whereas the remaining acids are removed during fermentation as part of the foam cover. The α -acids isomerize to iso- α -acids, e.g., *cis*- and *trans*-isohumulone. All α -acids and their isomerisation products have approximately the same bitterness.

The isomerisation products are significantly more soluble than the original α -acids, and are extremely stable at the pH value of beer. During the isomerisation process the following α -acid derivatives also are formed: *cis*- and *trans*-humulones, abeoisohumulones (oxidized isohumulones), antiisohumulones, spiroisohumulones, humulinic acids, and their various homologues.

The lupulones (β -acids) are insoluble at the normal pH value of the wort. They do not isomerize during boiling, and are largely removed with the spent hops and the trub without being utilized. Lupulone differs from humulone by a side chain on C_3 of the six-membered ring and gives rise to the same homologues as humulone. During storage, lupulones are oxidized to β -soft resins, which are soluble in the wort and in beer and impart a pleasant bitterness to the latter.

2.2.2. Aroma Substances

The volatile and nonvolatile aromatic components of hops also determine hop quality. The aromatic content of hops is influenced not only by the variety but also very much by both the drying and storing conditions as well as by processing.

The relative amounts of the almost insoluble sesquiterpenes, such as humulenes, farnesene, and β -caryophyllene, can be used to distinguish between the different varieties. The mono- and sesquiterpenes become more soluble by oxidation, i.e., as epoxides; during fermentation they are partly converted by the yeast to the corresponding sesquiterpene alcohols and can therefore contribute to the aroma of the beer. Linalool was found to correlate with the hop aroma of a beer.

Volatile compounds (aldehydes, ketones, alcohols, and esters) are typically produced during aging of the hops by side-chain breakdown of the bitter acids. Most of these, however, evaporate during wort boiling.

2.2.3. Other Components

Hops contain a number of phenolic components and derivatives of low molecular mass, such as phenolic acids (e.g., p-hydroxycoumaric acid, gallic acid, protocatechinic acid, caffeic acid), coloring components (catechins, flavones, and anthocyanidines), and polycondensed substances with strong tanning properties, which can originate from procyanidines. During wort boiling, these substances and the tanning substances from the malt adsorb onto constituents of the hot trub; they are subsequently eliminated at the wort cooling stage. Together with the proteins, the tanning substances may cause nonbiological haze in filtered beer. The polyphenols have reducing power, and they contribute to the flavor stability of the beer. Xanthohumol, a prenyl flavanoid, shows positive physiological properties, for instance, cancer-preventive activity.

2.2.4. Processing of Hops and Hop Products

After harvesting, the hop cones must be dried from a moisture content of 75-80% to a level of 10-12% at low temperature with strong air circulation. Afterwards they are packed into bales or compressed into ballots. Hops should be stored in cool, dry, dark areas at about 0 °C to preserve their quality. Vacuum packing followed by impregnation with an inert gas is necessary if prolonged storage of the hop product is anticipated. High temperature, oxygen, moisture, and light will cause changes in the oil fraction of hops; bitter acids become resins and lose part of their bitterness potential, and polyphenols transform into higher condensed products.

Various hop products find acceptance nowadays in the brewing industry because of their improved storage capacity, longer preservation of quality, and simpler handling in the brewery. Regulations control the use of these products in various countries.

Hop Powders. By drying hops to a moisture content of 6-8 % (depending on the variety) and grinding, a powder is obtained. This usually is pelleted and packed under vacuum into foil bags, which are then filled with an inert gas. Compared with natural hops, these powders show few variations in analytical data. Because they present greater surface area, their components are more readily soluble. Therefore, their use offers savings of 10-15 % in terms of α-acids. Pellets also occupy a considerably smaller volume by comparison with raw hops.

Enriched Hop Powders. After drying, hops are deep-frozen to about -30 °C and ground. Lupulin is separated from the cones and from other nonessential parts of the leaves by sieving at the same low temperature. This treatment also reduces the polyphenol concentration in the resulting hops, depending on the extent of removal of nonessential components. Moreover, nitrate and residues of plant protection agents are reduced. The powder, which usually is pelleted, offers savings in terms of α -acids of about 15 % when compared with natural hops.

Hop Extracts. Solvents used for the extraction of hops include alcohols, ethers, and supercritical (or fluid) carbon dioxide. For the production of the extract the hops are ground, the valuable components are dissolved, and the solution is separated from the solid substances. In all production methods, the solvent is finally evaporated at about 40 °C and reclaimed. The extracts have a consistency like honey and are packed in cans.

Carbon dioxide and ethanol dissolve the α -acids quantitatively. During extraction with 90 % ethanol, isomerisation of 10 % of the α -acids takes place. Carbon dioxide dissolves only about one-third of the hard resins under the prevailing extraction conditions for the removal of bitter substances and aroma contributors.

The aroma-contributing components are quantitatively dissolved; losses caused by evaporation of the solvent are minimal in the case of carbon dioxide and more substantial with ethanol. In the process employing supercritical carbon dioxide, the extraction conditions are controlled by pressure and temperature. There may be other parameters, as yet unknown, which

control the composition of the resulting extract of aroma-contributing substances and resins.

Carbon dioxide does not dissolve tannins and hop proteins. These may be obtained during a secondary extraction step by the use of hot water. During one-step procedures using methanol or ethanol as solvent, a small proportion of tannins also is extracted, which can easily be removed by centrifugation.

Ethanol extract is also a pure resin extract, although a small amount of polyphenols is dissolved during extraction. The polyphenols can, if desired, be removed by centrifugation. The composition of ethanol extract is: total resins 92 %, α -acids 42 %, iso- α -acids 1 %, but also the full amount of soft and hard resins.

Water extracts, which were used in former times to "standardize" the hop extract to a certain content of α -acids, are no longer of interest. They contain polyphenols, nitrogenous material and minerals, which might be of interest to the brewer, but also nitrates, residues of plant protection agents, and environmental contaminants. Thus, water extract is no longer in use. The savings in bitter substances when using extracts are 15 – 20 % in terms of the amount of the α -acid.

Hop-Extract Powder. Extract powder can be obtained by blending super extract with silica gel approved for the stabilization of wort or beer. The large specific surface of the silica gel causes rapid isomerisation of the α -acid. The savings in terms of α -acids when compared with raw hops amount to nearly 25 %.

When mixing extract and powder to obtain a free-flowing hop extract powder, α -acid savings are about the same as with normal hop extracts. Commercial hop pellets are available also in combination with a beer-stabilizing agent such as bentonite. In addition this product offers better utilization of the bitter substances and is especially effective when hops are added late during wort boiling.

Isomerized hop extracts are produced from CO_2 extract in three product forms. *Isomerized kettle extract* (IKE) is produced by mixing and heating the pure resin extract with magnesium oxide (3 - 6%) to give magnesium salts of iso- α -acids. After removal of the magnesium by means of a strong acid, iso- α -acids are present in their free form and used like normal resin

extract in the boil. *Potassium isomerized kettle extract* (PIKE) is obtained by heating resin extract with aqueous potassium carbonate/hydroxide solution, which converts the iso- α -acids to potassium salts. The third product consists of reduced iso- α -acids, rho-iso- α -acids, and other components of the resin extract such as β -acids and hop oils (LIKE). These iso-extracts are added to the boiling wort; they give a yield of about 73 % because of losses on the trub and on the yeast surface.

In more widespread use are the downstream or post fermentation bittering products (PFB): they are added during transfer from maturation to coldstorage tank or later on the way to the beer filter. Hence the losses are very low (5 - 10 %), and they offer the opportunity to produce various kinds of beer from a single brew. Generally, the "normal" iso-extract is added, or especially developed reduced iso-α-extract. Hydrogenation of the side chain of its five-membered ring avoids the formation of 3-methyl-2-buten-1-thiol (MBT), which causes the lightstruck flavor of beer in colorless and green glass bottles. The reduced rho-dihydroiso- α -extracts are produced by using a solution of borohydride or by hydrogen gas in the presence of a catalyst (tetrahydro-iso-α-extract) or by a combination of both procedures (hexahydro-iso-α-extract). The perceived bitter taste of these extracts is different to normal iso- α -extracts, e.g., rho extract only 70 %, tetra extract 100 – 170 %, hexa extract 130 %. The last two, in particular "tetra" already improve beer foam if as little as 3 - 5 ppm are added to the beer.

Light-stable beers must be produced with reduced extracts exclusively (e.g., LIKE already in the kettle). To prevent infections, part of the iso-extract is added during wort boiling and the final bitterness is built up late in the process.

To impart a hoppy aroma and taste, hop oil extracts can be used, mostly later in the process.

2.3. Brewing Water

Water is feedstock number one and the basis for a successful brewing process [23]. Different compositions of water were the reason why different beer types developed in different regions.

Natural water always comes as a highly diluted mineral salt solution; its chemical composition and concentration usually are determined by the

geology of the specific region of origin. In addition, impurities, organic substances, and organisms may subsequently enter the water. Because of their low concentration, the salts are almost completely dissociated into ions, which indirectly influence the quality of the beer.

Today almost any water can be made suitable for brewing but at a corresponding cost. Expensive water treatment is unavoidable if certain ions are present in such high concentrations as to be detrimental to the beer, e.g., an excessive amount of sodium chloride or more than 30 mg/L of nitrate ions. Nitrate is reduced during fermentation to nitrite, which is toxic to yeasts.

2.3.1. Salts

The total solids content of natural water usually is 50 - 2000 mg/L, with an average of ca. 500 mg/L. The following ions are predominantly found in water:

$$Cations: H^+, Na^+, K^+, NH^{4+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}$$

Anions :
$$OH^-, CI^-, HCO_3^-, NO_3^-, NO_2^-, CO_3^{2-}, SO_4^{2-}, SiO_3^{2-}, PO_4^{3-}$$

Calcium and magnesium salts are most commonly found in natural waters. The sum of these two cations determines the total hardness of the water, which is expressed in milliequivalents per liter (mval/L). Carbonate, hydrogencarbonate (HCO₃⁻), and free carbon dioxide must be controlled carefully because of the corrosive nature of free carbon dioxide. The non-carbonate hardness is accounted for by salts of acids other than carbonic, e.g., sulfates. These salts remain dissolved during boiling.

Effects During Mashing. At the concentrations of mineral salts normally found in water, interactions with soluble components of the malt as well as various effects on the enzymes of the malt and on the ingredients derived from the hops are of practical importance, especially with regard to the net effect on the solubility of the α -acids. It is essential to observe how different ions present in the water, together with the malt ingredients, influence the pH values of the mash, the wort, and the beer. The phosphates of sodium, calcium, and magnesium are most effective in

this regard. Further reactants include the potassium and calcium salts of organic acids such as lactic, malic, and succinic. The various hydrogencarbonates influence the acidity to varying extents, because the solubilities of the corresponding secondary or tertiary phosphates are different. Accordingly, the effect of magnesium hydrogencarbonate is greater than that of calcium hydrogencarbonate, because the secondary magnesium phosphate will remain in solution. The effect of sodium hydrogencarbonate is even more marked, because strongly alkaline tertiary sodium phosphate is formed, which remains in solution together with the secondary sodium phosphate. In addition, precipitation of phosphates by calcium and magnesium ions results in decreased buffering capacity of the mash, so that the pH may drop too rapidly during fermentation.

The alkalinity of the wort caused by hydrogencarbonates also affects the solubility behavior of the bitter substances present in hops. On the one hand, when the pH is increased, the solubility is increased, but an unpleasant, harsh bitterness is created in the beer. On the other hand, the ions of the alkaline earth metals can compensate for the increase in pH caused by hydrogencarbonate. The following equation demonstrates this effect:

$$3 \text{ Ca}^{2+} + 4 \text{ HPO}_4^{2-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2 \text{ H}_2 \text{PO}_4^{-}$$

Calcium ions convert the secondary phosphate to the acidic primary phosphate. Magnesium ions are only half as effective by comparison with calcium ions.

Alkalinity. The term alkalinity is used to designate the concentration of the hydrogencarbonate ions in water. The "residual alkalinity" is calculated by subtracting the effect of the acidity-improving alkaline earth ions from the effect of the acidity-destroying hydrogencarbonate ions:

residual alkalinity = total alkalinity

$$-\left(\frac{\text{Ca hardness}}{3.5} + \frac{\text{Mg hardness}}{7}\right)$$

Hardness is given in degrees German hardness (°dH).

The total alkalinity is equal to the hardness linked to the presence of hydrogencarbonate ions. The residual alkalinity indicates the suitability of the brewing water for the various varieties

of beer. The residual alkalinity for pilsener should be below 35 ppm CaCO₃, and 90 – 110 ppm CaCO₃ for pale beer. Decreasing the residual alkalinity by 90 ppm CaCO₃ will lower the mash pH by 0.15 units. Should the residual alkalinity increase substantially, considerable disadvantages can be expected. The brewhouse yield is reduced by 2 % when the residual alkalinity is in the range of 180 – 210 ppm CaCO₃. Similarly, high values for residual alkalinity resulting in a mash pH of over 5.8 will reduce the effectiveness of most of the hydrolytic enzymes. A high pH value causes molecular dissolution of the α -acids, which will impair the bitter flavor of the beer. The release of polyphenols from the husks of barley malt will occur with greater ease in this pH range, and is acceptable only in the case of dark beer.

2.3.2. Brewing-Water Treatment

Water used for brewing should correspond in quality to drinking water; it should be clear, colorless, and neutral in taste and smell. It should not contain heavy metals, especially iron and manganese, and should not be corrosive. Natural waters originate from many different geological formations and therefore very rarely conform to the quality required for brewing water. For this reason treatment is required before water from such sources can be used for brewing. The actual extent of water conditioning is governed by the concentrations of anions, the dissolved organic substances, and the presence of aggressive gases in the untreated water. Processing of brewing water also depends on the specific needs of the brewer and on the requirements of the particular beer. Selection of a treatment method also is influenced by the prevailing laws.

Attention is directed to both the carbonate hardness and to the ratio of carbonate to non-carbonate hardness, which should be around 1 to 2-2.5. Bearing profitability in mind, the following treatment methods can be applied:

Heat Precipitation. Carbonates can be precipitated by boiling. However, this method is not economical.

Decarbonation. The simplest procedure for the precipitation of carbonates is to add milk of

lime. The following components can be removed by Ca(OH)₂: free CO₂, Ca(HCO₃)₂, Mg(HCO₃)₂, and MgCO₃. For the last-named, however, a pH of 10.5 – 11 is required. If the non-carbonate hardness in the raw water is higher than the magnesium hardness, quick or pressure decarbonation may be used. In this case, water and milk of lime are intensively mixed in a reaction vessel, whereby calcium carbonate precipitates as a coarse product that sediments well.

Variations in magnesium hardness are more problematic. If the magnesium hardness exceeds the non-carbonate hardness, slimy magnesium hydroxide will partly precipitate and clog the gravel filter bed; it can also contaminate the brewing water. To overcome this problem, a two-step precipitation – decarbonation process is used. In the first step, the calculated amount of milk of lime that is needed for decarbonation and for removal of magnesium is added to a partial stream of the raw water (two-thirds) in a superliming reactor, in which both calcium carbonate and magnesium hydroxide are precipitated. This alkaline water subsequently reacts with the remaining one-third of the raw-water stream in a refining reactor. In this reactor, the excess lime is used to precipitate calcium carbonate whereas the magnesium carbonate of this 30 - 40 %stream remains in solution. The total water is finally collected in a storage tank after filtration through a gravel bed.

In order to control variations in the composition of raw water, hydrogen ion exchange facilities can be installed at the end. This equipment will automatically be activated whenever the pH rises above a predetermined value. The procedure ensures extensive removal of the magnesium hardness. The brewing water thus obtained is very poor in carbonates, and does not contain an excess of free carbon dioxide after irrigation.

Ion Exchange. (\rightarrow Ion Exchangers). Brewing water can be readily deionized by using ion-exchange resins, which require little space and facilitate quicker throughput. The availability of food-grade ion-exchange resins enables raw water to be processed to give water of any desired composition.

Cation exchangers can be either weakly or strongly acidic, depending on the anticipated load. Weakly acidic exchangers remove only the hydrogenearbonates (of Ca²⁺ and Mg²⁺) from

the raw water. During this process a large amount of free, corrosive CO_2 is liberated, which must be removed by blowing a countercurrent of air through the water. The remaining CO_2 reacts with milk of lime or marble to form $Ca(HCO_3)_2$; in this way slight hardening is achieved. Alternatively, the deionized water can be blended with raw water.

Strongly acidic ion exchangers operate in a similar manner. All cations are removed from the raw water, even those of the strong acids, and are replaced by hydrogen ions. These exchangers are especially effective with hardness caused by magnesium. The free mineral acids that are thus formed are neutralized with saturated milk of lime.

Anion exchangers can be used to remove SO_4^{2-} , Cl^- , and NO_3^- ions; this will decrease non-carbonate hardness. Even though total deionization is not desirable in the production of brewing water, complete ion exchange enables the brewer to prepare brewing water from sources with widely differing compositions.

Electroosmosis. For total deionization by electroosmosis, investment and operating costs are much higher than in the treatment procedures described above. In addition, this procedure may be applied only if combined with other deionization methods. In a continuous-current field the salts in the water migrate towards the electrodes, which are separated by membranes. The water trapped between the membranes is appreciably lower in its content and can be run off.

Reverse Osmosis. Ions, molecules, and other small particles can also be removed from water by reverse osmosis. Additionally, table waters may be obtained from the resulting concentrate by proper sterilizing and carbonating procedures, provided that the ionic composition is appropriate.

Acid Addition. The addition of mineral acids such as hydrochloric, sulfuric, or phosphoric acid changes the carbonate hardness into noncarbonate hardness, but the total hardness remains unaltered.

Other Processes. Malodorous or bad-tasting substances can be removed by installing an activated-carbon filter upstream of the deionization equipment. Suspended matter is removed

with flocculants and gravel bed filters, so as to avoid clogging of the downstream equipment.

Furthermore, such mineral salts as are found in natural water may be added to brewing water. Acceptable food-grade salts are CaCO₃, MgCO₃, CaCl₂, CaSO₄, and NaCl.

2.4. Beer Yeasts

Brewery yeasts belong to the family of Saccharomycetaceae and the genus *Saccharomyces*. They have the main advantage that their cells propagate by budding. For the production of bottom-fermenting beers, *Saccharomyces carlsbergensis* are used, and for top-fermenting beers, *Saccharomyces cerevisiae*.

After the malt enzymes have been destroyed during wort boiling, the yeast provides the original wort with its enzyme system. Wort is not an ideal nutrient medium for yeast. In order to metabolize actively, the yeast must synthesize those substances it needs according to the wort composition. Depending on the syntheses required, the amounts of the metabolic products that are found in the fermenting substrate will differ. References to taxonomic and technological structure, morphological characteristics, chemical composition, propagation, metabolism, and yeast enzymes can be found under the appropriate keywords (\rightarrow Ethanol; \rightarrow Yeasts) and [9–11].

The pitching yeast should be selected as carefully as the other raw materials. Furthermore, its introduction into production, its crop after fermentation, and its further handling should be managed with great care. Short-term storage of yeast and aeration before pitching retain fermenting power and keep the yeast in good physiological condition. If an infection with organisms detrimental to beer occurs, the yeast must be removed quickly from the production process.

2.5. Auxiliary Materials and Brewing Aids

This group comprises all those chemicals that come into contact with the raw materials, the wort, and the beer; they are not essential for the production of beer, and are used for the correction of deficiencies. No general directions exist in

the various countries where beer is brewed regarding the use of these materials.

Malting Auxiliaries. Various chemicals may be added to the steeping water. Hydrogen peroxide decreases the sensitivity of barley to water, and reduces the danger of mold formation. Alkaline additives such as Ca(OH)₂ or NaOH will increase the leaching out of husk tannins.

Gibberellic acid is an effective growth agent; it stimulates enzyme formation and accelerates germination. The amount of growth factor that is added to the final steeping water should not exceed 0.05 - 0.1 mg/kg of barley because of the danger of overmodification and additional coloration.

To avoid excessive losses of extract during germination, it is possible to add growth inhibitors during the later stage of germination. For this purpose potassium bromate may be used.

Sprinkling the green malt towards the end of the germination phase with an aqueous glucose solution will increase the amount of extract to a greater extent than would be expected from the amount of sugar used.

The addition of sulfur dioxide to the air flow during kilning will result in a lighter color and a higher extract yield by lowering the pH. Furthermore a heat-stable endo- β -glucanase can be added to improve cytolysis. It also blocks the formation of nitrosamines during drying and kilning.

Other aids to water treatment are described in Section 2.3.2.

Brewhouse Auxiliaries. The first concern of the brewer is to eliminate differences in quality of the raw materials which have remained through insufficient modification in the malthouse and which could not be compensated for during mashing. These cytolytic, proteolytic, and amylolytic deficiencies, or the use of an excessively high proportion of adjuncts, are compensated in the mash by adding enzyme preparations that originate from sources other than malt. The hard, raw aftertaste that frequently occurs in such beers can be reduced by adding mineral acid (HCl, H₂SO₄, H₃PO₄) or concentrated lactic acid to the mash.

During wort boiling, protein-precipitating substances such as tannin, carrageenan (Irish moss), or protein-stabilizing substances may be added in order to improve the clarification process and stability of the end product. The addition of cross-linked polyvinylpyrrolidone (polyvinylpolypyrrolidone; PVPP) reduces the polyphenol concentration. Synthetic additives based on polyester result in compact separation of the unpleasant, coarse, and bitter-tasting hot trub.

Numerous advantages can be gained by using a lactic acid culture propagated in the brewery (biological acidification). The lactic acid bacteria obtained from malt ferment at 47 °C in 10-20 % unhopped first wort and produce lactic acid (concentration 1.0-2.0 %) within 12-20 h. The culture is added in the brewhouse during mashing or wort boiling to obtain the desired pH value.

Fermentation and Maturation Aids. Deficiencies in yeast nutrients can be counteracted by addition of yeast food, which contains amino acids, minerals, vitamins, and zinc salts, to the substrate in order to achieve a vigorous fermentation. Because all enzymes of the malt are denatured during wort boiling, one may wish to add enzymes with a wide activity spectrum, which may additionally enhance clarification and filtration of the beer in the fermenting room. This becomes necessary if the naturally occurring enzymes achieve insufficient hydrolysis of high molecular mass malt components.

If foam production is impaired by this enzymatic action, which is rather difficult to control, foam stabilizers [alginates, poly(propylene glycol), or polysiloxane] can be added.

After fermentation, bacterial 2-acetolactate decarboxylase may be added to the fermentation substrate, which will transform diacetyl directly to acetoin (see Section 3.3.2). In this way the maturation rate can be increased considerably.

Antifoaming agents based on silicones have come into use in order to reduce the headspace needed during warm fermentation in tall, cylindrical vessels. A small amount (4 – 8 g/hL) of these agents is sufficient to prevent the formation of a fermentation cover. The foam inhibitor is removed completely by kieselguhr filtration, so that the final foam quality of the beer will not be impaired.

Clarification Aids. Before bottling, the beer is filtered through a filter cake. Proven materials for this purpose are kieselguhr (mud-free,

calcined, and screened diatomaceous earth) of various particle size distributions and perlite (ground and calcined glassy rock of volcanic origin).

Activated carbon may be used to correct a mild off-taste; it is usually used in the treatment of rest beers. Shortly before filtration, silica hydro- and xerogels may be added, which selectively affect the high molecular mass nitrogen fraction and also contribute to buildup of the filter cake.

Stability Improvers. The stability of beer is defined as the ability to preserve its characteristics from bottling to consumption. To ensure an adequate biological stability in zones of moderate climate it is sufficient to clarify the beer through kieselguhr and sheet filters, provided that the beer is delivered to the consumer quickly.

Higher demands can only be met either by the use of insoluble substances which act mechanically or adsorptively, or by pasteurizing the bottled beer (with 12 - 14 pasteurization units), or by hot bottling at 68 – 75 °C. However, heat treatment results in early aging of the beer. Oxygen trapped during filling reacts quickly with the beer. As a result a nonbiological haze may be formed sooner or later. This is derived from tannins and from proteins. Tannins can be removed by adsorption onto polyvinylpyrrolidone. Haze-forming protein particles can be removed with silica preparations or bentonite. Proteolytic enzymes such as papain, bromelain, and ficin decompose high molecular mass proteins to nonhazing components.

During the breakdown of proteins, two characteristics, stability and foam, again run counter to each other. Metal ions accelerate haze formation; they can be complexed with ethylenediaminotetraacetic acid (EDTA).

During long-term storage beer becomes vulnerable to other dangers including flavor changes, particularly through oxidation, different climatic and mechanical conditions, and effects due to light. The most effective remedy is low-oxygen bottling; if this is not possible, the beer must be protected against oxidation by the addition of antioxidants such as ascorbic acid, sulfites, and sugar reductones, or by enzymes such as glucose oxidase or catalase. The influence of oxygen during bottling can also be overcome by evacuating the bottles two- or even

threefold, by pressurizing the bottles with fermentation carbon dioxide, and by allowing fobbing. For additional safety the cleaned beer barrels, kegs, or bottles can be treated with peracetic acid or other products based on hydrogen peroxide, iodine-releasing chemicals, or sulfur dioxide. The cleaning and disinfection of food containers are treated under a separate keyword (\rightarrow Cleansing Agents).

3. Production Technology

3.1. Malting

Malting is defined as allowing grain to germinate under well-controlled conditions. The main purposes of malting are the development of enzymes in the grain with simultaneous degradation of high molecular substances in the cell walls (modification), the achievement of a distinctive character by color and aroma compounds, and removal of undesired aroma compounds (i.e. S-methylmethionine and dimethyl sulfoxide). High extract yield and low malting loss are economic goals. A schematic of malt production is shown in Figure 1.

After thorough cleaning in various separators and grading machines, the brewing barley is dried to a moisture content of ca. 12 %, which allows storage without damage to the embryo. If proper drying equipment is not available, cooling of the barley can help prevent spoilage to a certain extent. Before malting is actually started periodic aeration is necessary to remove the carbon dioxide emanating from the grains, so as to keep the germinating facilities healthy and to maintain germinative ability.

3.1.1. Steeping

Upon addition of water germination of the grain begins. No particular requirements are placed on the steeping water during malting, but it should be of potable quality. The uptake of water into the center of the kernels depends on the temperature and the grain size. The grain begins to respire with increasing moisture content. This process requires oxygen, which must be supplied in sufficient amounts during the entire steeping period.

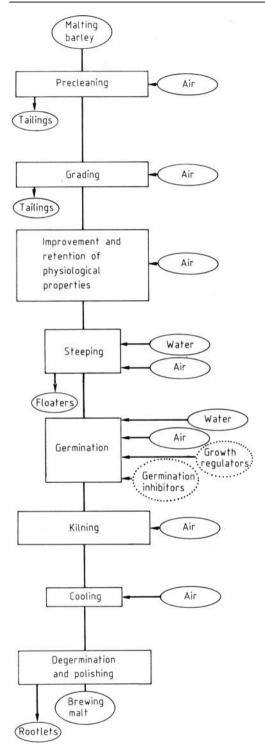


Figure 1. Flow sheet of malt production Additives that are shown in dotted ellipses are not necessary

Steeping Equipment. The round or rectangular steeping tanks with conical bottoms (capacity $2.2 - 2.4 \text{ m}^3$ per ton of barley) must be equipped with a water inlet and outlet, discharge valves, overflow for floaters, a carbon dioxide exhaust vent, and an air inlet for pressure aeration and recirculation. Recirculation pumps and sprayers are optional.

In units of higher capacity, and in particular for the second day of steeping, flat-bottom steeps are used. They are equipped with aeration equipment for climatization, similar to a germination box. Loading and casting is performed with horizontal screws.

Steeping Technology. Rapid moisture uptake and enhanced germination is possible in pneumatic steeping, in which wet steeping periods alternate with extended dry steeping periods (the latter during 50 - 80 % of the total period). First of all, steeping provides a definite moisture content appropriate to the physiological characteristics of the barley. During subsequent dry steeping (16 – 24 h) at a moisture content of 30 % the water sensitivity of the barley declines. After further increasing the moisture content to 38 %, uniform germination of the kernels can be expected within a period of 14 – 20 h. The moisture content is then raised to the final level in the germination box by adequate spraying (Fig. 2).

When the temperature is raised from one wet steeping period to the next, the temperature of the steeping materials is taken into account. Casting of steeped barley at 18 °C permits the use of a germination procedure with decreasing temperature, as shown in Figure 3. Other steeping methods exist based on similar principles: the flushing procedure, the re-steeping procedure, and the water-saving spray steeping.

3.1.2. Germination

Germination is a physiological process during which the embryo develops rootlets and acrospire. During this process, the nutrients stored in the endosperm are partly consumed. The aim of controlled germination is to produce a green malt of a definite composition, but not to allow the development of a new plant.

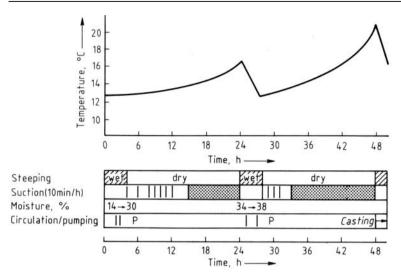


Figure 2. Steeping

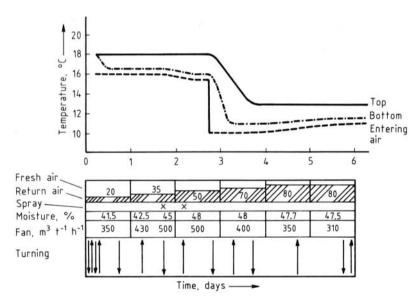


Figure 3. Germination

Germination Conditions. Germination takes place only under appropriate conditions in order to achieve the desired metabolic changes during the time necessary for germination. Parameters are moisture, temperature, ratio of air to carbon dioxide, and time. The moisture content must not decrease during the entire germination period. Temperatures favorable to uniform germination range from 14 to 18 °C.

A sufficient supply of air must ensure both normal respiration and removal of carbon dioxide. Germination will manifest itself first in noticeable changes in the appearance of the kernel. After "chitting" (breakthrough of the rootlet), the rootlet divides into a main root and secondary roots (forking). The acrospire also breaks through the aleurone layer and pericarp, and begins to grow under the husk towards the tip of the kernel.

During malting the development of the germ buds is desirable only to a certain degree.

Besides these manifestations of growth, chemical transformations occur in the endosperm; stored materials are broken down by enzymes and changed into soluble matter. These are either used as an energy supply, or are built into new tissue in the germ buds. The growth factors which develop during germination cause the formation of a number of enzymes in the scutellum and the aleurone layer.

Enzyme Formation. In addition to certain modifications to the substances of the barley, the main purpose of malting is the induction and increase in hydrolytic enzymes. The most important groups of these are: hemicellulases, proteolytic enzymes, amylases, and phosphatases (see Table 3). Of the cytolytic enzymes, which break down the hemicelluloses to low molecular mass materials, the β -glucanases are considerably

more effective than the pentosanases. The degree of cytolysis can be determined empirically by the continuous increase in friability of the endosperm; analytical measurements of the difference between coarse and fine grind extract and the viscosity of the congress wort can be made. Excellent cytolysis is achieved under conditions of high moisture, average temperatures of up to 18 °C, plenty of oxygen, and long germination periods. Before the cell wall is broken down, proteins must be hydrolyzed to a certain extent by proteolytic enzymes. The proteolysis is favored by high moisture content, low temperature, and an optimum germination period; if germination periods are too long, low-molecular protein substances will be consumed for growth of the rootlets and the acrospire. The modification of the proteins can be quantified by the degree of protein hydrolysis (ratio of soluble nitrogen to total nitrogen) and by the total amount of soluble nitrogen.

Table 3. Malt enzymes and their behavior during mashing

	CAS registry number	E.C. number	Optimum conditions in mash		
Enzyme			pН	t, °C	Inactivation temperature, °C
Oxidoreductases					
Peroxidase	[9003-99-0]	1.11.1.7		40 - 50	65
Lipoxygenase	[9029-60-1]	1.13.11.12	6.5	40	70
Polyphenoloxidase		1.14.18.1		60 - 65	80
Hydrolases					
Lipase	[9001-62-1]	3.1.1.3	6.8	35 - 40	60
Acid phosphatase	[9001-77-8]	3.1.3.2	4.5 - 5.0	50 - 53	70
α-Amylase	[9000-90-2]	3.2.1.1	5.6 - 5.8	70 - 75	80
β-Amylase	[9000-91-3]	3.2.1.2	5.4 - 5.6	60 - 65	70
<i>endo</i> - β (1 \rightarrow 4)- Glucanase	[9074-99-1]	3.2.1.8	4.7 - 5.0	40 - 50	55
Cellulase	[9012-54-8]	3.2.1.4	4.5 - 5.0	20	20
Laminarinase	[9025-37-0]	3.2.1.6	5.0	37	50
Limit dextrinase	[9025-70-1]	3.2.1.11	5.1	55 - 60	65
Maltase	[9001-42-7]	3.2.1.20	6.0	35 - 40	40
β-Mannosidase	[9025-43-8]	3.2.1.25	3 – 6	55	70
Invertase	[9001-57-4]	3.2.1.26	5.5	50	55
exo- and endo-Xylanases		3.2.1.37	5.0	45	
endo- β -(1 \rightarrow 3)- Glucanase	[9044-93-3]	3.2.1.39	4.7 - 5.0	40 - 45	55
exo- β-Glucanases		3.2.1	4.5	40	40
Pullulanase	[9012-47-9]	3.2.1.41	5.0 - 5.2	40	70
Arabinosidase	[9067-74-7]	3.2.1.55	4.6 - 4.7	40	60
β-Glucan-solubilase					
with esterase activity		3.2	6.6 - 7.0	62	73
with carboxypeptidase activity		3.4	4.6 - 4.9	62	73
Aminopeptidases		3.4.1	7.2	40 - 45	55
Carboxypeptidases		3.4.2	5.2	50 - 60	70
Dipeptidases		3.4.3	7.2 - 8.2	40 - 45	55
Endopeptidases		3.4.4	5.0 - 5.2	50 - 60	70

The protein content of barley decreases somewhat during germination, because the protein-rich rootlets are removed after kilning. The modification of starch by the action of α - and β -amylases occurs to only a moderate degree. The liberation, activation, and formation of β -amylase, as well as the de novo formation of α -amylase during the germination process, are both important. α -Amylase can be formed only in the presence of oxygen; its production is favored by a high moisture content during germination, low to medium germination temperatures, and long germination periods.

Germination Technology Practice. The control of the batch is governed by the malting system, and is also determined by the steeping method and by casting. *Germination with increasing temperature* proceeds between 12 and 16 °C; for barley grown in hot, dry climates, the temperature may rise as high as 20 °C towards the end of germination. Slow but even growth, slow enzyme formation, and low enzyme activity characterize the germination process. Green malts are sometimes kept warm in the second half of the germination period in order to attain the desired extent of cytolysis.

During germination at constant temperature, respiration and temperature increase are facilitated; this results in a more active metabolism and in strong growth. Maintaining the grain bed at 14-15 °C results in the most even modification.

With modern steeping and germination equipment it has become common practice to *germinate with decreasing temperature* (Fig. 3). The relatively warm initial germination phase at a still low moisture content favors quick hydrolysis and high enzyme activity. Enzyme formation is further stimulated by quick cooling of the grain bed and a simultaneous increase in moisture content. Because of the high moisture level, modification occurs satisfactorily in spite of the low temperature. The embryo tries to maintain its original growth rate, and compensates for the impaired living conditions by increased enzyme formation.

In the steep tank and during the early "biological" phase of germination, sufficient oxygenation of the grain bed is necessary for the formation of endo enzymes. In the subsequent "modification phase", a moderate increase of

carbon dioxide in the grain bed (up to 4 %) will inhibit too vigorous growth and improve cytolysis. Germination usually takes six days. The different modification properties of the various types of malt can be compensated by varying the germination parameters, especially the moisture content.

Malting Equipment. Floor malting is the oldest and simplest malting method, but it is found only very rarely today. The metabolic activity of the steeped grain, which has been spread on the floor, is controlled by the temperature of the room, by the height of the grain bed, and by turning. The temperature is allowed to rise steadily from the "young pile" through the "growth" and "matting pile" up to the "old pile".

All methods that use aeration (pneumatic systems) are characterized by malting in deep beds. The most important and most difficult task in this type of malting is the constant maintenance of effective cooling of the grain bed by means of an air stream saturated with moisture. Besides supplying oxygen and removing carbon dioxide resulting from respiration, the air stream must also inhibit excessive loss of water during germination. This is not easy to accomplish, because the air in the grain bed warms up and therefore removes moisture. Each pneumatic germination facility consists of aeration installations equipped with temperature control and moisturizing capabilities, ducts for fresh air, exhaust air, and recycled air, and fans. In addition the germination box is fitted with perforated floors, turning and spraying devices, and discharging equipment.

The various pneumatic malting installations originate from drum or box malting. Drum malting is practically only to be found in the various forms of the Galland drum, or malting box drum. Box malting, with the further development of tower malting or moving grain bed (German: *Wanderhaufen*), is almost the only method that has survived. The specific load of a box is 350 – 500 kg/m²; this corresponds to a depth of the green malt bed of 0.7 – 1.25 m. Among the special malting systems, either the combined germination – kilning system or malting systems in which steeping, germination, and kilning occur in one combined installation are used in practice.

3.1.3. Kilning

In order to stop the chemical and biological transformations that take place during germination, the green malt is dried. This procedure yields a storable product. Another function of drying is to remove the vegetable-like (cucumber-like) flavor of the green malt and to impart to the kilned malt a specific aroma and a defined color characteristic for the type of malt required. Finally, the rootlets, which are highly valued as nutritional feed for cattle, are also removed.

The control of drying processes (withering and kilning), together with the quality and modification of the green malt, determine the character and color of the product.

Withering and Kilning. Moist green malt is very sensitive to high temperature. In order to make allowance for this sensitivity, withering is carried out at high aeration and low temperature. This step decreases the moisture content from the green malt stage to the hygroscopic point (18 - 20%).

Further drying is accomplished somewhat more slowly, but is still relatively easy to handle up to the point of "breakthrough", at which the temperature above the kiln floor is higher than that of the wet bulb temperature. Breakthrough occurs when the moisture content is ca. 10 %. The subsequent drying procedure at higher temperature and low aeration becomes progressively more difficult, because the internal moisture must be conveyed from the interior of the grain

to the surface. The progress of withering and kilning for pale and dark malts in single-floor, high-capacity kilning equipment is shown schematically in Figures 4 and 5.

During the drying of malt the moisture content, volume, weight, and color of the grain change. Dehydration of the green malt lowers the moisture content, which ranges according to the malting technique from 41 to 50 % initially, to 3.5-4 % for pale malt and 1.5-2 % for dark malt. Careful dehydration ensures that the original volume of the green malt remains unaltered.

The chemical and biological changes encompass three stages with relatively different reactions: natural growth, breakdown, and buildup. The formation of aromatic and colored compounds is most important (Maillard reaction). During withering most enzyme levels increase and then decrease during kilning, depending on the temperature.

Malt Kilns. During malt kilning the grain bed is aerated with drying air. The most primitive, directly heated, single-floor kilns were further developed to the indirectly heated double-floor and triple-floor kilns. Later single-floor, high-capacity kilns were built.

The combined germination – kiln boxes have a specific loading capacity of 420 – 500 kg/m². Indirect heating systems, the type being built today, require big heating ovens with large heat-exchange surfaces. The use of recirculated air offers various technological and energy-saving advantages.

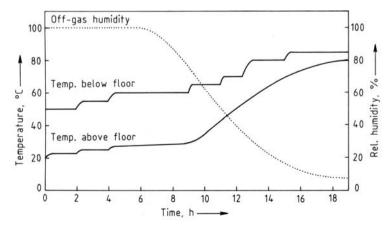


Figure 4. Withering and kilning of pale malt (single-floor kiln, no air recycling)

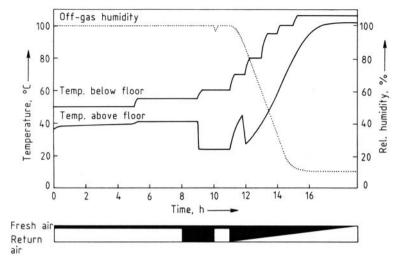


Figure 5. Withering and kilning of dark malt (single-floor kiln, air recycling)

Modern double floor kilns or "reverse air systems" allow the maltster to use the energy capacity of the exhaust air of the kiln side to heat the inlet air of the withering or drying side. The longer exposure to the temperatures on the drying process improves cytolysis and α -amylase activity.

After cooling the kilned malt, the rootlets are removed, and the malt is polished. The malt should then be stored before use in the brewhouse for at least four weeks.

Malt Loss. The changes in weight and volume occurring during steeping, germination, and kilning are shown in Table 4.

The maltster is mainly concerned with the quality of the malt and the production costs. The production costs are also influenced by malt loss. Losses arise during steeping, respiration, and germination; they amount to 16 - 25% (average 20%) and 5 - 12% (average 8%) on a dryweight basis. For quality control standards, see 20.

Special Malts. Wheat malt is produced according to the processes followed for barley malt.

Table 4. Volume and mass changes during malting

	Moisture content, wt %	Volume, hL	Mass, kg
Malting barley	14	100	100
Steeped barley	41	145	145
Green malt	48	220	147
Kilned malt	3.5	118	79
Stored malt	4.7	120	80

Chit malt and short-grown malt are exposed to short germination periods and have a low degree of modification. These malts enhance the foam properties of the beer. Caramel (crystal) malt is saccharified in a kiln or roasting drum and dried according to the desired color at temperatures between 80 and 180 °C. Roasted malt is made of well-modified, already kilned pale malt, which is conditioned (10 % increase of water content) and then heated to 180 – 220 °C in a roasting drum until the desired color appears. Scalding malt is heated to 50 °C at the end of germination and is subsequently kilned. Acid malt is enriched with lactic acid bacteria to lower the pH value in the mash. Smoked malt imparts a special "smoky" taste and flavor to the beer (or whisky).

3.2. Technology of Wort Production

The high molecular mass substances of the malt and of adjuncts must be solubilized by grinding and mashing. The extract solution is subsequently separated from the solids by lautering. The lautered wort is then boiled with hops, clarified, and cooled. The basic procedures are shown in Figure 6.

3.2.1. Grinding of the Malt

The manner in which this purely mechanical procedure is carried out is of critical importance

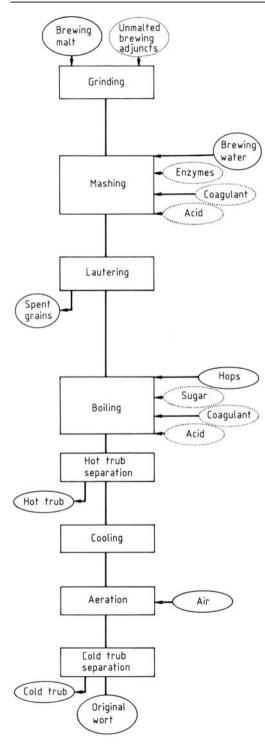


Figure 6. Flow sheet of wort preparation Additives that are shown in dotted ellipses are not necessary

both to the chemical and biological transformations during the mashing process and to the composition and yield of the wort. The husks should be crushed as little as possible in order to prevent the undesirable dissolution of tannins, bitter compounds, and coloring substances, which could have an adverse effect on the taste of the beer. Furthermore, the husks must serve the specific purpose of forming a filter layer during lautering when a lauter tun is used. In contrast, the endosperm requires fine grinding, because it contains the extract components that are to be dissolved.

Nonuniform modification and the resulting differences in hardness of the individual parts of the malt grains cause the products of grinding to differ in size, extract yield, and ease of breakdown. Particles located at the tip of the kernel are undermodified; they are therefore tough and hard, and result in a coarse grind. The portion near the embryo is more friable, and yields a finely ground flour. Grinding also is the basis for wort preparation, because the fineness of the grist determines the grist volume, which in turn determines the volume of the spent grains. During lautering of the wort, the technique of sparging and raking depends on the characteristics of the spent grains. The extent of modification and the moisture content of the malt, the mashing procedure, and the lautering equipment determine the degree of grinding. Proper sampling is most important when particle size is assessed by sieving.

Gristing Mills. The grinding of malt is accomplished by using smooth or fluted cast-iron rollers which rotate either at the same or at different speeds relative to each other. The grinding process may be accomplished in one step, or in such a fashion that certain particles are subjected to repeated grinding. Accordingly, the number of rollers ranges from two to six.

The simplest grinding equipment is the tworoller mill, which, however, can be used satisfactorily only on malt that is well modified. When four rollers are used, the two upper rollers function as crushers, while the lower rollers accomplish the final grinding. Modern types of mills use shaking screens after the first pair of rollers; smaller particles and husks are thus removed, and only the harder coarse particles are ground twice.

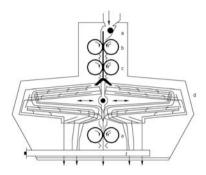


Figure 7. Six-roller malt mill a) Feed roll; b) Pair of precrushing rolls; c) Pair of husk rolls; d) Sieve box; e) Pair of grits rolls; f) Sampler

Mills with three passages adjust best to the variations in malt quality. To obtain higher capacities, five- and six-roller mills are exclusively employed (Fig. 7). After crushing, the grist is separated into three main fractions: husks, grits, and flour. The husks are directed to the two-husk rollers, where they are freed of the rough particles clinging to them. The coarse grits from the first and second grinding are finally milled in the grits roller pair. Mills with five rollers work similarly. Mills with several milling stages also permit removal of the husks, which are added to the mash at a later stage of mashing. Conditioning of the malt with low-pressure steam or warm water (increasing the water content by 1 - 1.5 %) during multiple-roller milling proved advantageous. In this way, the husks remain elastic and are not destroyed even with thorough grinding.

In wet milling the malt is steeped and then ground in simple double- or quadruple-roller mills; in the older systems this is accomplished in one vessel, whereby a moisture level of about 30 % is reached within 10 or 20 min at a water temperature of 50 or 30 °C, respectively. In modern systems the moisturizing is accomplished continuously by a vertical shaft combining nozzles and cascades to give a moisture content of 18 - 20 %.

3.2.2. Mashing

During mashing the solid particles are solubilized by the action of the brewing water and the enzymes formed during malting. The optimum conditions under which these enzymes act on the individual compounds are shown in Table 3.

Starch breakdown is most important during mashing. The solubilization of the starch granules during mixing with water and heating proceeds in various steps. After swelling of the starch kernels, gelatinization of the starch occurs as the enzymatic hydrolysis starts. Starch hydrolysis is allowed to continue until no more α -glucans (dextrins), which give a color with iodine, are present, and the desired attenuation limit is achieved.

Protein hydrolysis is as important as starch hydrolysis, even though smaller amounts are transformed. During mashing, numerous endoand certain exopeptidases (e.g., carboxypeptidases) attack the proteins that were already extensively modified during germination. Depending on the degree of protein modification, the enzyme content of the malt, and the mashing conditions, peptides and amino acids are formed, as well as proteinaceous substances of high molecular mass; the last-named are responsible for foam, palate fullness, and nonbiological haze.

The hemicelluloses are hydrolyzed during mashing only after they have been released at temperatures up to 50 °C. The endo- β -glucanases are inactivated already at temperatures of 50-55 °C, so that substances of high molecular mass which are released at temperatures of 60-70 °C by the action of β -glucan solubilase cannot be broken down any further. For this reason, uniformity and extent of cytolytic modification is of greatest importance.

The acid phosphatases which occur in the malt hydrolyze the organic phosphates; during this process phosphoric acid is released, which decreases the pH and increases the buffering capacity of the malt, wort, and beer. Excessive buffering, however, aggravates the drop in pH during fermentation.

Lipids are degraded to glycerol and longchain fatty acids. The unsaturated linolic and linolenic acids undergo oxidation by lipoxygenases to hydroperoxides.

Increasing the temperature of the mash and the duration of mashing increases the release of polyphenols and anthocyanidines. Both groups are subjected to oxidation, catalyzed by peroxidases and polyphenol oxidases.

Mashing Parameters. The amount of brewing water used for dissolving the grist and for the chemical and biological transformations constitutes the mash liquor; *spargings* are used to yield

the residual extract compounds, which remain in the spent grains after lautering the first wort. The amount of brewing water employed is basically different for all-malt pale and dark beers. For pale beers, a greater volume of mashing-in water is used in order to obtain thinner mashes and to speed up the enzymatic processes. The volume of brewing water is about 4 hL per 100 kg of malt for pale beers, and 3 - 3.5 hL per 100 kg malt for dark beers (mash ratios 1:4 and 1:3-3.5, respectively). The spargings (4 - 5 hL per)100 kg malt) must be added in such a manner that the remaining extract can be yielded as completely and quickly as possible. The last runnings (end of spargings) should always be analyzed for economic usefulness and beer quality (tannins, boiling time).

The intensity of the mashing process is determined by the mashing-in temperature. Temperatures of 35-40 °C facilitate dissolution of the substrate and the enzymes, so that these can be more effective at their optimum temperature. At around 50 °C the breakdown of proteins, gums, and phosphates is increased; thoroughly modified malts can be mashed in even at 62 °C, the optimum temperature for β -amylase.

The dissolution of the ingredients of the brewing materials is already initiated by grinding. Further parameters include the rest periods at different temperatures, the pH value of the mash, and the choice between decoction mashing (boiling parts of the mash) and infusion mashing (no boiling of mash portions).

Mashing Vessels. For mashing-in and for the storage of partial mashes a heatable mash tun, equipped with an agitator, is used. In a similar mash kettle, which is usually smaller, the decoction mashes are heated and boiled. In breweries with a two-vessel brewhouse, the lauter tun is also used as mash tun, and the brewing kettle is also used as mash kettle.

Mashing Procedure. The brewer determines the composition of the various specific beer types by the choice of the mashing procedure. All mashing methods can be derived from the three-mash decoction procedure shown in Figure 8. In two-mash procedures, one of the decoction mashes is eliminated. Single-mash procedures can be accomplished with infusion before drawing off the decoction mash, with infusion

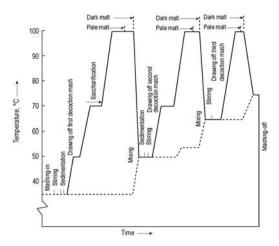


Figure 8. Three-mash method
—— Temperature of decoction mash
- - - - Temperature of rest mash

after drawing off the decoction mash, or as kettlemash procedure (boiling of the total mash, cooling, and saccharification with an enzyme extract that was drawn off at the beginning from the top liquid layer). When the malt is overmodified and enzyme-rich, then a high-temperature two-mash method can be used to advantage. Due to energysaving and even emission-reduction reasons the mashes are no longer boiled; instead they are kept slightly below boiling temperature. The *infusion* methods require good malt modification. The access of air should be avoided to minimize oxidation reactions. The so-called temperatureprogrammed infusion mash uses the same main rests as the decoction mashes, e.g., at 50, 62, 70, and 75 °C, to promote the individual enzymes or coenzyme groups. Infusion-mash methods with decreasing temperature have become popular for extremely modified malts and certain beer types such as ale. Mashing-in at 75 °C enhances the activity of α-amylase. During mashing-in the temperature drops to 65 °C. Grist mashing methods are intended to treat the different grist fractions on the dual basis of their enzyme content and their convertibility. In the process involving husk separation, the boiling of the husks, and therefore their extensive leaching, is avoided.

Processing of Adjuncts. Unmalted cereals must be treated thermally before enzymatic breakdown takes place, thus ensuring the conversion of extract-forming components. Malt amylases facilitate the gelatinization of the finely

ground adjuncts. The grinding of the malt grist must correspond in fineness to the grist part of the adjuncts, and the concentration of the malt mash must be kept very high because a large amount of water is required for optimum adjunct gelatinization (1:4-5).

Pale barley malt gelatinizes at temperatures between 58 and 67 °C depending on variety and climatic conditions; unmalted cereals need higher temperatures: barley 65 – 69 °C, corn 73 – 79 °C, and rice 67 – 91 °C.

Corn can be added to the first decoction mash without any special treatment up to 15 %. If higher proportions of corn are added, a special adjunct mash will be required, in which the ratio of corn to malt is 2:1. When almost complete gelatinization and liquefaction have been achieved, the adjunct is boiled and subsequently added to the malt mash.

Some varieties of *rice* will gelatinize completely only at 88 - 91 °C, even if malt is added. After gelatinization, sufficient malt mash held at temperatures of 30 - 40 °C is added; liquefaction then takes place within 10 min at 78 °C. The liquefied material is subsequently boiled and added to the actual malt mash. After that, the mashing procedures described above can take place. The processing of 10 - 15 % unmalted barley will be possible only if the brewing malts are rich in enzymes. Higher proportions of unmalted barley (30 - 40 %) require the addition of enzyme products.

3.2.3. Separation of Wort

After mashing, wort is obtained in two steps: (1) lautering of the first wort by filtration, (2) washing out of the extract that remains in the spent grains with hot water (sparging).

Lauter Tun. Commonly used lauter tuns have a total capacity of 8 hL/100 kg and spent grain depths of 25 - 50 cm. They have a slotted false bottom with an open surface representing about 6 - 20 % of the plate area. Rotating, height-adjustable raking machines loosen the spent grain bed, and a spray device delivers the sparging water. During lautering, aeration of the wort should be avoided. The mash should remain homogeneous during pumping in, so that a loose, even filter cake can form. Finally, the wort that runs off should be as clear as possible,

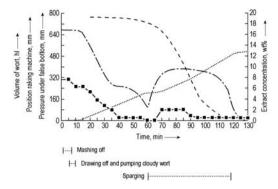


Figure 9. Idealized lautering diagram using a lauter tun
---- Extract concentration, wt %
----- Pressure under false bottom, mm
--- Volume of wort, hL
-■-■- Position raking machine, mm

so that no particles which could disintegrate further during wort boiling (filterability), and only small amounts of the long-chain fatty acids, which destroy foam, can get into the kettle.

Because of the danger of washing out iodinereactive α -glucans, the sparge water should have a maximum temperature of 78 °C. In order to avoid channeling, it should be delivered evenly. The ideal performance of a lautering process in a modern lauter tun is shown in Figure 9.

Mash Filter. In place of the lauter tun, some brewers employ mash filters to separate the mash into solids and liquid. The total mash is transferred into a vertically arranged filter press. The frames are covered on both sides with filter cloth made of synthetic material. At the same time, the air must escape quickly when the homogeneous mash is pumped into the chambers. After yielding the first wort, the grain cubes are pressed together by membranes which separate the chambers of the filter. Because very low volumes of sparging water (0.5 hL/100 kg) are necessary, this facility is very suitable for high-gravity brewing.

Characteristic differences between well-automated mash filters and lauter tuns are the following: (1) independence from the quality of the malt and from the proportion of adjunct, (2) quicker lautering of the more highly concentrated first wort, (3) higher yields, and (4) a slightly hazier filtrate.

Strainmaster. The strainmaster consists of a rectangular vessel, the bottom half of which is conically shaped. In the lower part of the vessel

perforated sieve pipes of triangular cross section, which have an open surface area of 10%, are arranged on top of each other. After pumping off the first wort the sparging water can be pumped in from the top and/or the bottom. A very high first-wort concentration of 20-23% is necessary in order to achieve a homogeneous mash. Even with large amounts of sparging water it is not possible to achieve yields as high as those obtained with the lautering systems previously discussed, primarily because the spent grains must be withdrawn while very wet. The major advantages of the strainmaster are its large capacity and rapidity in action – lautering is finished in 70-80 min – and its simple, automatic operation.

As modern lauter tuns and mash filters manage the same number of brews per day without any drawbacks, strainmasters are still in operation in a declining number of breweries, but no new ones are being installed.

Continuous Lautering. Equipment that allows continuous wort lautering has not been successfully introduced into breweries because the wort that runs off is very hazy. The most important features of such equipment include a rotary mash filter, a screen-conveyor centrifuge, a belt filter, a vacuum drum filter, the Pablo system with screen centrifuges and separators, and hydrocyclones.

Spent Grain Removal. Spent grain is usually sold to farmers with a moisture content of 78 - 80 % and provides a protein-rich nutrient feed for cattle. Spent grains obtained from a strainmaster must first be demoisturized in a screw press. Spent grains obtained from mash filters have a moisture content of only 68 - 70 %. An amount of 100 kg of barley malt yields 120 - 130 kg wet spent grains from lauter tuns, whereas wheat malt yields 10 - 15 % less. Dry matter consists of 23 - 28 % protein, 5 - 9.5 % fat, 40 - 47 % nitrogen-free extract materials, 16 - 21 % crude fiber, and 4 - 6 % minerals.

3.2.4. Wort Boiling and Hopping

The wort obtained by lautering (full kettle wort) is boiled; during this time hops are added. The process can be divided in two steps: thermal reactions and evaporation [24]. During boiling,

chemical reactions such as isomerization of the bitter substances of the hops and formation of aroma, reducing, and coloring substances take place, as well as dissolution processes, inactivation of the malt enzymes, and the sterilization of the wort.

Evaporation removes undesired aroma components [myrcen from hops, carbonyl compounds, and sulfur compounds like dimethyl sulfide (DMS)] and allows the desired wort concentration (original gravity) to be achieved. A high efficiency of the boiling systems guarantees high quality, which can be determined from total DMS (< 120 μ g/L), the thiobarbituric acid number (TBN < 45 in the cast wort) and the heat-coagulable nitrogen content (20 – 30 mg/L).

Wort Boiling. The kettles must have a capacity of about 9 hL per 100 kg of malt grist in order to achieve the desired effect through boiling. The most important part of the kettle is its heating device. At first, direct firing was used; this was later changed to oil heating, and then to steam-jacketed kettles with two-zone heating and a cone-shaped central core.

Today hot-water (125 - 140 $^{\circ}$ C) or saturatedsteam (107 - 115 °C) systems with internal or external heaters are used. In conventional kettles the evaporation rate was 12 – 14 % (i.e., 8 % per hour), relative to the final volume. Modern internal or external heaters allow boiling times of about 60 min, due to slightly elevated temperatures in the heaters, homogeneous circulation, and large evaporation surfaces. To avoid too strong protein coagulation, a "rest" is taken in the middle of the boiling process. However, degradation of dimethylsulfide precursor (DMSP) to free dimethyl sulfide proceeds. Thus, the total evaporation can be reduced to 4-6%. By installation of an efficient vapor condenser and an energy store, the wort can be heated from 72 to 93 - 95 °C by heat exchange. This system is almost balanced.

The denaturation and subsequent coagulation of proteins will lead to coarse, flaky precipitation products (break) and non-opalescent worts only if the finely distributed protein complexes have sufficient chance to come into contact with each other for agglutinization; this is achieved by using small steam bubbles and an efficient circulation. Boiling by means of various external heating systems provides proper mixing and control of the wort.

Further decrease of the boiling time is not possible because of the length of time required for the isomerization of the bitter substances. However, heating at 108 - 112 °C enables the boiling time to be further reduced to less than 60 min at an evaporation of 4 - 6 %.

Continuous Wort Boiling. At a maximum temperature of 135 °C, the hot holding time required is claimed to be only 150 – 160 s. At higher temperature, heterocyclic nitrogen compounds will increasingly form; these have a very low flavor threshold, and impart a bread-like or cracker-type aroma to beer. After the hot holding period, evaporation proceeds in tandem flash evaporators, and should amount to at least 6 % of the original volume in order to drive off such undesirable aromatic substances as aldehydes, ketones, sulfide, and dimethyl sulfide. When these parameters are carefully observed, beers can be produced with high-temperature wort boiling which are of the same quality as those produced under normal boiling conditions.

The Schoko process separates wort boiling into two processes: keeping at slightly below boiling temperature for 50-60 min (0.5 % evaporation) and exposure to a vacuum in an expansion evaporator down to 65-70 °C to eliminate undesired aroma compounds which are formed during the holding time in the kettle and in the whirlpool. The total evaporation amounts to about 6 % after the whirlpool rest.

Hopping. The dissolution of the bitter substances is very dependent on pH. At a pH of 5.9, the α-acids are molecularly dispersed, partly as salts (humulates); their solubility is 480 mg/L. However, at a pH of 5.2 only 84 mg/L can be dissolved in a colloidal state. At the normal wort pH of 5.4 - 5.6, the colloidal solution prevails. During wort boiling, up to 40 - 60 % of humulone, cohumulone, and adhumulone isomerize; 5 - 1 % remain unisomerized. A proportion of the bitter substances is oxidized, which also contributes to the bitterness of the beer. The major part of the loss must be attributed to incomplete extraction from the hop cone or hop products, and to precipitation. The remaining α-acids are rendered insoluble as a result of the fall in pH during fermentation and are expelled in the fermentation cover. The β-acids are not transferred to the wort, but the soft and hard

resins are dissolved during boiling and also impart a certain bitter taste.

The isohumulones are more soluble at low pH values, e.g., about 2000 mg/L at pH 5. Boiling and hot-stand times are essential for isomerization. In addition, extraction speed, the age of the hops, the amount of α-acids added, and the wort pH all affect isomerization. If additional contact surfaces are available (as in hop extract powders), the isomerization will occur faster. Separate addition of tannin extracts at the beginning of boiling and of extracts of bitter substances later will result in a higher bitter substance yield, because the bitter substances otherwise are adsorbed onto the hot trub particles and are lost. In the brewhouse, about 60 % of the bitter substances can be transferred to the wort: only 30 % of the amount originally added remains in the finished beer because of further precipitation during fermentation.

The amount of bitter substances added is expressed in milligrams of α -acid per liter of finished wort, and it varies according to the hop product used and the beer type and variety. For pale lager beers about 65 mg/L are added, for export 80 mg/L, and for pilsener 80 – 160 mg/L. The addition of hops according to variety and timing also influences the bitterness. For the latter, the yield of aroma compounds is crucial, which depends on the time of addition: late in the boil or even later in the whirlpool.

Color. Coloring and reducing substances are formed during kilning and mashing. Others develop during boiling of the wort. The numerous amino acids react with reducing sugars to form intermediary products which undergo further transformation to brown melanoidines. The products thus formed possess reducing properties and give acid reactions. Polyphenols also contribute to color formation by nonenzymatic oxidation and polymerization. Strong formation of coloring compounds leads to broad and harshtasting beers which age quickly.

The Finished Wort. The hopped beer wort obtained after boiling is designated as finished wort (cast wort, hot wort). Its extract content and volume are analyzed. The brewhouse yield can be determined from these values; the extract yield is expressed as a percentage of the amount of malt used (range between 78 and 81 %). Table 5 shows the composition of a pale 12 % finished wort.

Table 5. The composition of pale lager wort (12 %) made from barley malt

Carbohydrates (100 %):	
Hexoses	7 – 9 %
Sucrose	3 %
Maltose	43 – 47 %
Maltotriose	11 – 13 %
Lower dextrins	6 – 12 %
Higher dextrins	19 – 24 %
Pentosans	3 – 4 %
Gums	0.2 %
Nitrogen compounds:	
Total nitrogen	950 - 1150 mg/L
High molecular	200 - 300 mg/L
mass nitrogen	
Low molecular	550 - 700 mg/L
mass nitrogen	
Free amino nitrogen	200 – 250 mg/L
	(about 22 % of total N)
Bitter substances	25 - 35 EBC bitter units
	(pils 40 – 50 EBC)
Polyphenols:	
Total polyphenols	180 – 250 mg/L
Anthocyanidines	70 – 110 mg/L
Minerals	15 - 20 mg/L
	(80 % inorganic, 20 % organic)
Zinc	0.1 - 0.25 mg/L
pH	5.0 - 5.7
Viscosity (20 °C)	$1.7-2.0 \text{ mPa} \cdot \text{s}$

Wort Concentrates. In some countries it is permitted to manufacture hopped wort concentrates and unhopped malt extracts from wort made by the usual brewing method. Concentration to 70-80% dry matter is achieved either by vacuum evaporation or by lyophilization. These concentrates can be diluted back to the desired extract content in the kettle; they are processed subsequently in the normal manner.

3.2.5. Wort Treatment

Hot Trub Separation. The hot trub contains the nitrogen compounds that coagulate during boiling. These must be removed completely before fermentation, or else the beer will taste wort-like, bitter, and even harsh. The hot trub consists of 40 - 70 % protein, 7 - 15 % bitter substances, 20 - 30 % of other organic compounds, such as polyphenols, and mineral substances. Hot trub yield is between 400 and 800 mg of extract-free dry matter per liter of finished wort. When whole hops are used, the cast wort must first be cleared of spent hops by passing it through a hop back. In the past, the wort

was pumped into the flat coolship, where it cooled immediately to ca. 80 °C and during the following hour to ca. 65 °C; the colder seasons allowed the wort to cool down to pitching temperature overnight. Because of the danger of infection on the large surface of the coolship, the heat loss, and the great expenditure of work, other methods of hot trub separation have been developed.

The *settling tank* (hot wort receiver) permits good separation of the trub and spent hops, but the amount of sludge collecting on the bottom of the vessel creates problems because 2-5% of the wort is trapped in this sludge. It can, however, be recovered by centrifuging the mixture of trub, spent hops, and wort in a chamber or plate centrifuge. The wort recovered in this way can be added to the same batch of wort or to the next brew.

The total hot wort is frequently clarified by means of efficient, self-cleaning centrifuges; these, however, will only work reliably if the wort – trub mixture is added homogeneously. This can usually be achieved by means of an intermediate hot wort tank with a stirring mechanism. The most thorough removal of trub and spent hops can be achieved by filtering the hot wort through kieselguhr.

An inexpensive solution is the *whirlpool tank*, wherein the wort is pumped tangentially into a cylindrical vessel. This creates an even, rotating stream. The solid particles suspended in the rotating liquid will separate due to friction (tea cup effect), migrate to the bottom center, and coalesce to form a cake. It is also possible to achieve this effect in whirlpool kettles, where both boiling and trub separation take place, provided that the bottom of the kettle is appropriately shaped.

Wort Cooling. The wort, which has been freed of hot trub, is cooled to 4-7 °C for cold bottom fermentation, to 10-15 °C for accelerated bottom fermentation, and to 12-18 °C for top fermentation. The capacity of the plate heat exchanger should be sufficient to cool the whole wort from 97 °C to pitching temperature within 50 min. Thus, the total time between the end of boiling and the end of cooling should not exceed 90 min, to avoid excessive color pick-up and formation of Maillard and Strecker degradation products, which are apt to deteriorate the character and the flavor stability of the later beer.

Cold Trub Removal. The very finely flaked cold trub appears at temperatures of 70 – 55 °C. It consists of around 50 % protein, combined with 15 – 25 % polyphenols and 20 – 30 % carbohydrates of high molecular mass. At 0 °C about 150 – 300 mg/L of cold trub is formed. Opinions are divided regarding the necessity of cold trub separation. The presence of cold trub can, under certain circumstances, accelerate fermentation because of the presence of long-chain unsaturated fatty acids. The yeast will contain a higher level of impurities and the filterability of beer brewed in this manner may be poorer.

Fairly good separation of the cold trub can be obtained in the starting vessel by sedimentation after pitching. Even more effective are cold sedimentation with or without the addition of kieselguhr, cold centrifugation, and, very elegantly, flotation not only with aeration but also simultaneous addition of pitching yeast. Filtration of the wort removes the cold trub quantitatively; however, a deficiency of minerals and fatty acids could be created by this method. Blending of unfiltered wort can be helpful in this case.

Aeration. The oxygen necessary for yeast propagation (7 - 8 mg/L), corresponding to 80 % saturation of the wort with O_2) is usually introduced in the form of air at the pitching temperature. If pure oxygen is used, it must be added carefully, so that the oxygen level does not exceed 15 mg/L; a higher level is detrimental to the yeast. Optimum aeration can compensate for the disadvantages of extensive wort clarification. All closed cooling systems require separate aeration of the wort. During normal wort aeration 5 - 15 L of air per hectoliter of wort is needed; flotation requires 40 - 60 L/hL.

Sterile air may be introduced on the cold wort side of the plate cooler with even dispersion by air nozzles or venturi jets, or in the hot wort centrifuge, provided the wort is cooled immediately. A combined hot and cold aeration in the ratio of 1:5 also is possible.

3.3. Bottom Fermentation

The flow sheet of Figure 10 describes the basic operations for popular beer varieties from fermentation to finished beer.

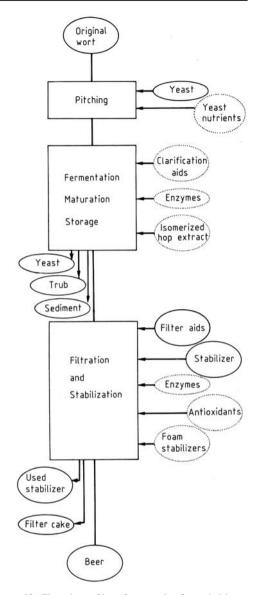


Figure 10. Flow sheet of beer fermentation from pitching to final product

Substances that are shown in dotted ellipses are not necessary

3.3.1. Fermentation

The fermentation process is initiated by the addition of 0.5 - 0.7 L of a heavy yeast slurry per hectoliter of wort, corresponding to $15 - 20 \times 10^6$ yeast cells per milliliter of cooled and aerated wort. This procedure is called *pitching*. The batchwise addition of original wort to

fermenting green beer is called doubling. The main products resulting from the fermentation are ethanol and carbon dioxide. Other reaction products include higher aliphatic and aromatic alcohols, esters, organic acids, carbonyl compounds, sulfur-containing compounds, and polyhydric alcohols, all of which are important for the properties and quality of the resulting beer (for details on alcoholic fermentation, see → Ethanol). All the compounds formed have different taste and odor thresholds. Their combined contributions make up the flavor or offflavor of the beer; the amounts produced can be influenced to some degree by brewing technology. Further changes in the wort are caused by the fall in the pH value (see below). The pH drop leads to the precipitation of nitrogen compounds of high molecular mass, of polyphenols, and of bitter agents. The result is a decrease in color and a debittering effect.

Yeast has the ability to adjust its metabolism to aerobic as well as to anaerobic conditions. The yeast doubles or triples its mass during fermentation. For the build-up of cell substance (proteins and enzymes) the yeast needs mostly amino acids, which are taken either from the fermentation substrate or synthesized by itself. Besides proteins, lipids are also synthesized for yeast propagation because they are important components of the cell wall, and are needed for the uptake of nutrients. For the synthesis of these lipids from acetyl coenzyme A, molecular oxygen is needed; after lautering, wort itself contains only few lipids. Finally, the yeast also requires minerals for the stabilization of its enzyme systems.

The many bottom- and top-fermenting yeast strains differ in their ability to ferment and to form byproducts, but the yeast can develop the ideal pattern only if it is in a healthy state (viability >95 %, intracellular pH > 6.2). The safest method is to pitch with freshly propagated (or assimilated) yeast which is multiplied from a small population to the necessary cell count for the start of fermentation. Under normal conditions (i.e., without infection and performing according to the desired pattern) the yeast can be repitched several times. But in order to achieve this the yeast must be cropped as early as possible, freed from CO₂ (and ethanol), cooled to below 3 °C, and stored for as short a time as possible. This is particularly important with large cylindro-conical fermenters from which the

yeast is cropped under the pressure of the liquid column plus some additional overpressure. For top-fermenting yeasts, horizontal fermenters are more favorable for development of the typical aroma (especially for wheat beer yeasts). Cylindro-conical fermenters require young (i.e., propagated yeast cells).

If the yeast deteriorates it undergoes autolysis. Even at a very early stage, the yeast excretes short-chain fatty acids and amino acids, which increase the pH of the beer. This and the release of yeast proteases impairs beer foam, aroma, taste, and flavor stability.

Fermentation **Byproducts.** During main fermentation, the pH value decreases by one unit because volatile (acetic, formic) and nonvolatile *organic acids* (pyruvic, malic, citric, lactic) are formed. The pH of beer ranges from 4.3 to 4.6. The intensity and speed of acid formation is determined by the buffering action of the wort, the amount of easily assimilated nitrogen, the yeast strain, and the fermentation schedule used. If the pH drops quickly, gums that retard filtration will precipitate, but valuable colloids also are lost. The pH has a direct effect on the flavor and the liveliness (sparkle) of the beer. Short-chain fatty acids are formed during the fatty acid synthesis at the beginning of the main fermentation process: butyric, isovaleric, hexanoic, octanoic, and decanoic acid. Their amounts can be controlled by the wort composition, aeration, yeast strain, and general fermentation conditions. During pressure fermentation, increased levels of these compounds can be expected during maturation. Even in very low concentrations, they cause a yeasty odor and impair head retention.

The higher *aliphatic alcohols* (1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol) and *aromatic alcohols* (especially 2-phenyl-1-ethanol) represent the largest fraction of the compounds responsible for the aroma of the beer; at concentrations which are too high, they will adversely affect taste and quality. Their levels can be controlled to some extent by manipulating the content of free amino nitrogen, wort concentration, pitching rate, yeast strain, pitching temperature, and fermentation temperature.

Because of their low taste threshold values, esters strongly influence the organoleptic

properties of the beer. Esters are products of enzymatic catalysis and their formation is very closely related to yeast propagation and lipid metabolism. Wort aeration, pitching rate, fermentation temperature, the yeast strain, and the counterpressure during fermentation all have great influence on ester formation. Measures intended to intensify yeast propagation will lower ester concentration.

Most sulfur compounds like hydrogen sulfide, dimethyl sulfide, 3-methylthio-1-propanol, and thiols are not desirable in beer because of their specific odor and taste. Efficient hot trub removal and speedy main fermentation are the most important factors in the formation and removal of these compounds. However sulfur dioxide formation up to a level of 10 mg/L is desirable because of its antioxidative properties and thus its influence on the flavor stability of beer. To obtain a sufficient amount of SO₂, the rate of yeast multiplication should be controlled by reduction of the wort aeration; in particular, several brews are fermented in a large fermentation vessel. Along with the degree of aeration, the yeast strain plays an important part.

Glycerol (1300 – 2000 mg/L) is formed as a byproduct during glycolysis; its concentration depends on the amount of fermented sugars.

Aldehydes and ketones are responsible for the aroma of green beer and for the stale flavor. Acetaldehyde formed in the green beer does not present any technological difficulties. Off-flavors in beer are usually caused by a high level of diacetyl and 2,3-pentanedione; these compounds are responsible for unfavorable, buttery flavor in the beer. The taste threshold of diacetyl depends on beer type, and ranges from 0.10 to 0.12 mg/L; that of 2,3-pentanedione is 0.5 – 0.6 mg/L.

3.3.2. Maturation

The total diacetyl concentration is used to judge the maturity of purged beer, and it must be decreased below the flavor threshold by means of brewing technology. The diacetyl precursor 2-acetolactate is called "potential diacetyl", because it transforms into free diacetyl only in the filtered, yeast-free beer, and can then not be broken down any further. In calculating the total diacetyl concentration, 2-acetolactate must be added to the amount of free diacetyl.

Diacetyl Metabolism During the propagation phase the yeast cells need numerous nitrogen compounds for the formation of yeast protein. If there is not sufficient fixed nitrogen present in the wort in the form of compounds which can be assimilated, the yeast will use a combination of carbohydrate and protein metabolism. During valine synthesis diacetyl can be formed via 2-acetolactate by oxidative decarboxylation, as shown in Figure 11. This step, which is catalyzed by yeast enzymes, is highly temperature dependent and occurs very slowly below 10 °C. Diacetyl itself is present in very small quantities in fermentation samples and in green beer, because its reduction to acetoin is much faster than its formation. The final product 2,3-butanediol is, as far as taste is concerned, unobjectionable; its concentration in beer never exceeds its flavor threshold. Bacteria, which may occur in the brewery as infections, also are likely to promote the formation of diacetyl by the route shown in Figure 11. Some bacterial types contain an enzyme which can decarboxylate 2acetolactate directly to acetoin while avoiding the limiting maturation step.

Fermentation Conditions. The formation and reduction of 1,2-diketones is dependent on (1) a sufficient supply of free amino nitrogen and other yeast nutrients, (2) proper pitching and doubling conditions (sufficient aeration, low pitching temperature, optimization of pitching rate regarding yeast quantity and timing), (3) a careful selection of the yeast (yeast strain, physiological condition of the yeast, no infection), and (4) control of the fermentation and maturation conditions favorable for the degradation of diacetyl. The most effective parameter in this respect is temperature control during fermentation and maturation, which is the basis for the fermentation procedure shown in Figure 12.

Using the combination of *cold fermentation* – *cold maturation* allows a tasty beer can be produced by simple means. It is advantageous to remove most of the yeast at the end of fermentation and to achieve secondary fermentation by the addition of "krausen" (green beer in its initial fermenting stage).

With the combination warm fermentation – warm maturation, the formation of fermentation byproducts is increased at the prevailing high fermentation temperatures. The rapid pH drop results in losses of bitter substances, decreased

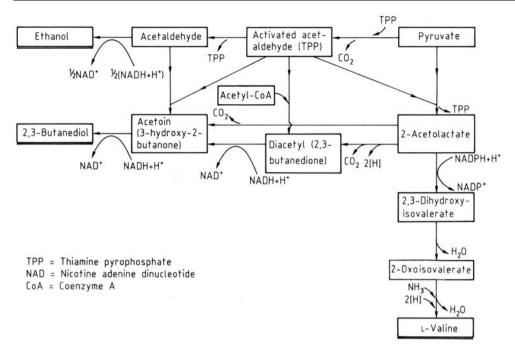


Figure 11. Synthesis of diacetyl by yeast and bacteria

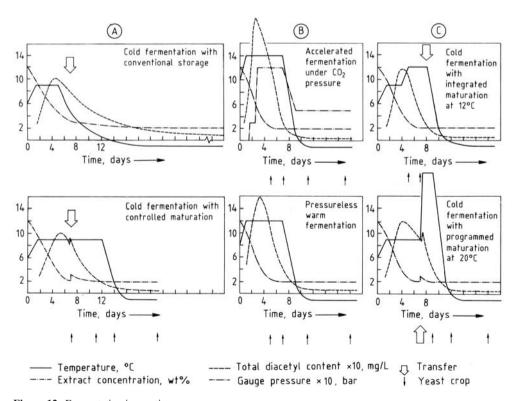


Figure 12. Fermentation in practice
A) Cold fermentation – cold maturation. B) Warm fermentation – warm maturation. C) Cold fermentation – warm maturation

foam stability, and sometimes a yeasty flavor. Pressure fermentation using the higher buildup of carbon dioxide is a remedy. This will slightly decrease the fermentation rate and control yeast propagation, thus curbing the formation of fermentation byproducts.

The combination cold fermentation - warm maturation avoids the formation of undesirable flavors and decreases the level of diacetyl safely; it leads to beer of constant quality. In this case, temperature control is optimally adjusted to the metabolism of the yeast. In programmed maturation, heat exchangers are used to raise the temperature to 20 °C. The addition of 10 % "krausen" with an apparent degree of attenuation of 20 - 30 % is practiced at the beginning of this maturation phase. Accelerated fermentation and maturation are also achieved by stirring fermentations and then maintaining a maturation step and subsequently purging green beer with carbon dioxide. However, an excess of fermentation byproducts is formed by this method.

Modern practice uses combined fermentation and maturation at 12 - 14 °C. At an attenuation degree of 50 % a slight pressure is built up to 0.5 - 1 bar overpressure to enrich CO_2 . After attaining end-fermentation, the yeast is cropped and the main temperature maintained until the total diacetyl load is below 0.12 ppm. During this time of 3 - 4 d after end-fermentation the yeast is purged twice and eventually cooled to 0 to -1 °C. During cooling, CO_2 is injected for several hours at a rate of 3 g hl⁻¹ h⁻¹.

Fermenters. Fermentation and maturation are carried out in open or closed fermenters, horizontal tanks, or vertical fermentation tanks with conical bottoms. In two-tank processes, fermentation, maturation, and storage occur separately; vertical tanks with conical bottoms are used in this case.

The capacity of the cooling equipment and heat exchange surface of the tanks should be designed for maximum heat development or, in the case of single-tank processes, for a maximum cooling rate.

Fermentation Stages. The brewer identifies the changes occurring in the green beer by carefully observing the individual fermentation stages: creaming, head formation, rocky head, and the decreasing of head at the end of fermentation. Extract decrease and temperature level

must be checked constantly. Attenuation also is indicated by a drop in pH value, by a phase of cell propagation and cell sedimentation (turbidity), by a decrease in coloration, and by a lowering in redox potential.

The carbon dioxide formed during fermentation amounts to 2 - 2.5 kg per hectoliter of beer. It is collected and can be used for carbonation of soft drinks or for low-oxygen bottling and racking.

3.3.3. Cold Storage

During cold storage the beer must be carbonated to the desired CO₂ level (0.48 % for draft beer, 0.50 % for canned beer, 0.55 % for bottled beer). This can be achieved in the conventional procedure by using a bunging overpressure of 0.2 – 0.6 bar, depending on hydrostatic pressure and temperature. Beers that underwent warm maturation require either higher pressure, or carbon dioxide to be added during transfer from warm to cold storage tanks. During storage, the beer must clarify by allowing the yeast and other hazecausing materials to settle, and its taste must refine and round off. In order to achieve these requirements, the beer must be stored at 0 to -2 °C during the last week or two. When warm maturation is practiced, the storage period cannot be as easily defined. Frequently fermentation, maturation, and storage take place in the same vessel (one-tank process).

By using separate tanks for the sedimentation of the yeast after fermentation (flocculation tanks), yeast content and degree of attenuation are further balanced. During transfer to the cold storage tanks krausen is added. Separate storage tanks also are used when the beer is stabilized with bentonite during the second half of the storage period.

Continuous fermentation may be accomplished by through-flow or by tributary-flow systems or in a bioreactor. These methods are rarely found in large production facilities.

3.3.4. Filtration

For filtration theory and beer filtration see [25].

Besides an impeccable taste, perfect clarity is expected of a stored and matured beer. Solid and hazy particles still present in the beer (yeast,

protein – tannin particles, and hop resins) are removed by filtration. Filtration also improves biological and chemical-physical stability. Filtration is carried out at low temperature (possibly at 0 to $-2\,^{\circ}$ C) under a counterpressure of carbon dioxide above its saturation level, and with minimum uptake of oxygen.

Filtration systems used for pre-clarification were formerly pulp filters; today brewers use mostly plate and frame filters, pressure leaf filters, or candle filters for cake filtration with a filter aid (diatomaceous earth, perlite), or centrifuges. For subsequent final clarification and sterile filtration, sheet filters made from cellulose and diatomaceous earth are used. For sterile filtration filter membranes made from cellulose esters of definite pore size may be used.

The choice of the clarification method depends on capacity, technical considerations, and economic conditions. Another factor is the filterability of the beer, which is not always proportional to the viscosity, but also depends upon the nature and amount of filtration-retardant materials present, such as α - and β -glucans, proteins, and a high yeast content.

3.3.5. Stabilization

In bright beer high molecular proteins and tannins tend to aggregate and form haze. This process can be delayed by removing one of these fractions which improves the chemical-physical shelf life of the product. Most common is the removal of part of the tannins by adding polyvinylpolypyrrolidone (10 – 50 g/hL) as an adsorbent. Polyvinylpolypyrrolidone is dosed in the filtered beer and retained in a pressure leaf filter. The loaded polyvinylpolypyrrolidone is subsequently reprocessed and reused.

It is also possible to remove the haze-forming fraction of proteins by precipitation with silica gels or agarose or by enzymatic breakdown.

3.3.6. Types of Bottom-Fermented Beers

In many countries, bottom-fermented beer is designated as *lager beer*. Its extract of original wort varies according to local laws (tax classification) from 7 to 14 %. Lagers are the most popular beers, and they have an average bitter

substance content of 20 EBC bitter units (see Table 6 and Section 5.3).

Beer with an Extract of Original Wort of 10 – 14 % This range comprises an extraordinarily large variety of beer types, including pale and dark beers, export beers (more than 12 % extract of original wort), Märzen beers, special beers, and festival beers (13 – 14 % extract of original wort). Within these limits there are such different beer types as Pilsener, Dortmunder, Munich, as well as smoky-flavor beers and cellar beers; these are, however, restricted to certain localities.

Strong Beer In Italy, pale and dark beers of more than 15 % extract of original wort are classified as strong beers; in Austria and Germany beers from 16 % up to a maximum of 28 % extract of original wort also belong to this class.

3.4. Top Fermentation

Top-fermented beers differ from bottom-fermented beers by their special aroma which is primar-

Table 6. The composition of bottom-fermented pale lager beer brewed by 100 % malt and 12 % extract of original wort

Extract of original wort Attenuation limit (apparent) Real degree of attenuation Apparent residual extract Real residual extract* Alcohol concentration Fermentation by products Higher alcohols Acetic acid Formic acid Esters Aldehydes Diacetal and 2-aceolactate Attenuation imit (apparent) 78 - 85 % 80 - 85 % 1.7 - 3.0 wt % 2.0 - 3.5 wt % 80 - 120 mg/L 120 - 200 mg/L 20 mg/L 20 - 50 mg/L 40 - 10 mg/L
Fermentation by products Higher alcohols 60 - 120 mg/L Acetic acid 120 - 200 mg/L Formic acid 20 mg/L Esters 20 - 50 mg/L Aldehydes 5 - 10 mg/L Diacetal and 2-aceolactate < 0.1 mg/L
Higher alcohols 60 – 120 mg/L Acetic acid 120 – 200 mg/L Formic acid 20 mg/L Esters 20 – 50 mg/L Aldehydes 5 – 10 mg/L Diacetal and 2-aceolactate < 0.1 mg/L
Acetic acid $120 - 200 \text{ mg/L}$ Formic acid 20 mg/L Esters $20 - 50 \text{ mg/L}$ Aldehydes $5 - 10 \text{ mg/L}$ Diacetal and 2-aceolactate $< 0.1 \text{ mg/L}$
Formic acid 20 mg/L Esters 20 – 50 mg/L Aldehydes 5 – 10 mg/L Diacetal and 2-aceolactate < 0.1 mg/L
Esters 20 - 50 mg/L
Aldehydes $5-10 \text{ mg/L}$ Diacetal and 2-aceolactate $< 0.1 \text{ mg/L}$
Diacetal and 2-aceolactate < 0.1 mg/L
Acetoin < 3.0 mg/L
Total nitrogen 700 – 900 mg/L
Heat coagulable nitrogen 15 – 22 mg/L
High molecular mass nitrogen 150 – 250 mg/L
(21 - 22 % of total N)
Low molecular mass nitrogen 300 - 600 mg/L
Free amino nitrogen 80 – 160 mg/L
Bitter substances 16 – 25 EBC bitter uni
Total polyphenols 130 – 180 mg/L
Anthocyanidines 40 – 80 mg/L
pH 4.3 – 4.6
Viscosity (20 °C) $1.4 - 1.7 \text{ mPa} \cdot \text{s}$
Surface tension $42 - 48 \text{ dyn cm}^{-1}$

*Consisting of 80–85 % carbohydrates; 4 – 5.2 % proteins; 3.5 % glycerol; 3 – 4 % minerals; 2–3 % tannins, bitter substances, and coloring malt; 0.7 – 1 % organic acids; and a small amount of vitamins.

ily induced by the top-fermenting yeast strains of *Saccharomyces cerevisiae*. The particular yeast strain employed has a higher optimum fermentation temperature, and therefore the fermentation proceeds between 12 and 25 °C. During fermentation, the yeast rises and can be skimmed off the top. In large vessels, especially the cylindrical fermentation tanks with conical bottoms, the yeast is, however, cropped in the same manner as in bottom fermentation. The number of yeast generations is considerably greater. At the higher fermentation temperature, the amount of diacetyl is usually easily decreased. Because of the fast rate at which fermentation proceeds, a relatively low pH value of 4.1 – 4.3 results.

Types and Production of Top-Fermented **Beers.** The extract of original wort in wheat beer is 11 - 14%; the wheat malt portion can range from at least 50 to 100 %. An intensive two-mash decoction procedure is needed in the brewhouse in order to ensure satisfactory protein modification, because an increase in wheat malt proportionally decreases the concentration of assimilable nitrogen compounds in the wort. Because of the higher pitching temperature (12 – 18 °C), the pitching rate required will be lower (0.3 - 0.5 L) of yeast per hectoliter of original wort, corresponding to $7-15\times10^6$ yeast cells per milliliter). The aeration should ensure an oxygen concentration of 6 – 8 mg/L. The initial fermentation stage is characterized by the rise of trub particles and hop resins to the surface. After their removal, yeast rises to the top and can be cropped; this continues until the end of fermentation. The special wheat beer yeast can be repitched as often as 200 – 500 times. Wheat beer is characterized by a typical spectrum of fermentation byproducts, such as 4-vinylphenol and 4-vinylguajacol; these two compounds are responsible for the typical aroma of wheat beer. A more rapid and extensive pH drop, an increased formation of higher alcohols and esters, together with a greater decrease in nitrogen and bitter compounds, mark the course of wheat beer fermentation as compared with lager beer procedures. A higher bunging pressure during storage ensures a carbon dioxide concentration in wheat beer of 0.6 - 0.9 %. If wheat beer is marketed as "naturally hazy", the secondary fermentation can be accomplished in the bottle

by adding unfermented wort and bottom-fermenting yeast or bottom-fermented krausen. Crystal-clear wheat beer remains in the tank until mature and is subsequently filtered and bottled.

Alt beer also has an extract of original wort of 11-14 %. Methods vary widely for the production of the dark Alt beer which gives readings of 25-40 EBC coloring units: the wort may be produced from pale malt with the addition of caramel coloring or colored beer, 100 % dark malt, or 90 % pale malt and 10 % dark caramel malt. A proportion of 10-15 % pale wheat malt sometimes is used to round off the taste. The black malt which is used as a substitute for caramel may also be produced from wheat. The bitter substance concentration of Alt beer amounts to 25-40 EBC bitter units. The fermentation temperature is 12-22 °C.

Kölsch beer (extract of original wort 11-14%) may be produced only in the town of Cologne. It is brewed with pale barley malt by adding up to 10-20% wheat malt, and fermented at 12-22 °C, but sometimes up to 28 °C. The character of Kölsch and Alt, formerly designated as top-fermented bitter beers, is strongly determined by the properties of the specific yeasts; a large variety of flavors results.

Berliner Weisse (White) also is named after its place of origin; it has an extract of original wort of 7-8 %. Its very low pH value of 3.2-3.4 originates from the combined yeast and lactic acid fermentation. A degree of attenuation sometimes exceeding 100 % results in an alcohol concentration of 2.5-3 % and a lactic acid concentration of 0.25-0.8 %. The bitter substance content amounts to 4-6 EBC units, whereas the carbon dioxide concentration lies between 0.6 and 0.8 %. The beer has an acidic taste, which is marked by a pleasant estery – flowery quality, depending on the production method and the particular type of beer; it is frequently served with raspberry or woodruff syrup.

Sugar and sugar syrup may be used in the production of top-fermented nutrient *malt beers*. The malt beers are brewed with 7 – 8 % extract of original wort, and are enriched after filtration with sugar until an extract of original wort of 12 % results. The alcohol concentration of malt beer must be under 0.5 %. The pH lies between 4.5 and 4.9 depending on the method of wort production and

the degree of attenuation; the carbon dioxide concentration is 0.4 - 0.5 %, the color rating ranges from 50 to 80 ECB units (65 – 80 % dark malt, 3 – 5 % dark caramel malt, 3 – 5 % acid malt, and the remainder pale malt) and the bitter substance content is 6 – 10 EBC units. Malt beers are pasteurized on account of their high content of fermentable sugar.

British ales have an extract of original wort of 7-13 %, according to the tax category. Different sorts of malt, raw grains (roasted barley) and hops are use for the different ale types. English ales can be classified in following types:

- Mild Ale: The denomination Mild refers to the hop character and describes a slightly hopped beer. Mild is brewed as pale or dark ale and therefore can feature a strong malty character.
- Bitter Ale: In comparison to mild ale, bitter ale
 is a more strongly hopped ale, which is brewed
 with a higher hopping rate. In order to impart
 the desired hoppy aroma not only very late
 kettle hopping is usual, but also the addition of
 particular aromatic hop varieties during maturation or even cold storage.
- Pale Ale: The characteristics of pale ale and bitter ale strongly overlap. This beer also shows a stronger hop note, which can be somewhat milder than in the case of bitter ale. The color can be described as amber; the original wort can be slightly higher than in case of bitter ale.
- India Pale Ale: The name India pale ale (IPA)
 has its origin in the Victorian Age, when ales
 were exported from England to India by sea.
 These beers were often very strongly brewed
 (16 % o.g.) and hopped to avoid infection and
 aging during the long sea voyages.
- Brown ale designates a dark, very malt-aromatic ale.
- Old ale is mostly a dark type of ale which is not completely fermented so that the sweetness and taste of maltose are preserved in the beer. A historic interpretation of the name consists in the fact that these beers were already brewed in the wintertime for the summer months. According to this, the beer was already several months old by the time it was drunk.
- Scottish ales are very aromatic beers with a higher amount of residual extract, so that the full character is brought out. The color of these beers is described as gold-brown to dark

brown. The name derives from the original geographic location of the brewing region.

- Irish ale is characterized as malt-aromatic with a typically red color.
- Normal ales (keg ales) are those whose brewing process is finished in the brewery.
- Real ales (cask-conditioned ales) are draft or bottled beers brewed from traditional ingredients, matured by secondary fermentation in the container from which they are dispensed, and served without the use of extraneous carbon dioxide. The ale types described above or other ale types used as basis are transferred into barrels, if necessary with addition of finings, secondary fermentation sugar, and hops. The secondary fermentation is executed under control of the brewery or of an expert and trained pub staff. After delivery, the barrel is stored on a rack and should not be moved any more for clarification and sedimentation purposes. The carbon dioxide developed during secondary fermentation produces, beside carbonation of the beer, pressure in the barrel, which must be reduced in a controlled manner. The beer is traditionally dispensed through a beer pump (beer engine) without use of dispensing gas. Air replaces the beer in the same way as by tapping directly from the barrel.
- Stout is a dark, strongly hopped beer, with an extract of original wort between 11 and 18 %. The weaker stouts also are called *porter*. Some of these are treated with a special post-fermentation yeast (*Saccharomyces brettanomyces*), which imparts a typical aroma to the product. Stout is traditionally brewed with a certain amount of roasted barley that imparts a dark color of > 60 EBC and a specific roast barley/ roast malt flavor. It is also strongly hopped. It is often dispensed by nitrogen gas or a blend of N₂ and CO₂. Thus, a very creamy foam is generated.

Lambic, gueuze, and fruit lambic are Belgian spontaneously fermenting beers with an extract of original wort of 11 - 12 %. They are produced from certain admixtures of raw materials other than malt. The hop content varies widely, as does the method of wort production. Fermentation is not caused by a definite yeast strain, but by the airborne organisms of the fermentation rooms and vessels. Because of this spontaneous fermentation, the beers vary not only in their alcohol

level, but also in their lactic acid concentration. According to the amount of acidity, the beers are either left in a natural state and consumed with added sweeteners, or a specific amount of sweet mash is added. The most famous fruit lambics are kriek (cherry) and frambozen/framboise (raspberry).

Top-fermented strong beers with an extract of original wort of more than 16 % include the German pale and dark *Weizenbock* beers as well as the different varieties of stout.

3.5. Special Production Methods

A number of special production methods have been designed to produce beers with very specific properties. The legal regulations covering such products differ in various countries.

3.5.1. Dietetic Beer

Dietetic beers are pale beers of Pilsener brewing type; in Germany they may contain only 0.75 g biologically available carbohydrates and 0.5 g protein per 100 g of beer. In order to achieve these figures, wort of 11 - 12 % extract must be fermented until the apparent degree of attenuation is more than 100 %. Brewhouse procedures are adapted towards achieving this aim by employing mashing with extended rest periods at 60 -66 °C. During cold fermentation (7 – 12 °C), a small proportion of malt extract that has been drawn from the mash at 50 °C is added. This causes breakdown of the remaining high molecular mass carbohydrates and proteins. The addition of malt flour also has proved successful in obtaining the properties of dietetic beer. The beer must be carefully stabilized because the addition of unboiled extracts increases considerably the amount of coagulable nitrogen compounds. Almost complete breakdown and fermentation of the extract results in the alcohol concentration rising to 4.8 - 5%. This is partly viewed as a disadvantage. Thus, the alcohol concentration is subsequently lowered by either distillation in film evaporators or reverse osmosis. It is much easier to produce dietary beer with a lower extract of original wort because the control of both alcohol concentration and fermentation is simpler. The intensive fermentation leads to pH values in the

range of 4.1 - 4.5; the bitter substance content varies between 22 and 40 EBC units.

With regard to the nutritionally relevant composition of these beers different national regulation are in force. In the USA the so-called low carb beers may not have more than 20 g carbohydrates per liter, in Germany and Switzerland the value must be below 7.5 g/L, and in Austria these beers are forbidden.

3.5.2. Nutrient Beer

Nutrient beers are bottom-fermented beers which are brewed with 100 % malt. They are classified either as "low-alcohol" (alcohol concentration below 1.5 %) or as "alcohol-free" (alcohol concentration below 0.5 %). The extract of original wort of these very dark beers (60 - 80 EBC coloringunits) is between 11.5 and 12.7 %; the apparent degree of attenuation is 25 - 30 % in the lowalcohol beer and 8 – 10 % in the alcohol-free beer. The pH is 4.7 - 4.9, according to the degree of attenuation and other technological steps (acid malt); the bitter substance content is low (6 - 10)EBC units). The flavor of alcohol-free nutrient beers may be improved by increasing the alcohol concentration to 0.7 % and then blending with first-wort extract before filtration. It is also possible to remove the alcohol partly. Complete pasteurization of such beers is mandatory.

3.5.3. Low-Alcohol Beer and Alcohol-Free Beer

In case of the term "alcohol-free" national laws differ. Some countries allow an alcohol content of up to 0.5 vol %, other countries less, if a beer is declared as alcohol-free.

The techniques for the production of alcoholfree beers can be classified into two groups. When physical techniques are applied, the developed alcohol is removed after fermentation. In the case of biological methods, the development of alcohol is inhibited or kept within the limit mentioned above.

 Physical techniques: Beers that are fermented almost normally, but where part of the alcohol is later withdrawn by thin-film evaporation, vacuum distillation, reverse osmosis, or dialysis.

Biological techniques: Beers whose fermentation is interrupted by filtration and pasteurization. An alternative to heat treatment is a cold-shock process, during which a beer has just started to ferment is rapidly cooled in a thin film. This produces a spectrum of fermentation byproducts similar to that of normal beer.

Besides these, procedures are used in which special microorganism ferment selected parts of the fermentable extract. For instance *Saccaromyces ludwigii* metabolizes only hexoses and sucrose. The major fraction of the malt sugars, such as maltose and maltotriose, remains unfermented.

In the case of beers with absolutely no alcohol, no contact with industrial yeast is allowed.

Beers from physical techniques are more common, because the taste of the dealcoholized beer is more similar to that of normal beer.

3.5.4. Xan Wheat Beer

Xan wheat beer features a higher content of xanthohumol. Xanthohumol is a prenyl flavonoid (polyphenol) which is only found in the lupulin glands of hops and shows health-positive properties in in vitro examinations. Cancer-preventive activity and a growth inhibition of certain tumor cells were reported, as well as a strong antioxidative effect towards radicals, which can lead to cell damage. As xanthohumol is relatively unstable and easily eliminated during the brewing process, a special brewing procedure had to be developed to enrich xanthohumol in beer.

Xanthohumol is an nonpolar substance which dissolves in polar media only in low quantities and isomerizes to isoxanthohumol during boiling. Enrichment therefore is achieved by brewing with higher original gravity, by late and high hop addition, and by addition of cold brewing water. Rapid cooling of the wort to below 80 °C prevents isomerisation of xanthohumol. Another important factor is the roasted malt. Roasted substances are regarded as responsible for improving the solubilization of xanthohumol during the brewing process. Without roasted products, xanthohumol contents of 1 - 3 mg/L are possible in unfiltered beers; in beers with roasted products up to 10 mg/L can be reached even in filtered beers.

3.5.5. Gluten-Free Beer

Some people suffer from intolerance to gluten, a protein found in barley, wheat, and oat. This disease is called celiac disease or endemic sprue.

The production of gluten-free beer must be carried out with great care; even the yeast must be cultivated in gluten-free wort. For beer production sugary raw materials can be used which do not originate from gluten-containing sources, such as honey, sugar, and syrup. Here the definitions of beer and wine are mixed up, so in many countries such a product may not be sold as a beer.

A better way to produce a gluten-free beer is to use cereals which do not contain gluten. These are the pseudocereals amaranth (e.g., Amaranthus hypochondriacus), buckwheat (Fagopurum esculenum) and quinoa (Chenopodium quinoa), as well as the grain types sorghum (e.g., Sorghum bicolor), millets (e.g., Panicum miliaceum), maize (Zea maize), and rice (Oryza sativa) in unmalted or in malted form.

3.5.6. High-Gravity Brewing

This procedure is popular because existing installations can be better utilized and because a higher capacity can be achieved without new investment. In general, the wort is brewed as strongly as the brewhouse equipment will permit, e.g., with 13 - 18% extract of original wort instead of 11 – 12 %. Concentrations of 16 – 18 % are only attainable without loss of yield if syrups are added at the end of wort boiling. After fermentation and maturation (mostly during filtration), these stronger beers are adjusted to the desired extract of original wort with carefully processed water (deaerated, carbonated, and sterilized). The wort concentrations are usually not higher than 16 - 17% so as to maintain the ratio and level of byproducts and, thereby, the normal beer taste. High-gravity beers always have poorer head retention.

3.5.7. Beermix Beverages

Beermix beverages can be produced with all kinds of beer together with lemonade, cola, juice, or other ingredients. In most cases they consist of

50 % beer and 50 % of an alcohol-free refreshment. The alcohol content then lies in the range of 2.5 vol %.

Several variations are found on the market:

- Alcohol-free or with alcohol
- With one or more additives
- With functional ingredients
- Isotonic
- · Clear or hazy
- With minerals
- · With flavors
- Sweetened with sugar or artificial sweeteners [e.g., acetosulfame (E950), aspartame (E951), cyclamate (E952), saccharin (E954)].

3.6. Filling

After filtration, all operations must be directed to maintain the quality of the beer. Mistakes made at this point are very hard to rectify and will only become noticeable much later (re-infection and aged taste caused by a high oxygen concentration). Furthermore, the beer must be bottled under an appropriate pressure to prevent the release of carbon dioxide. Filling and packaging are subject to various legal regulations, just like the production of beer itself. These regulations pertain to labeling, container capacity, and volume tolerance [26].

The amount of beer lost depends on the production facilities, and to a certain extent on capacity, and ranges between 3 and 10 %. Examination of beer loss provides an insight into loss of volume, which occurs from casting to the actual process of bottling, and into loss of extract.

Kegging. Barrels are manufactured of oak wood, aluminum alloys, stainless steel, or plastics lined with stainless steel; their size ranges from 10 to 250 L. After the barrel has been thoroughly cleaned, it is purged with carbon dioxide or, less advantageously, with air, and filled under counterpressure (isobarometric). Bowless filling units not only avoid the danger of infection, but they also protect the beer from extensive contamination with oxygen.

Barrels with a cylindrical edge are called *kegs* or *system barrels*; they have a permanently installed fitting for cleaning, sterilization, filling, and tapping. With such a device, the barrel

remains sealed and under a pressure of carbon dioxide even after it has been emptied. In this fashion the drying-up of beer remnants is avoided, and cleaning is facilitated. Cleaning and filling under sterile conditions are easily automated. Kegs and fittings are standardized.

Cellar Tanks. For larger distributors stationary draft beer tanks which hold 10 to 30 hL can be installed. The beer is delivered from the brewery in large tank trucks. The cellar tanks are equipped with cooling devices. They are lined with disposable polyethylene bags, which make it possible to store the beer under impeccable sanitary conditions without the need to clean the cellar tank. The excess pressure necessary to dispense the beer is created by gas which is admitted between the inner wall of the tank and the polyethylene bag.

Bottling. Bottles may be made of glass or plastics (PET, PEN). Whereas glass is diffusion-proof, not only can carbon dioxide escape from plastic bottles, but also oxygen can diffuse into the beverage, and cause an undesirable oxidation taste. A metal crown with synthetic liner is widely preferred over other means of sealing the bottles. Returnable bottles must be cleaned to a microbiologically impeccable standard before refilling. Disposable bottles are relatively expensive because their manufacture requires more energy and raw material than multiple-use bottles.

Isobarometric bottling is best carried out by pre-evacuation of the bottles and pressurizing with carbon dioxide. After filling fobbing is induced by various means; this provides for a maximum displacement of air. The crown closure machine presses the crimped edges of the crown around the mouth of the bottle, which is then labeled automatically. Modern bottling machines fill up to 120 000 bottles per hour. Brown glass bottles are preferred to those made of green or colorless glass, because they protect the beer letter against light of short wavelengths, which causes photodegradation of the bitter acids of hops, and hence gives rise to lightstruck beer.

Canning. Cylindrical cans of aluminum or tinplate are closed with a flat lid equipped with a ring pull-tab. A nonporous synthetic resin coating is applied to the inside of the can to prevent a

chemical reaction occurring between the metal and the liquid. Pre-evacuation is only possible with stable tinplate cans. Otherwise cans are blown out with an inert gas; alternatively, carbon dioxide is blown under the lid of the can after filling.

3.7. Labeling and Declaration

The options for product dress today are many and varied: body, shoulder, neck-around, back, and wrap-around labels made of numerous different materials are available. Casein-based glue, whose basic constituent is obtained from milk protein, is the most widespread choice for applying paper labels or aluminum foils on glass.

Bottlers have to mark the label with the bestbefore-end date and an internal batch number, which is necessary for the identification backward and forward. This can be done by inkjet or laser printer, stamping, or perforating.

3.8. Beer Dispensing

After filling and transportation the beer should be stored at a temperature of 6 - 9 °C without movement. Bottled beer should be stored in the dark. For draft beer it is important to maintain the carbon dioxide level established in the brewery right up to the end of dispensing, and moreover to transfer the carbonation into the glass without loss. This is achieved by dispensing the beer with a carbon dioxide pressure higher than that of the saturation pressure in combination with a pressure compensator. The clean, thin-walled glasses used exclusively for beer drinking should be rinsed with fresh, cold water just before the beer is tapped so as to equalize the temperature. Special care should be taken in the cleaning of beer glasses in order to remove traces of fat which might otherwise cause premature collapse of the sensitive foam, and also to maintain the good flavor of the beer.

4. Properties and Quality

Foam. More than any other beverage, beer is marked by its natural ability to form foam. The release of carbon dioxide during tapping is responsible for foam stability whereas the

sparkling of carbon dioxide bubbles in the tapped beer is responsible for head retention. Both foam stability and head retention, as well as the liveliness of the beer, depend largely on the carbon dioxide concentration. A foam-stabilizing effect is ascribed to colloids, such as proteins, glycoproteins, tannins, β -glucans, and isohumulone complexes; on the other hand, fatty acids, glycerides, and ethanol in an amount in excess of 7-8 wt % destabilize foam.

Color. The color of beer is first of all determined by the malt type and ranges from the pale Pilsner type to the dark Munich type with a lot of variations in between. During the brewing process an increase in color is caused by temperaturedependent, nonenzymatic color reactions of the Maillard type, but also by nonenzymatic and enzymatic reactions of the polyphenols. In pale beers the increase in color should be limited. This may be difficult when kilning overmodified green malts, possibly heated with gibberellic acid. Further color pickup occurs during mashing, wort boiling, the hot wort stand in the whirlpool, and also by oxidation reactions during wort production and bottling/canning. A reduction of the color takes place during fermentation due to the pH drop, as well as later during filtration.

Buffering and Reduction Potential. The buffering substances present in the beer are chiefly weak acids and their salts, primary and secondary phosphates, and proteins. Depending on their chemical identities and concentrations, they can counteract the pH changes that occur during malting and during wort preparation, and they can aggravate the pH drop during fermentation. The reductones that are formed during malt, wort, and beer production are of great importance for the stability of the beer. Furthermore polyphenols from malt and hops build up a reduction potential during wort production. By adding antioxidants, the reduction potential can be increased further.

Sensory Qualities. The odor and the taste of the beer, as well as the mouthfeel, are evaluated with regard to quality and intensity by tasting experts. The temperature of the beer during tasting should be 6-10 °C. In a taste evaluation one differentiates between the initial impression, for which the aroma and palate fullness are mainly

responsible, the liveliness, where the impression of freshness emerges (a function of carbon dioxide release and the organic acids present), and the aftertaste, where the quality and intensity of the bitterness are put to the test. Tasting experts must be selected carefully and kept in constant practice. An international nomenclature with guidelines for the description of the impressions of beer flavor has been developed.

Flavor Stability. After bottling the beer, numerous changes in its original properties occur. The changes in palate fullness and in liveliness are caused by an agglomeration of colloidal particles, which in turn is facilitated by oxygen and by changes in temperature. Palate fullness declines, and the bitterness becomes coarser and broader. Beer aroma undergoes a change due to numerous reactions contributing to an "aged" quality, which is also described as oxidation or bready flavor.

Careful selection of the raw materials, wort production without any oxidation, control of the formation of carbonyl compounds during wort production, and an optimal fermentation are the prerequisites for a flavor-stable beer, which must be packaged without any access of oxygen.

5. Analysis

5.1. Analysis of Raw Materials

5.1.1. Water

In the food-processing industry, drinking and process water must comply with certain quality standards from the bacteriological, hygienic, and chemical points of view. The hardness of water can be determined by complexometric titration, which gives an idea of the concentrations of carbonate, hydrogencarbonate, and hydroxide in the water. The calcium and magnesium hardnesses must be determined to estimate the residual alkalinity.

5.1.2. Malt

The congress mashing method is used to study the parameters that determine the modification properties of the malt. In this method, ground malt is subjected to a simple infusion mash process whereby the temperature must first be maintained at 45 °C for half an hour, and is then gradually increased at the rate of 1 K/min to 70 °C; this temperature is finally maintained for one hour.

The cytolysis of the malt is defined by its friability, which is determined physically or by the viscosity of the congress wort. The former fine – coarse grind difference has proved to be less reliable and reproducible. The proteolysis is defined by the ratio of dissolved nitrogen compounds to the total nitrogen content of the malt (as determined by the Kjeldahl method). The amylolysis is expressed by the saccharification time of the congress mash at 70 °C and the final attenuation of the congress wort.

Microscopic staining in combination with statistical methods is being increasingly used to estimate the uniformity of modification. Other qualitative characteristics are the enzyme potential, friability, and purity of the barley variety.

5.1.3. Hops and Hop Products

The bitter compounds can be isolated by fractionation of resins or by using HPLC. During the fractionation of resins, hop ingredients are distributed between an acidic aqueous methanol phase and diethyl ether. The bitter ingredients, which are extracted into the ether phase, are classified according to their solubility in methanol and hexane into total resins, soft resins, and hard resins. Depending on their ability to form lead salts the soft resins are further classified into α - and β -fractions. Using the HPLC method each of the homologues of the α - and β -acids and their oxidation products can be separated.

5.2. Brewhouse Control

The yield of the as-is extract (air-dried) from the congress mashing method is a measure of the yield achieved in the brewhouse during large-scale preparation of the wort. For this the extract of original wort and the quantity of the cast wort must be determined.

Nowadays in brewhouses of high capacity the yield in the cast wort is difficult to determine. Thus overall brewhouse yield (OBY) is determined by measuring the volume and extract of

the cold wort prior to fermentation. Exact inductive flow meters and measurement of the cold wort extract are necessary. Spent-grain analysis gives an indication of the effectiveness of the extraction process during wort filtration.

5.3. Wort

The chemical composition of the wort is also of interest; amylolytic degradation and saccharification of starch components should be advanced in such a manner that only very few compounds that are stainable with iodine remain in the wort. When turbid lautering occurs, further stainable starch particles are solubilized during wort boiling. Furthermore, turbid lautering also leads to an increase in the long-chain fatty acids content in the wort.

The gum content of the wort (determined by precipitation with salts, or precipitating agents or after isolation, using gel permeation chromatography) can only slightly be influenced by the choice of the mashing procedure. It depends mainly on the modification and the enzymatic capacity of the malt.

The degree of protein degradation during mashing can be measured from the contents of amino acids and dipeptides in the wort and from fractionation of the nitrogen compounds. The amount of coagulable nitrogen and the quantity of precipitated trub give information on the intensity of wort boiling. An idea of the various Maillard reactions, which take place during boiling, is given by the concentrations of the aroma compounds in the wort (carbonyl compounds, alcohols, Maillard products), which are quantitatively determined by GC.

The isohumulones are the most important bitter compounds in the finished wort and in the beer. They are extracted from the acidified sample with isooctane, and their concentration is determined by spectrophotometry. The extinction of the isooctane extract at 275 nm is multiplied by 50, and the value thus obtained is taken as the bitterness (in EBC bitter units) according to the standards of the European Brewery Convention (EBC) and the American Society of Brewing Chemists (ASBC).

The attenuation limit is determined by fermenting a wort sample with an excess of yeast at room temperature.

5.4. Fermentation

The most important parameters during fermentation are the decrease in extract, the pH, and the temperature. The practice of keeping a record of the yeast cell concentration from pitching to the end of fermentation using the electronic Coulter counter or microscopic count methods (Thoma chamber) is gaining increasing importance.

Gas chromatographic methods have proved to be useful in estimating the aroma components. Whereas the more concentrated fermentation byproducts in the ppm range can be used to judge the fermentation and possible organoleptic deviations, certain trace components in the ppb range can serve as indicator substances for identification of the process technology. The acetoin concentration is used as an indicator for the vitality of the yeast. After a relatively simple workup method (steam distillation of the sample followed by extraction of the distillate with dichloromethane) about 60 individual components can be detected in a single run by using modern GC and high-resolution capillary columns. Along with selective detectors (sulfur detector, nitrogen detector), this figure can be increased considerably.

5.5. Microbiological Process Monitoring

In a brewery the main contaminants are lactobacilli, *Pediococcus cerevisiae*, and "wild yeasts" (*Saccharomyces* species). Gram-negative bacteria (genus *Megasphaera* or *Pectinatus*) may also be dangerous.

Direct viewing under the microscope, biological shelf-life tests, and enrichment methods are used. Shelf-life tests show microbiological stability of the beer during storage at 27 °C. The yeast sediments of samples taken from the fermentation and the storage cellars are observed under the microscope after a period of about 20 days. In the case of filtered samples, trace infections are detected by enrichment on a solid or liquid nutrient medium. By using membrane filtration techniques, the microorganisms on the filter are incubated anaerobically under optimal growth conditions on solid agar. The samples can be evaluated after an incubation period of two

days with aerobic incubation (wort agar) and five days (NBB agar; NBB = culture medium for bacteria harmful to beer) with anaerobic incubation. Color changes in liquid NBB broth or solid NBB agar indicate the presence of harmful bacteria.

The number of biological controls and the choice of culture media depend on such factors as selectivity, specificity, and output of the brewery. As a routine procedure, the pitching yeast as well as bottled beer stored for a specific period should be analyzed.

5.6. Beer

The extract of original wort of the finished product can be calculated from the density and refractive index of the decarbonated beer or from the densities of beer distillate and the distillation residue.

The methods described in Section 5.3 are also used for beer. The carbon dioxide content is determined by measuring the total pressure of beer after vigorous shaking at a specific temperature.

The physicochemical stability of the beer is estimated from an accelerated aging process. In this method filled beer bottles are kept alternately at 40 °C (or at 60 °C for stabilized beer) and at 0 °C until an increase of turbidity by 2 EBC formazine units occurs after cooling. By multiplying the obtained stability period, expressed as number of 40 °C (or 60 °C) warm days, by a factor that is specific to each brewery, one can calculate the period of time during which the beer would not become turbid under normal storage conditions.

The carbon dioxide content of the beer determines its foaming capacity. The head retention is dependent on the composition of the beer. The methods of foam measurement are classified according to the way the foam is generated: (1) free fall, (2) shaking, (3) bubbling of a gas, and (4) catalytic release of carbon dioxide.

Color can either be measured by visual comparison under defined conditions or spectrophotometrically by measuring the extinction of the sample at 430 nm and that at 700 nm; this difference, multiplied by 25.5, is defined as the color in EBC color units.

Flavor stability can be judged by storing the packed beer at 20 or 30 °C for three or two months, respectively, and comparing it with beer from the same batch stored at 0 °C. A quicker result is obtained by the "forcing test" (one day at 20 °C, four days at 40 °C, one day at 0 °C) and comparing to a beer kept at 0 °C. The beers are then tasted and the degree of aging denoted. GC analysis gives a possible hint to the causes of flavor deterioration.

5.7. Legally Required Controls

In order to comply with the requirements of the food laws, the extract of original wort or the alcohol content must be within certain limits. Further, the filling volume in the bottles must be within required tolerances. Nevertheless, it is still indispensable that the brewmaster is responsible for determining by taste test as well as the beer is ready for filling and as before it leaves the brewery.

6. Economic Importance

Sinceca.1998 beer consumption increased by more than 20 % worldwide. Despite stagnation in several major beer-consuming nations the total market size of 1.698×10^6 hL reached a new peak in 2006. Consequently the per capita consumption increased, too, to reach 26.4 L in 2006 [27].

The most popular product is the pale, bottom-fermented lager of typically 4.5 - 5.5 vol % alcohol. Worldwide 65 % of beer is marketed in bottles, 20 % in cans, 12 % in kegs or barrels (draught beer), and 3 % in PET.

The Barley and Malt Market. Barley takes rank four in the production of cereals worldwide. The annual production of barley is about 140×10^6 t. For 1.7×10^6 hL of beer production a quantity of 28×10^6 t of barley (ca. 23×10^6 t of malt) and 6×10^6 t of other cereals are necessary [22]. The largest malting companies are listed in Table 7.

The Hop Market. The world hop crop in 2006 was 85 569 t with an average α content of 8.3 % (7102 tons α). Fine aroma hops took a

Table 7. The largest malting companies

Company	Country of origin	Production capacity, 10^6 t/a	Global market share, %
Groupe Soufflet	France	1500	8.2
Groupe Malteurop	France	1330	7.3
Cargill Incorporation	USA	1290	7.1
United Malt Holdings	USA/Canada	1125	6.2
IMC	USA	925	5.1

share of 17.0 %, aroma hops 26.3 %, and bitter hops 56.7 %. Table 8 lists the utilization of the different hop products.

When looking at the key players in the global hop market it is noteworthy that 85 % of the total volume is controlled by only four companies (Table 9).

The Beer Market. Table 10 lists production and consumption figures and also the number of breweries in each country.

The consolidation in the global beer industry has only begun during the last 15 years and has not yet come to an end. Besides a few brewers which left their home markets very early, the industry was affected by national and not by international groups. After the recent mergers between Interbrew and AmBev, SAB and Miller, or Coors and Molson global players are gaining more and more weight. The top ten brewers worldwide are listed in Table 11.

Third ranked Anheuser-Busch, whose growth has always been internal, sells more than 86 % in its home market. In comparison, Carlsberg and Heineken are selling approximately 5 % and

Table 8. Utilization of hops and hop products

Hop cones	5 %
Hop pellets	45 %
Pre-isomerized hop pellets	10 %
Hop extract	27 %
Pre-isomerized hop extract	3 %
Downstream products	10 %

Table 9. Top hop companies and their global market shares

35 %
30 %
10 %
10 %

Table 10. Beer production volume, per capita consumption and number of breweries in 2004

Country	Production volume, 10 ⁶ hL/a	Per capita consumption, L/a	Number of breweries
China	291	17	500
USA	232	79	1800
Germany	106	117	1279
Brazil	86	50	43
Russia	85	58	300
Mexico	69	53	22
Japan	66	56	33
UK	59	99	60
Spain	31	88	21
Poland	28	77	65
Americas	492		
Europe	529		
Asia	440		
Africa	71		
Australia and Pacific	21		

SAB Miller around 18 % in their respective domestic markets.

Table 12 shows the leading brewers by region. When comparing the market share of single brands with those of their owners, a "global brand" is hardly evident Table 13.

A survey of the productivity and quantities of energy and water consumed for breweries of different sizes is given in Table 14.

Taxation. The varieties of beer are classified into various tax groups on the basis of their extract of original wort or alcohol content. The groups differ from country to country. There are different means of tax collection: (1) raw-material taxation, which is based on weight or volume of the brewing materials used; (2) intermediate

Table 11. World top ten brewers in 2004

Company	Country of origin	Annual output, 10 ⁶ hL	Global market share
InBev	Belgium/Brazil	183.7	11.9 %
SAB Miller	South Africa/USA	178.3	11.6 %
Anheuser-Busch	USA	144.2	9.3 %
Heineken	The Netherlands	117.5	7.6 %
Carlsberg	Denmark	67.6	4.4 %
Coors	USA/Canada	57.6	3.7 %
and Molson			
Scottish	UK	51.4	3.3 %
& Newcastle			
Modelo	Mexico	42.8	2.8 %
Tsingtao	China	37.1	2.4 %
(group)			
Kirin	Japan	36.0	2.3 %

Table 12. World top brewers by region 2004 (10⁶ hL)

Europe		The Americas		Asia/Pacific		Africa/Middle East	
Company	Sales	Company	Sales	Company	Sales	Company	Sales
Heineken	80.0	Anheuser-Busch	124.9	SAB Miller	37.3	SAB Miller	33.1
InBev	69.1	InBev	91.2	Tsingtao (Group)	36.9	Heineken	13.5
Carlsberg	58.2	SAB Miller	73.1	Kirin	34.6	Castle/BGI	12.2
Scottish & Newcastle	50.0	Coors and Molson	45.1	Asahi	31.6	Diageo (Guinness)	7.7
SAB Miller	34.8	Modelo	41.8	Beijing Yanjing	28.9		
Radeberger	16.8	FEMSA	25.6	InBev	22.9		
Anadolu Group (Efes)	13.6	Heineken	14.5	San Miguel Corps	20.7		
Coors and Molson	12.4	Polar	14.4	Anheuser-Busch	16.2		
Mahou	10.6	Schincariol	13.4	Henan Gold Star	12.3		
Diageo (Guinness)	8.4	Papst/S & P	8.8	Suntory	11.4		
	353.9	-	452.8	-	252.8		

Table 13. World Top ten beer brands (2004)

Rank	Brand name	Brand owner	Sales, 10 ⁶ hL	Market share
1	Bud (range)	Anheuser-Busch	48.20	3.12 %
2	Budweiser	Anheuser-Busch	47.40	3.07 %
3	Skol (Brazil vol. only)	InBev	31.20	2.02 %
4	Corona	Modelo	28.20	1.83 %
5	Heineken	Heineken	22.80	1.48 %
6	Coors Light	Coors and Molson	21.20	1.37 %
7	Miller LITE	SAB Miller	20.70	1.34 %
8	Brahma Chopp	InBev	19.70	1.28 %
9	Super Dry	Asahi	19.60	1.27 %
10	Busch (range)	Anheuser-Busch	15.80	1.02 %

product taxation, which is assessed according to the volume of the wort; and (3) finished product taxation, which is levied on sale

7. Physiology and Toxicology

According to standard definitions, beer is classified as a food. In addition, it acts as a stimulant. The calorific content of beer as a nutrient may be calculated from its concentrations of protein, carbohydrate, and alcohol, as well as organic acids. A rough estimate in kJ/L can be obtained by multiplying the extract of original wort

Table 14. Productivity and specific energy and water consumption as an a function of brewery size

Annual brewery output	$>$ 10 6 hL	>10 ⁵ hL	>10 ⁴ hL
Productivity, hL per employee Current consumption, kW h/hL	10 000 7	4 000 9	2 000 11
Heat consumption, kW h/hL	23	30	40
Water consumption, hL/hL	3.5	4.5	5

(in wt %) by a factor of 150. Hence beers with 10 – 14 % extract of original wort have an approximate calorific value of 1500 – 2100 kJ/L. From a nutritional point of view, the amino acids (on an average 140 mg/L) and vitamins (20 – 25 mg/L) are especially valuable. One liter of beer contains about 40 μg thiamine, 400 μg riboflavin, 7500 μg niacin, 650 μg pyridoxine, 1500 μg pantothenic acid, and 800 μg folic acid.

The consumption value of beer may be derived from its ingredients. Thirst quenching is accomplished by its high water content and its mineral concentration (total around 1000 mg/L, consisting of: sodium 20 – 30 mg/L, potassium 500 mg/L, calcium 30 mg/L, phosphorus 300 mg/L, and magnesium 100 mg/L). Carbon dioxide (4 – 8 g/L) and organic acids (up to 600 mg/L) have a relaxing, calming and, at the same time, stimulating effects. The dietetic effect of the beer is based mainly on its low sodium concentration. Because it also is free of fats, it will promote urination.

Pathogenic and toxic bacteria cannot survive in beer because of the presence of alcohol, carbon dioxide, bitter substances, and the low pH. A

proper balance between alcohol and assimilable carbohydrates, proteins, phosphates, and vitamins results in a lower increase in blood alcohol levels by comparison with other alcoholic beverages. The toxicology of ethanol is treated elsewhere (\rightarrow Ethanol).

A daily consumption of 60 – 80 g alcohol (corresponding to 1.5 - 2 L of beer) by a healthy, adult male, or of 40 – 60 g alcohol by a woman is not harmful. These guidelines vary according to body weight, age, nutritional habits, environment, and occupation as well as psychological condition. Moderate beer consumption also leads to longer life expectancy, has a lowering effect on blood pressure, and is beneficial to persons suffering from peptic ulcers. Moderate consumption of alcohol results in an increased level of cholesterol bound by high-density lipoproteins (HDL), which have a protective effect on blood vessels. These findings can be further explained by the antithrombocytic properties of alcohol.

Harmful Substances. Numerous nutritional regulations, especially the Reinheitsgebot, require the amount of additives in beer to be kept to a minimum.

Heavy metals derived from raw materials are mostly removed during the malting and brewing process; beer is one of the beverages lowest in heavy metals (lead, 1 – 3 μg/kg; cadmium, $0.1 - 0.5 \,\mu g/kg$; mercury, always less than 0.1 µg/kg). Mycotoxins and insecticides have not been found in beer until now. Fungicide sprays, especially dithiocarbamates, are used in hop growing. The residues contained in the hops are metabolized during wort boiling to ethylenethiourea and propylenethiourea, which are only partially removed in the further brewing process and remain in the beer. The necessary sprayings could be reduced considerably by breeding disease-resistant types as well as by an early warning system. The concentrations of residue can also be cut to less than 5 mg/kg by allowing a time lapse of several weeks between the last spraying and the actual harvesting. Various hop extraction procedures also can lower the concentration of dithiocarbamates.

The WHO recommends a limit of *nitrates* of 50 mg per liter of potable water. The nitrate in the wort originates mainly from water and hops. Nitrate is reduced to nitrite, which is poisonous

to yeast. However, its concentration is much below the threshold considered critical by the WHO. Nitrate can be most effectively removed from the brewing water by anion exchange. The nitrate content of hops is reduced in concentrated pellets, and it is zero in resin extracts.

The concentration of highly carcinogenic N-nitrosodimethylamines is virtually negligible, because kilns are fired indirectly nowadays. With average values of less than 0.5 μ g/kg, beer produced today is no longer significant as a potential source of nitrosamines.

The byproducts formed during fermentation, such as higher alcohols, esters, and aldehydes, are of more importance for the aroma of the beer than for its wholesomeness. No connection has been found between the level of higher alcohols, fats, and aldehydes and the incidence of hangover.

Sulfur dioxide is a true fermentation byproduct. Bottom-fermented lager or pilsener contains 0-10 mg/kg and top-fermented beers have 0-5 mg/kg, whereas strong beers may contain more than 10 mg/kg. The source cannot be traced back to the sulfur content of the malt, the hops, or the brewing water. It is formed during fermentation, which is adjusted such that to 5-10 ppm SO_2 is formed to ensure good flavor stability of the beer.

Histamine, a metabolite of histidine, occurs in beer in amounts of under 0.5 mg/kg and has no toxic effect at this level. The *nucleic acid components* of beer originate from the raw materials. The yeast needs adenine and guanine for its growth and removes part of these substances during fermentation. The purines of the finished beer are broken down to uric acid in the human body, which can cause gout if the amount exceeds the solubility in blood. Bottom-fermented lager beers contain 70 – 130 mg purine per kilogram; in wheat beers the figure is around 80 mg/kg.

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