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Barley malt substitutes – their role today and in near future. Part 1 – Sugar adjuncts and barley, corn and rice as cereal adjuncts

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Abstract

Although barley malt is considered a traditional appropriate raw material for beer production, there are several reasons to introduce alternative sugar or starchy materials into brewing. Economic and market demands play a crucial role in the selection of raw materials. However, different adjuncts bring various technological challenges due to their specific physicochemical properties as well as the degree of processing when entering to the brewery. This review is focused on the current practice as well as on innovations in the use of several barley malt substitutes. The beer production from various proportions of adjuncts is presented step by step and the pros and cons associated with technological changes and equipment are discussed. The impact on sensory character is also considered. The aim of the paper is to offer theoretical background and reveal the latest possibilities for practice.

Keywords: brewing adjuncts; barley malt substitutes; sugar adjuncts; starchy adjuncts; barley; corn; rice

1 Introduction

Beer as a cereal drink has accompanied mankind since ancient times. Especially in Europe, barley and wheat have gradually become the main cereal raw materials for beer production. Further evolution led to the preference of (malted) barley as a basic source of saccharides for beer production. Many factors contributed to this selection, particularly climatic changes along with agricultural aspects and practical reasons, e.g. wheat was preferred for nutrition particularly at the time of crop failure (Holub and Fiala, 2022). Moreover, barley has been found to be very suitable for the brewing technology firstly due to its high starch/protein ratio which promises favourable extract for yeast growth and fermentation, and secondly for it structure allowing easy and economical processing (Lowe et al., 2004; MacLeod and Evans, 2016). Thus barley full malt beers have come to the forefront and with their typical malt sensory properties they have been perceived as products of the highest quality up to these days (Basařová et al., 2021; MacLeod and Evans, 2016). Despite the above-mentioned points, today more than 80% of the world beer production uses barley malt alternatives and this trend is still continuing (Bogdan and Kordialik-Bogacka, 2017; Hertrich, 2013; Moll, 1994; Stewart, 2016a; Zarnkow et al., 2007). Stewart (2016a) reported that in the USA unmalted adjuncts accounted for an average of 38% of all brewing materials (except hops), with the most common being corn 46%, rice 31%, barley 1% together with sugars and syrups that constitute 22% of total adjuncts. Bogdan and Kordialik-Bogacka (2017) add that in European countries unmalted adjuncts make up to 10–30%, in Australia over 40–50%, and in Africa due to its different climatic conditions it is 50–75%.

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These "malt alternatives" or in other words "adjuncts" or "substitutes" are usually understood as a raw material providing such beer extract that is different from barley malt (Basařová et al., 2021; Stewart, 2016a). They are generally divided according to their state of matter into solid or liquid, or according to the type of extractive substances into starchy and sugar adjuncts (Basařová et al., 2021; Helstad, 2013). This division will be discussed in the following chapters.

The reasons for the worldwide and widespread preference of barley malt alternatives are as follows:

- economic;
- agricultural;
- socio-political;
- environmental;
- health and dietetic;
- sensorial;
- technological.

Malt substitutes are used in brewing mainly from the **economic** point of view and the pressure on production cost still raises. The fermentable saccharides originating from malt alternatives are considerably cheaper than those from malted barley, because malting is an energy intensive process and the price of beer has to reflect among others also this energy cost. For example, Poreda et al. (2014) reported that an added share of 30% of unmalted corn can save 8% of the beer cost in Brasil. Aastrup (2010) stated overall savings of 0.5–1.0 €/hl associated with 100% of unmalted barley grist, including changes in technology and differences in material costs. The real particular savings should be calculated based on local prices and the adopted technology.

Agricultural aspect is closely linked to economic reasons. In general, diverse crops including (pseudo)cereals can thrive in different geographical areas. Some territories are not suitable for barley growing but other (pseudo) cereals are abundant. The beer production there is based on local cheap raw materials rather than on expensively imported barley malt (Bogdan and Kordialik-Bogacka, 2017) or technically impossible storage, e.g. tropical areas (Dabija et al., 2021). Thus, barley and corn are typical for Europe, rice for Asia, corn for America and sorghum for Africa (Bogdan and Kordialik-Bogacka, 2017).

Other **socio-political** circumstances, such as economic crises or wars as well as tax regulations, also play an important role in a production strategy. For instance in Japan, the taxes on beer and beer-flavoured products are assessed on the basis of malt content, i.e. less malt equals lower taxes (Masayuki, 2018).The ban on imports of barley and barley malt into Nigeria between 1985 and 1999 caused the introduction and spread of malt alternatives, which persist to this day, even though the ban is no longer in force (Kok et al., 2019; Taylor et al., 2013). Also the famous Bavarian Beer Purity Law (*Reinheitsgebot*) regulates ingredients for beer production and precludes the replacement of malt by other sources of starch or sugar (Basařová et al., 2021). Currently, most breweries in Germany, Norway and Greece follow *Reinheitsgebot* (Stewart, 2016a) as well as many other breweries around the world claim to comply with this regulation mainly due to a marketing strategy (Beer Cartel, 2018; German Culture, 2022; Kok et al., 2019).

Further, malt substitutes have turned increasingly important in terms of **environmental** sustainability and the availability of raw materials due to climate change. Carbon emissions are principally in proportion to energy consumption, therefore unmalted (pseudo)cereal alternatives are an attractive choice for reducing the carbon footprint of malting and brewing chain. To give an idea, the intensive agricultural production of barley, which employ multiple tilling together with application of fertilizers and pesticides, accounts for 241 kg CO_2^e/t. Energetically demanding malting process add up other 217 kg CO_2^e/t (Muntons, 2020). Thus barley malt production accounts for a considerable proportion of total CO_2 emissions released during beer production. Numerical expressions differ significantly depending on a calculation method and the assumptions on which it is based (Amienyo and Azapagic, 2016). Just to give an idea: according to BIER (2012) CO_2 emissions for barley malt accounted for 39% of the entire malting-brewing chain in Europe and 33% in North America. Aastrup (2010) reported that a complete replacement of malt by raw barley can reduce CO_2 emissions by 8%. Also saving the water used for grain steeping and germination should be mentioned as a step for reducing of environmental burden (Kok et al., 2019).

The global climate change is expected to have important implications for barley production. Crop and economic models have predicted that extreme weather can cause a significant reduction in barley yields worldwide with a potential loss of up to 17% (Xie et al., 2018). The use of many barley substitutes may therefore play a role in securing the supply of raw materials for brewing in the future. One of the sustainable barley alternatives seems to be corn, because the climate change is not expected to have a serious negative impact on corn in the USA and China according to predictive models (Li et al., 2011).

Health and dietetic circumstances cannot be overlooked even in the case of beer. Malt substitutes represent important raw materials in the production of beers intended for a specific group of people such as celiacs. These gluten free beers cannot be produced from barley, wheat or rye but from gluten-free cereals such as sorghum, buckwheat, rice or corn. Oat, with its favourable protein composition, is on the threshold of safety for gluten intolerance, so it appears to be a promising raw material with low gliadin content (Kordialik-Bogacka et al., 2014).

The interest in malt substitutes is growing due to the effort to improve **sensory properties** or find new attractive ones, which is in line with the worldwide boom of innovative and completely different products (Bogdan and Kordialik-Bogacka, 2017). Also, several already existing and popular beverages cannot be produced without adjuncts, e.g. German wheat beers and similar Belgian and Northern European whites or Belgian lambics (Hertrich, 2013). The general **technological aspect** goes hand in hand with the focus on sensory properties. In this regard malt adjuncts can improve colloidal stability and shelf-life especially in case of low-alcoholic and lighter beers (Bogdan and Kordialik-Bogacka, 2017; Goldammer, 2008; Hertrich, 2013). They can greatly facilitate the beer stabilization due to the low content of soluble proteins and negligible amount of polyphenolic compounds (with the exception of unmalted barley) (Basařová et al., 2021; Goldammer, 2008; Hertrich, 2013). The use of substitutes enables to reach a higher attenuation degree, which is useful in the production of high-alcoholic or on contrary low-alcoholic beers (Basařová et al., 2021; Bogdan and Kordialik-Bogacka, 2017; Gallagher et al., 2004; Hertrich, 2013). Furthermore, it has been reported many times that a small portion of unmalted adjuncts can significantly alter the sensory profile of beer and this small change in recipe leads to a product with a completely new flavour (Kordialik-Bogacka et al., 2014; Piddocke et al., 2009; Yeo and Liu, 2014).

The impact of alternative raw materials on sensory characteristic can be positive as well as negative, depending on product specifics. For example, colour is usually lighter, mouthfeel and beer body are more delicate and less full, foaming is less intensive and less stable (Hertrich, 2013).

It must be added that despite the many aforementioned benefits, replacement of classical barley malt also brings some technological challenges including deteriorated fermentation due to the low level of free amino nitrogen (FAN) (Basařová et al., 2021; Hertrich, 2013; Kunz et al., 2012), higher temperatures needed for gelatinisation of starch not originated from malt barley or lower enzymatic potential and associated lower brewing yields (Basařová et al., 2021). However, scientific knowledge contributes to a deeper understanding of the brewing process and the undesirable consequences of the used malt substitutes can be minimized with modern means in particular due to a large selection of enzyme preparations (Kunz et al., 2012).

The objectives of this review are to present the current knowledge on the use of malt substitutes from a practical point of view. The latest scientific studies on the application of sugar adjuncts and three main cereal adjuncts are presented and discussed. The paper also deals with specifics of the technological processing of individual cereals, evaluation of positive and negative aspects of their use, possible degree of surrogation as well as sensory properties of the resulting beer. Nonetheless, more cereals, pseudo-cereals and less significant starchy tubers will be included and discussed in Part 2.

2 Sugar adjuncts

Sugar adjuncts are preparations based on the content of soluble saccharides, i.e. simple fermentable sugars such as glucose, fructose, maltose or saccharose that can be accompanied with more complex non-fermentable dextrins. They are available either as solids or as liquids. They usually come from agricultural sources rich in sugar (e.g. sugar cane/beet) or starch (e.g. cereals, potatoes). The latter starchy material enters the brewing process only after the conversion into soluble saccharides. The most used sugar supplements are the following:

- **Granulated saccharose** (solid) – comes from sugar cane or sugar beet. Chemically, it is a disaccharide composed of simple fermentable sugars glucose and fructose. Yeasts are not able to ferment this disaccharide directly but its hydrolysis to glucose and fructose is required. Hydrolysis occurs either by heating in acidic solution such as wort or by the yeast action. Yeast enzyme invertase cleaves the saccharose into building units, i.e. glucose and fructose, which can be transported into yeasts across the cell membrane. Granulated sugar can be applied directly to the wort kettle. A better yet practice is its dissolution in water before addition to wort.
- **Saccharose-based syrups** (liquid) – derived from sugar cane or sugar beet. A number of similar products are available on the market. For example, cane-sugar syrups are based on sugar cane but also sugar beet and can be supplemented with invert sugar; invert syrups which are hydrolysed sucrose syrups resulting in the mixture of glucose and fructose; or popular Belgian "candi sugar" which is sucrose syrups often highly caramelized and intended for special beers (Stewart, 2016a; Stewart, 2016b).
- **Starch-based syrups** (liquid) – are produced from various cereals or potatoes. Acidic enzymatic or combined hydrolysis of starch ensures to supply syrups with sim-

ilar carbohydrate composition to sweet-wort, i.e. 10–15% glucose, 2% fructose, 2% sucrose, 50–60% maltose, 10–15% maltotriose and 20–30% dextrins. The modern technology enables the production of special syrups with different properties and degrees of fermentability.

 * Glucose syrups are a product of acidic/enzymatic starch hydrolysis with a various degree of conversion expressed as dextrose equivalent units (DE). This indicates the amount of dextrose in the dry matter, i.e. the value of pure starch would be 0, while pure solid dextrose would be equal to 100) (Stewart, 2016a). However, DE shows only the level of reducing sugars but says nothing about the composition and technological properties. This glucose syrup is mainly produced from corn, so the well-known designation as corn syrup can be often found.
 * Maltose syrups – advisable for the production of special beers due to the possibility to choose and precisely define the content of fermentable and non-fermentable saccharides. The prevailing sugar is maltose.

- **Malt syrups/extracts** (hopped or unhopped) – are concentrated unfermented wort usually produced in the form of sweet viscous liquid. They are very popular for homebrewers and microbrewers. The market offers a number of variants based especially on different proportions of dark and special malts, thus resulting in products of various flavours and colours so that it is possible to produce beer according to the selected beer style. Moreover, extracts with added enzymatic power are also produced. These are intended for brewing with unmalted adjuncts. The main advantage of the extracts is the composition comparable to common wort. They contain a high level of well-fermentable maltose (60–70%) as well as other components necessary for smooth fermentation such as vitamins, lipids or trace elements (Basařová et al., 2021; Bogdan and Kordialik-Bogacka, 2017; Goldammer, 2008; Stewart, 2016a).

The sugar adjuncts are usually added directly into the kettle during the wort boiling stage and that is why they are sometimes called kettle adjuncts. The application of these highly concentrated sugar solutions substantially increases fermentability of the wort and thus very effectively expands the brewery capacity, which is successfully employed in high gravity brewing (HGB). Their application at later production stages is also possible, for instance in case of secondary fermentation in tanks, casks or bottles to obtain beer with finer sensory properties (Stewart, 2016a).

The advantages of sugar adjuncts usage lies in the smaller space requirements for their storage and almost no need to alter the technological equipment. Moreover, energy savings, together with costs associated with handling and pre-treatment of cereals, are not negligible (Bogdan and Kordialik-Bogacka, 2017). Sugar substitutes facilitate achieving a higher degree of attenuation associated with a higher alcohol content. Their use also leads to decreased level of nitrogenous and polyphenolic substances, which is reflected in reduced foaming (Basařová et al., 2021; Helstad, 2013; Lloyd, 1986).

However, the use of sugar adjuncts also brings some negative impacts such as high susceptibility to microbial contamination especially in case of malt extracts and syrups with high nitrogen contents. Therefore higher demands on the sanitation of storage of containers have to be taken into account (Basařová et al., 2021; Šavel, 2015). Also several cases of deteriorated syrup colour have been recorded and these were caused by a long-term storage at elevated temperatures, which triggered melanoidin formation. This applies to breweries storing large volumes of syrups or those far from suppliers (Stewart, 2016a). In addition, long storage of highly concentrated sugar solution can lead to sugar crystallization (Bogdan and Kordialik-Bogacka, 2017).

Table 1 A general overview of positive and negative effects of sugar adjuncts in brewing technology

	Advantages	Disadvantages
Technological	storage	↑ risk of contamination
	↓ modification of equipment	↑ sanitation requirements
	expansion of brewery's capacity	poor fermentation
	high gravity brewing	↑ nutrient needs for yeasts
	↑ attenuation degree	long-term storage temperature
Biochemical	↑ alcohol content	–
	↓ nitrogen content	↑ nitrogen content
	↑ polyphenol content	–
Sensorial	↑ colour – lighter beers	less full beers
	–	less foaming

Furthermore, a higher percentage of sugar-based supplements may slow down or completely stop the main fermentation due to suppressing maltose utilization at excessive glucose levels that is sometimes referred to as glucose effect, i.e. the yeasts prefer monosaccharide glucose to disaccharide maltose (Stewart, 2016b). Therefore, it is suggested to carefully monitor the course of fermentation and to supplement basic nutrients such as nitrogenous substances during fermentation if necessary or to increase the inoculation rate and not to re-inoculate with the used yeasts. To suppress the negative effect of sugar adjuncts on the fermentation, it is recommended to use them only up to 10% of grist (Helstad, 2013; Hertrich, 2013; Lloyd, 1986). A brief and clear summary of the advantages and disadvantages of using sugar adjuncts in brewing is given in Table 1.

3 Starchy adjuncts

There are numerous crops that can serve as an effective alternative to barley malt for beer brewing. Current technologies together with a wide offer of commercial enzymes, including thermostable ones, make it possible to brew beer with 100% unmalted barley and over 60% corn, rice or wheat (Stewart, 2016a).

Any raw materials rich in starch or other similar polysaccharides can constitute starchy adjuncts. However, it is necessary to take into account not only readily available starch, but also the nature of starch in terms of its processing in beer production (Hertrich, 2013).

The term "mash vessel adjuncts" or "cooker mash adjuncts" can be found in literature or heard among brewers in connection with starchy substitutes. "Mash vessel adjuncts" refer to a starchy material that is not pre-cooked in the brewery and can be added directly to the mash. e.g. wheat flour, corn flakes, rice grits as well as micronized or torrefied grains (Bogdan and Kordialik-Bogacka, 2017). While those products, whose starch is present in a native form and requires pre-gelatinisation in an additional cooker, are known as "cooker mash adjuncts" (Goldammer, 2008).

3.1 Cereal malted and unmalted alternatives in brewing

In general, unmalted cereal adjuncts offer more or less cheaper starch, little or no enzymatic activity as well as little or no soluble nitrogen. The effect on organoleptic properties is sometimes neglected, however a certain impact on sensory quality of beer has been proven. For instance unmalted barley contributes to a stronger and harsher character of beer. Corn, on the other hand, provides beer fullness and a clean taste and aroma, wheat offers dryness and rich aroma. Rice gives the beer a typical light taste with supported drinkability (Bogdan and Kordialik-Bogacka, 2017; Stewart, 2016a; Stewart, 2016b).

The cereal grain contains starch composed of approximately 25% linear amylose and 75% branched amylopectin. Variation in starch composition and structure across the species and varieties are common (Hertrich, 2013; Stewart, 2016a), although cereal plants are botanically closely related (Table 2) – all are currently classified in the same grass family – *Poaceae*. In addition to starch, cereals contain bran and germ components, i.e. non-starch polysaccharides, lipids and other substances potentially harmful in beer brewing (Hertrich, 2013).

The first requirement in the processing of cereal alternatives is to obtain starch and to eliminate undesirable components. Then the starch is hydrolysed into fermentable sugars, especially glucose, maltose and maltotriose. The cereal pre-treat-

Table 2 *Scientific classification of starchy cereals used as barley malt alternatives according to the Integrated Taxonomic Information System (ITIS, 2022)*

Taxonomy Hierarchy	*Latin*	English
Kingdom	Plantae	plants
Subkingdom	Viridiplantae	green plants
Infrakingdom	Streptophyta	land plants
Superdivision	Embryophyta	–
Division	Tracheophyta	vascular plants
Subdivision	Spermatophytina	seed plants
Class	Magnoliopsida	–
Superorder	Lilianae	monocots
Order	Poales	–
Family	Poaceae	grasses
Genus	Hordeum L.	barley
	Triticum L.	wheat
	Zea L.	corn
	Avena L.	oats
	Sorghum Moench	sorghum
	Secale L.	rye
	X Triticosecale Wittm.	triticale

ment and hydrolysis procedure depend on the form of cereal adjuncts. Several basic types of adjuncts can be used in brewing technologies:

- Raw cereal grain;
- Malted cereals;
- Unmalted cereals in the form of certain milling products such as:
  - Flours;
  - Coarse grits;
  - Flakes – whole grains or coarse grits heated and rolled;
  - Extruded flakes – the material in an extruder turns into paste thanks to the combined effect of high temperature and pressure. These conditions crack and gelatinise the starchy granules and at the end of the process the mass is extruded into an environment with normal temperature and pressure, which leads to a rapid expansion of the product;
  - Torrefied cereals – the grain passes through a stream of hot air at 260°C, which disrupts the cell structure, followed by direct rolling and cooling. No handling or dust problems are associated with the use of torrefied cereals (Stewart, 2016a);
  - Micronized cereals – the grain is subjected to infrared radiation that heats and vibrates the starch molecules, causing their swelling and softening, followed by immediate rolling or flaking;
- Refined starches, starch extracts, syrups and concentrates;
- Special malt substitutes, e.g. green malt (Basařová et al., 2021; Goldammer, 2008; Helstad, 2013; Hertrich, 2013; Kok et al., 2019; Stewart, 2016a).

Pre-treatment of grain starch practically requires its solubilization, which is based on two fundamental principles, i.e. gelatinisation and liquefaction. This means that the starch granules absorb water until they rupture as a result of hydration. The grain content goes into solution, increasing its viscosity. At this stage, amylose and amylopectin molecules come into contact with amylolytic enzymes (Hertrich, 2013). Gelatinisation takes places over a range of certain temperatures. These temperatures are specific to the different cereal species (Table 3), their varieties and even to a particular growing year determining the harvest quality. As for the brewing purposes, gelatinisation can be performed either in a separate cereal cooking vessel, typically for corn, rice, and sorghum or the process can take place directly in a main mash tun, usual for unmalted barley or wheat (Goldammer, 2008; Hertrich, 2013; Lloyd, 1986; Stewart, 2016a). If a cooking vessel is not available in the brewery, then any cereal supplement is processed directly in a mash tun, but a different schedule with prolonged rest periods must be included (Goldammer, 2008; Lloyd, 1986).

The above-mentioned milling products are also added directly into a mash tun, since the starch gelatinisation took place during its production process outside the brewery (Stewart, 2016b).

In addition to starch pre-gelatinisation, there is also a need to focus on removing non-starch undesirable components such as β-glucans and lipids. β-Glucans are non-starch polysaccharides typical of barley cell walls of the aleurone layer. They are particularly undesirable due to the raise of wort viscosity and the difficulties they cause during separation processes (Lowe et al., 2004). Lipids are generally considered harmful in brewing, mainly in conjunction with deteriorated flavour during beer ageing. The high lipid contents are typical for cereals other than barley. However, there is no common approach to lipid reduction because their distribution varies between cereals (Hertrich, 2013).

The important and probably the most discussed point in the technology of unmalted cereal substitutes is a lack of necessary enzymes including the enzymes of amylolytic, proteolytic and cytolytic nature. They developed during malting, and therefore their deficiency is substantial, especially at a higher percentage of unmalted adjuncts in grist (Yorke et al., 2021). Thus, mashing (an operation based

Table 3 *The range of gelatinisation temperatures of cereal adjuncts according to Briggs et al. (2004) and Hertrich (2013) and % of achievable extract (Briggs et al., 2004)*

Cereal adjunct	Gelatinisation temp. (Briggs et al., 2004) [°C]	Gelatinisation temp. (Hertrich, 2013) [°C]	Extract (Briggs et al., 2004) [%]
Barley	60–62	58–65	70
Corn	62–77	72–78	78
Rice	60–82	70–85	84
Wheat	52–66	55–60	75
Sorghum	69–75	69–75	82
Oats	52–64	57–72	72
Rye	50–62	55–60	74

on enzymatic breakdown of high molecular compounds) must take place either in the presence of the relevant proportion of high quality malt that provides the enzymes, or they are supplemented in the form of exogenous microbial enzymes (Bogdan and Kordialik-Bogacka, 2017).

This chapter can be concluded by summarizing that the chemical composition of various cereals is crucial for brewing industry because different proportions of several substances will impact the whole technological chain such as milling, mashing, wort composition, fermentation, etc., as well as organoleptic properties of beer. In particular, the impact of cereal adjuncts on beer aroma and flavour has recently been a hot topic in scientific literature.

3.2 Barley

In traditional brewing countries, barley malt is an essential raw material, which at the same time determines the beer quality (Lowe et al., 2004; MacLeod and Evans, 2016; Šavel, 2015). Nevertheless, the application of lower shares of unmalted barley, i.e. up to 40% of the total grist, is a well-described and established practice in the beer production. The advantages of using unmalted barley lie mainly in its significantly lower price compared to malted barley as well as in its composition similar to barley malt, which allows to preserve the organoleptic properties of beer (Dongmo et al., 2013; Šavel, 2015). However, higher proportions of unmalted barley, i.e. 50% and more, lead to deterioration of the technological process and the beer character (Kunz et al., 2012).

At first the enzymatic deficit of unmalted barley must be taken into account. Insufficient (unmalted barley) or no (pre-gelatinised starch) cytolytic, proteolytic and amylolytic activity are associated with technological obstacles such as lower extracts yields, impaired filterability and fermentability of wort (Dongmo et al., 2013; Kok et al., 2019). Adding commercial enzymes derived from bacterial cultures can solve these complications. At the same time, the enzyme application can improve other parameters, including filterability or antioxidant potential of beer, which is associated with ageing stability (Grooth et al., 2013; Kunz et al., 2011; Steiner et al., 2012). The industrial production of enzymes responds to the increased demand caused by extended employment of unmalted adjuncts. Due to the already well-supplied market, nowadays it is possible to compensate for the malting process and to replace malt with 100% of unmalted barley, while the malt quality is comparable to wort made of malt (Aastrup, 2010; Dongmo et al., 2013; Goode et al., 2005; Kunz et al., 2012; Schoenenberg and Kreisz, 2010; Steiner et al., 2012; Stewart, 2016a; Zhuang et al., 2017). Endogenous enzymes of raw barley (e.g. β-amylase, proteases) together with commercial microbial preparations make it possible to achieve very efficient beer brewing, while the technological process and sensory character are comparable with full-malt beers (Dongmo et al., 2013). The only issue is the price and its reflection in the overall production cost and legislative measures that may restrict the use of enzyme preparations in some countries. It is stated that adding up to 40% or even 50% of unmalted barley can be performed without enzyme supplements because malt enzymes deliver the sufficient enzymatic activity (Dongmo et al., 2013).

Table 4 presents scientific studies published over the last 10 years that have focused on the replacement of barley malt with a varying proportion of unmalted barley. Their authors monitored and evaluated a number of parameters and/or tried to find optimal solutions for specific obstacles. Thanks to such research, it is therefore possible to successfully apply higher proportions of unmalted barley in industrial practice with an acceptable effect on sensory quality.

Pre-gelatinisation. Unmalted barley may be pre-treated with cooking under mild pressure or with steaming at atmospheric pressure. Then the pre-treatment is followed by rolling in which flakes are formed and their final humidity is 8–10%. Also torrefied, micronized or extruded barley may be included in brewing recipes (Yano et al., 2008). However, due to the low gelatinisation temperatures, pre-gelatinisation is not necessary. This practice is typical for instance for some popular stouts (Stewart, 2016a).

Milling. Grain milling is a necessary pre-mashing operation so that the starch and other barley components could be exposed to an intense contact with enzyme molecules. There are roller mills ensuring coarser grist and preserved husk integrity for subsequent lautering, in which the husks form the basis of a filter cake. Hammer mills provide finer grist with unintegrated husks (Kok et al., 2019), whereby the wort is further separated on a mash filter. Unmalted barley grain is noticeably harder with low friability comparing to barley malt (Steiner et al., 2012). Therefore, more efficient hammer mills or six-roller mills are usually employed in processing of unmalted barley. It is expected that a hammer mill providing very fine grist/flour is more advantageous because its larger surface can ensure easier and faster hydrolysis and more efficient extraction. However, also the extraction of undesirable compounds such as polyphenols must be taken into account.

In general, milling can be performed in dry or wet form, alternatively in dry form with grain conditioning/moistening. Dry milling leads to high crushing of grain and very fine flour ensuring higher extract recovery together with higher levels of β-glucans (de Moura and Mathias, 2018; Yano et al., 2008). This dry procedure is also associated with higher energy requirements, greater wear of mills as well as higher dust. On the other hand wet or conditioned milling promotes greater grain elasticity accompanied by greater adhesion of the starchy fraction to the husks, which may cause a reduction in extract yield (de Moura and Mathias, 2018). Wet or conditioned milling is recommended for tough raw barley grain (Bogdan and Kordialik-Bogacka, 2017). Curin et al. (1977) mentioned that the main advantages of wet milling unmalted barley is the reduction or even elimination of a number of negative consequences, such as prolonged lautering or negative impacts on the organoleptic character of the final beer.

Dongmo et al. (2013) studied the effect of milling setting (grist quality) of two unmalted barley varieties with regard to filterability and other wort parameters using 100% of unmalted barley in grist. They tested four-roller, six-roller and hammer mill with and without grain conditioning. All experiments exhibited prolonged lautering times, with the longest time recorded when a mash filter was included. The lautering performance was improved considerably when the husks were conditioned and milling resulted in a coarse grist size. The type of milling device depended on the barley variety, i.e. four-roller was effective for Beatrix variety, while six-roller mill for 2300/Irlbach variety. The main conclusion of the work monitoring many parameters is that the barley variety together with milling settings have great impact on the wort quality and course of lautering using 100% unmalted barley. Even if the optimal conditions for lautering are found, some other obstacles can appear, e.g. higher turbidity in wort or beer. Dongmo et al. (2013) decreased the turbidity formation by addition of protease and pullulanase during mashing.

Van Donkelaar et al. (2016) focused on pearling – a method of abrasive milling in barley, which reduces some undesirable components, while maintaining β-amylase activity. The authors tested different barley/malt ratios degree of pearling and two different filter types and found that increasing barley percentage decreases the process performance and the extract yield. Thus, it can be stated pearling brings several benefits such as decrease in the amount of arabinose, S-methylmethionine and anthocyanogen but the mentioned negative effects should be considered as well.

To summarize, milling effectivity depends mainly on grain hardness which is probably determined by the interaction of starch, proteins and β-glucans. High content of proteins and β-glucans is correlated with harder grain, while more starchy barley is on contrary softer (Kok et al., 2019). The milling parameters should be therefore set on the basis of the grain properties of a suitably selected variety, taking into account the weather conditions during growing year.

Mashing. Milled unmalted barley as well as pre-treated barley in the form of gelatinised starch (e.g. flakes or micronized grain) can be added directly to the mash tun due to reasonable gelatinisation temperatures (Table 3). In general, mashing temperature profiles and rest periods depend on the degree of endosperm modification of the particular employed grain. Therefore, raw barley requires included and prolonged mashing rests at lower temperatures such as ~45°C and ~52°C, which corresponds to optimal activity β-glucanases and proteases, respectively. The prolonged temperature delays give the enzymes a chance to come into contact with the relevant substances and thus catalyse their hydrolysis. These enzymes are quite sensitive and a rapid transition to higher temperatures can cause them to be inactivated (Kok et al., 2019). It is well known that (un)malted barley contains high levels of β-glucans and arabinoxylans, which make solutions too viscous and thus complicate wort separation. The optimal wort viscosity is ensured primarily by enzymes, which either come from malt or from commercial production. Enzymatic degradation can be enhanced by acidification of mash using lactic acid or lactic acid bacteria (Lowe et al., 2004).

Wort separation. This brewing operation is usually a rather problematic stage due to the filtration efficiency affecting the entire production and yield of the extract. The lautering effectivity is mainly affected by husk integrity, size of grist and sweet wort viscosity (Kok et al., 2019). As mentioned above, when choosing a hammer mill, the husk is crushed and then usage of mash filter is advantageous. On the contrary, when grinding takes place in roller-mills, then lautering is usually integrated.

Implementation of raw barley is accompanied by a higher wort viscosity which occurs either due to the presence of unmodified parts of cell walls, such as hemicelluloses and arabinoxylans, or is caused by ungelatinised starch granules in the mash. Increased viscosity of sweet wort leads to slow and problematic lautering.

Wort and beer. The wort composition depends mainly on the quality of barley, but also on the kind and amounts of added exogenous enzymes as well as on technological procedure.

It was found that increasing a proportion of unmalted barley in grist leads to a decrease in glucose level in the wort. At the same time maltose and maltotriose remain almost maintained when an appropriate mixture of commercial enzymes is used (Kok et al., 2019; van Donkelaar et al., 2016; Zhuang et al., 2017).

Another frequently described characteristic is a lower FAN, consisting of free amino acids, low molecular weight peptides and ammonia, which can cause problematic fermentation (Evans et al., 2014; Kunz et al., 2012). The higher was the proportion of unmalted barly, the lower FAN was detected (Kunz et al., 2012). Neither commercial enzymes (Zhuang et al., 2017) nor sufficiently prolonged protein rest (Aastrup, 2010; Kunz et al., 2012) helped to increase FAN.

Only Lowe et al. (2004) recorded successful results when proteolytic lactic acid bacteria (LAB) in wort prepared from 50% unmalted barley was used. LAB application led to a satisfactory FAN and an overall positive effect on the wort quality including a significant reduction in β-glucans associated with improved separation processes.

Increasing level of β-glucans is also a typical feature accompanying rising share of raw barley (Kunz et al., 2012; Lowe et al., 2004).

There are different opinions with respect to the influence of unmalted barley on beer quality and flavour (Kunz et al., 2012). Early studies quite often stated that beers prepared from high proportions of unmalted barley are harsh and astringent. Reportedly, lowering the wort pH to 4.9 before boiling helps to avoid these undesirable sensory perceptions (Šavel, 2015). Sensory properties of beer made from unmalted barley are determined by a number of factors. The literature describes several common features that can be more or less generalized. Certainly, it is true that the higher percentage of unmalted barley, the greater is the risk of sensory defects in beer. For example, Kunz et al. (2012) stated that the taste of beers produced from raw barley up to 50% were rated slightly better than whole malt beers. Furthermore, the share of unmalted barley up to 75% showed equivalent rating with all-malt beers. Only beers with a barley proportion of 90% demonstrated astringent and abrasive bitterness. Steiner et al. (2012) pointed to not enough body or mouthfeel at beer brewed with 100% barley. On the other hand,

Table 4 *An overview of the latest studies discussing brewing with unmalted barley*

Grist*	The aim of study	Enzymes	Brewing Scale	References
5, 10, 15, 20, 25 and 30% UB	metal ions in wort	barley malt enzymes	laboratory	Sterczyńskaet al. (2021)
15, 25, 35, 45, 55, 65, 100% UB	proportions of optimal ingredient	Ondea Pro®	laboratory	Cooper et al. (2016)
25 and 45% UB	beer quality	barley malt enzymes	pilot plant (~60 l)	Yano et al. (2008)
25, 50, 75 and 90% UB	beer quality – mainly oxidative stability	amylase, pullulanase, protease, glucanase and xylanase	pilot plant (1–2 hl)	Kunz et al. (2012)
30 and 60% UB	sensory and analytical profiles of lager beer	barley malt enzymes	25 l	Yorke et al. (2021)
35% UB+30% corn+35% MB	qualitative parameters of beer	commercial enzyme mixes: Ceremix, Ultraflo, Neutrase, Fungamyl, Promozyme, Finizyme	full scale	Loiko and Romanova (2018)
40% UB	technology and wort properties	exogenous enzyme mix Brewers Compass®	laboratory	Demeester et al. (2021)
50% UB	a mash bioacidification	proteolytic LAB	laboratory	Lowe et al. (2004)
50, 65, 80 and 100% UB	barley pearling + optimisation of raw materials with regard to wort quality	enzyme mixture Ondea Pro® (Novozymes)	laboratory (~5 l)	van Donkelaar et al. (2016)
100% UB	benefits of using commercial enzyme mix Ondea Pro	Ondea Pro®	full scale	Aastrup (2010)
100% UB	lautering performance + wort quality	Termamyl® SC (a heat-stable α-amylase) Ultraflow Max®(β-glucanase and arabinoxylanase) Neutrase® (protease) pullulanase and lipase	60 l	Dongmo et al. (2013)
100% UB	the influence of barley quality on wort parameters	enzyme mixture Ondea Pro (Novozymes)®	laboratory	Evans et al. (2014)
100% UB	barley use instead of malt – beer quality	enzyme mixture Ondea Pro (Novozymes)®	60 l	Steiner et al. (2012)
100% raw	brewing potential of unmalted grain	enzyme mixture Ondea Pro (Novozymes)®	10 l	Zhuang et al. (2017)

UB – unmalted barley
MB – malted barley
**where only % UB is given, there the relevant rest is MB*

Yorke et al. (2021) reported that implementation of two different barley varieties at 30% proportion did not considerably alter beer flavour profile. However, 60% of the barley substitute showed increased astringent and persistent bitterness, and these tones were evaluated differently between two tested varieties.

Despite some sensory disbalance, beers with increasing unmalted barley percentage in grist demonstrated a better oxidative stability, slower development of ageing compounds during beer storage and a higher antioxidant potential (Kunz et al., 2012). Steiner et al. (2012) described also an excellent foam stability in 100% unmalted barley beer, although nitrogen compounds were quite low.

Kunz et al. (2012) reported that their beers made from unmalted barley up to 50% displayed comparable or higher extract yields and final attenuation due to sufficient enzymatic activity provided by both malt and exogenous enzymes. Evans et al. (2014) noted that these parameters are considerably dependent on the selection of suitable and high quality barley. Their experiment showed that barley from food or malting varieties reached high values of extract and fermentability. Nevertheless, they also proved a seasonal effect of barley on brewing parameters.

We can conclude that current barley varieties and well-adapted technology make it possible to brew beer even from 100% unmalted barley with satisfactory quality and acceptable process efficiency, especially as far as the separation processes is concerned. The sensory characteristics seem to be very close to conventional all-malt beers, and further experimental batches are likely to improve the quality even more.

3.3 Corn/maize in brewing

Corn/maize is one of the most widely used barley malt substitutes in brewing especially in the USA and China (Basařová et al., 2021; Debyser et al., 1998; Glatthar et al., 2002; Jaukovic et al., 2017) or in subtropical and tropical areas such as Central America or Mexico, where it orginates (Dabija et al., 2021). Climatic conditions of these places make it difficult to grow barley or store barley malt. At the same time, corn is mostly a traditional crop in these areas, making it a more affordable and economically viable raw material (Farnham et al., 2003; Taylor et al., 2013). Other reasons for choosing corn may be the production of gluten-free, light colour or light beers (Hertrich, 2013; Kelly et al., 2008).

Regarding the corn adjunct, a new Chinese trend should be mentioned: the so called "Three High" brewing technology. This means high-gravity brewing with a high proportion of corn starch and a high material/water in the liquefaction process (Zhuang et al., 2017).

A number of corn varieties with different colour, nutritional or technological properties are grown and the variety portfolio in brewing is gradually expanding. For example, waxy (Taylor et al., 2013) or pigmented corn (Hernandez-Carapia et al., 2021; Romero-Medina et al., 2021) has recently become popular, especially in craft brewing. The starch of the waxy varieties is composed of almost 100% amylopectin. This composition causes slightly higher gelatinisation temperatures (by 1–2°C), but also a more intense desirable swelling of starch granules (Maia et al., 2021; Taylor et al., 2013). The pigmented varieties are in turn rich in anthocyanins and anthocyanidins (Taylor et al., 2013).

Unlike barley, corn kernel is naked without coating layers and it consists of endosperm (82–83%), germ (10–11%), pericarp (5–6%) and tip cap (0.8–1.0%) (Dabija et al., 2021). Corn endosperm is constituted by starch (62–80%) together with proteins (5.8–13.7%) and lipids (2.2–5.9%) (Dabija et al., 2021; Hernandez-Carapia et al., 2021). Cell walls are composed of proteins, phenolic acids and non-starch polysaccharides (cca 4.2%) such as arabinoxylans (particularly glukuronoarabinoxylans) and less β-glucans (Bogdan and Kordialik-Bogacka, 2017; Dabija et al., 2021; Taylor et al., 2013). Highly cross-linked arabinoxylans are not soluble in water, thus corn cell walls are not thought to be problematic during wort separation (Taylor et al., 2013). Corn grain processing must always involve a germ removal due to reducing the amounts of lipids and other precursors of an old flavour that adversely affect the foaming and sensory properties of beer (Hernandez-Carapia et al., 2021). Generally, corn is first cleaned, conditioned, rid of germs, crushed, sorted, milled and dried so that the resulting material reached less than 1% lipids in the dry matter. Corn substitutes are usually used in the range of 10–30% of whole grist with particle size 0.15–0.27 mm. When the proportion is increased, then the longer time required to achieve the needed degree of liquification has to be taken into account (Basařová et al., 2021; Błażewicz and Zembold-Guła, 2007; Šavel, 2015). Recent papers studying incorporation of the corn adjunct into beer production and its aspects are listed in Table 5.

The main disadvantage of corn or corn products is the low FAN (Šavel, 2015). Further, corn provides a slightly lower extract due to lower levels of dextrins after mashing compared to other unmalted adjuncts, e.g. rice. Despite careful processing, the higher levels of proteins and lipids and their impact on the sensory profile should be taken into account (Dabija et al., 2021).

Corn requires specific storage conditions at temperatures up to 20°C because of high levels of unsaturated fatty acids, and should be used immediately after milling to prevent oxidation of lipid components which is associated with sensory defects (Basařová et al., 2021; Šavel, 2015).

Forms. The usual forms of corn used in brewing and its specifics:

- Brewer's grits. They are obtained by dry milling (Hertrich, 2013; Stewart, 2016a). After mashing, they contain less dextrins, higher amounts of proteins and lipids (Stewart, 2016a).
- Refined grits, i.e. micronized, flaked, etc. These pre-gelatinised products considerably reduce mashing time (Dabija et al., 2021; Stewart, 2016b).
- Refined starch is a very fine powder and a highly pure product containing only traces of proteins (<0.3%) and no lipids. Its production involves wet corn milling, with an 11% final moisture content after drying. Detailed procedure is described in Hertrich (2013). Refined starch cooking is easier and shorter than for other corn products due to extremely fine granulation. On the other hand, this advantage is offset by a higher price and difficulties with powder manipulation. Conventional grain handling systems in breweries cannot be used. Storage tanks and handling lines must be well-grounded, as there is a risk of explosion due to electrostatic sparks. Moreover, starch may be too viscous, so that discharging the solution from the tanks is almost impossible without special fluidising bottom (Hertrich, 2013; Stewart, 2016a). The use of corn starch is not very common (Šavel, 2015), however this pure form of corn found its place in the high gravity brewing (Dabija et al., 2021) or as part of adjuncts combined with rice (Stewart, 2016a).
- Malted corn grain is rarely applied in brewing, nevertheless there are several traditional products using the ingredient, e.g. Chica de jora in South America (Dabija et al., 2021), Tesuino maize beer by Tarahumara Indians in Mexico or Xhosa traditionally homebrewed beer in South Africa (Jaukovic et al., 2017) and many others. Also current growing attention of South American and Mexican craft brewers in particular may increase its importance (Dabija et al., 2021; Romero-Medina et al., 2021).

Milling. Medium-coarse corn grits are needed for brewing purposes. Too coarse or too fine grain causes a number of technological problems. For this reason, the corn grist delivered to the brewery is sometimes reground to standardise dimensions of the coarsest corn pieces in order to optimise the extract yield (Hertrich, 2013). Wet milling is prevalent in African or Asian industries, but it is less common in the USA or Brazil (de Moura and Mathias, 2018).

Pre-gelatinisation. Corn requires higher temperature range of starch gelatinisation (Table 3); therefore, pre-mashing of corn is necessary. Pre-gelatinisation is performed either in a separate cooker, while this premash mixed with commercial enzymes or malt and joined to mash. Or the process may take place in a mash tun before conventional malt mashing and malt and water is added to the corn pre-mash (Briggs et al., 2004; Fumi et al., 2011; Poreda et al., 2014; Taylor et al., 2013).

Mashing. After cooling the pre-gelatinised corn is added to the barley malt mash at a temperature of 10–50°C and the conventional infusion mashing can follow (Koszyk and Lewis, 1977; Poreda et al., 2014). Sometimes a similar procedure is called American double mash (Hertrich, 2013). The implementation of a decoction mashing has also proved successful in breweries, e.g. in Italy (Fumi et al., 2011). The addition of commercially produced enzymes or barley malt is crucial to achieve sufficient enzymatic power required for optimal saccharification. When barley malt is used as a source of enzymes, the corn adjuncts are mixed with a mash portion that is heated up to boiling.

A key step in the mashing of corn enriched wort is the inclusion of a proteolytic rest, which can improve colour, increase reducing carbohydrates as well as total nitrogen and phenolic compounds. On the other hand, the elimination of the proteolytic step leads to a lighter colour, a reduction in proteins, phenolic compounds and antioxidant activity (Mathias et al., 2019). Moreover, the addition of exogenous proteases is recommended to improve the FAN levels and other technological parameters of the wort (Perez-Carrillo et al., 2012).

Lautering. Corn kernels differ from barley by a proportion of non-starch polysaccharides in the cell walls of the endosperm. These are predominantly arabinoxylans, mainly glucuronoarabinoxylans, which are insoluble in water and their structure is more complex. Still, no negative effect of corn arabinoxylans on lautering has been demonstrated (Taylor et al., 2013). Lautering obstacles can, however, occur with poor saccharification caused by enzyme deficiency (Dziedzoave et al., 2010), especially in case of a higher proportion (30–50%) of corn starch. Zhu et al. (2015) proved that the main cause of filtration problems is incompletely degraded corn starch, which forms a thick and viscous spent grain slowing down the filtration rate. They recommend application of amylolytic enzymes as one of the ways to help the lautering process.

Wort and beer. Blazewicz and Zembold-Gula (2007) described the properties of wort prepared with 20, 30 and 40% of corn in grist. They found that wort samples had a lower degree of attenuation, lower soluble nitrogen and FAN. Also Maia et al. (2021) found a significant decrease in FAN in beers made from 30 or 60% torrified corn. In addition, the author demonstrated that the lower FAN was correlated with a decrease in Strecker aldehydes. In general, soluble nitrogen is associated with good foaming and the FAN affects the yeast physiology and thus the whole fermentation process. Poreda et al. (2014), who applied 10 and 20% corn supplementation, found only a slightly lower FAN, which did not adversely affect fermentation.

Beers prepared with more than 20% of corn substitutes displayed an increased concentration of higher alcohols due to a low FAN. These higher alcohols negatively affected the sensory profile of beer (Jin et al., 1993). Lighter colour of corn beer is also related to low content of nitrogen substances, because they are one of the major player in Maillard reactions (Mathias et al., 2019; Poreda et al., 2014). Maia et al. (2021) and also Yorke et al. (2021) evaluated beers made from 60% torrefied corn with increased sour taste which was explained by weak buffering capacity of the wort. Moreover, Yorke et al. (2021) reported grainy aroma with sweetcorn tones. This typical undesirable "popcorn" flavour is given by the aromatic compound 2-acetyl-1-pyrroline, which is present in corn (Taylor et al., 2013).

He et al. (2018) tried to improve sensory properties of "corn beers" and they found that extruded corn starch was better than conventional starch. The beers prepared from extruded starch showed comparable values of desirable volatile substances as in lagers or ales. An interesting study by Maia et al. (2021) focused on the connection between an increased share of unmalted corn and beer stability. The authors of the study discovered that corn may be responsible for decrease in total pro-oxidant metal ions and staling aldehydes. On the other hand, the observation that wort produced from corn adjunct may exhibit lower total phenols and antioxidant activity (Fumi et al., 2011; Mathias et al., 2019) has also been reported.

Table 5 *Overview of recent papers dealing with incorporation of corn in brewing recipes*

Proportion and form of grist	The aim of study	Applied enzymes	Brewing Scale	References
10 and 20% corn grist	impact on quality of wort and beer (colour, DMS, proteins, alcohol, attenuation, filtration)	barley malt enzymes	3000 hl fermentation tanks	Poreda et al. (2014)
12.5; 25; 37.5; 50% corn grist	impact on flavour stability	β–glucanases, xylanases	400 ml	(Maia et al., 2021)
20; 30 and 40 % (fine) corn grist	impact on wort quality	barley malt enzymes	laboratory	Błażewicz and Zembold-Guła (2007)
30 and 60% flake torrefied maize	impact on sensorial beer profile	from barley malt	25 l	Yorke et al. (2021)
30% corn+70% malt	monitoring of qualitative parameters of beer	commercial enzyme mixes: Ceremix, Ultraflo, Neutrase, Fungamyl, Promozyme, Finizyme	full scale	Loiko and Romanova (2018)
33% extruded/cooked corn starch	monitoring of fermentable sugars and flavour compounds	barley malt enzymes	pilot plant (cca 100 l)	He et al. (2018)
38% corn grist	monitoring polyphenols during brewing process	barley malt enzymes	full scale (cca 200 hl)	Fumi et al. (2011)
45% corn grain	the effect of mashing changes on wort quality	barley malt enzymes	laboratory (cca 1 l)	Mathias et al. (2019)
extruded corn starch	optimization of FAN amount using protease	Termamyl, Neutrase	laboratory (~500 ml)	Perez-Carrillo et al. (2012)
10, 20, 30, 40, 50, 60, 70% corn starch	wort separation performance in high adjunct ratio brewing	thermostable α-amylase	laboratory	Zhu et al. (2015)
10,20,30,50,70,100% corn starch	enhancing the hydrolysis of corn starch uses amylases	thermostable, mesophilic α-amylase, isoamylase, β-amylase, raw-starch-digesting α-amylase, glucoamylase, pullulanase, Taka-Diastase, xylanase	laboratory (~200 ml)	Zhu et al. (2015)
100% corn starch	study of factors blocking filtration	α-amylase, β-glucanase	laboratory	Ma et al. (2014)

3.4 Rice in brewing

Rice is also one of the most widely used malt alternatives (Marconi, 2017). Breweries prefer rice mainly for its neutral taste and flavour, high volume of starch and lower protein and lipid content compared to barley malt. These properties allow the production of light colour, well-drinkable dry and clear beers with increased resistance to non-biological turbidity (Coors, 1976; Stewart, 2016a). Rice, like corn, has zero or negligible amount of prolamins, therefore it can be used for the production of gluten-free beers (Fitzgerald, 2004). The optimal course of the brewing process is given primarily by the choice of a suitable rice variety with the regard to the required properties (Stewart, 2016a). The rice composition depends on the particular variety, environment, cultivation and weather conditions. Generally, it is about 70% of starch, 5–8% of protein, 0.2–2.2% of lipids, and traces of inorganic substances. The protein content is the lowest when compared with other adjunct cereals – barley (8–15%), maize (~10%) and sorghum (~11%) (Taylor et al., 2013). Cell walls of rice endosperm are composed of arabinoxylans and β-glucans (47–48%), cellulose (23–28%) and pectin substances including polygalacturonides and glucomannans. Despite that, it seems that cell wall components do not have any impact on filtration processes (Marconi, 2017; Taylor et al., 2013). The rice husk that is fibrous as in barley is composed of 31–36% cellulose, 18% arabinoxylans, 10–18% lignin, 3–12% hemicelluloses and 13–21% ash (mainly silicon) and might serve as a filter bed during lautering (Taylor et al., 2013).

The main criteria for a suitable rice selection are the following: gelatinisation temperature, mash viscosity, mash aroma, moisture along with lipid, ash and proteins. For example, diverse types of rice have different gelatinisation temperatures. It is stated 65–68°C for short-grain rice and 71–74°C for long-grain rice. In addition, long-grain rice forms extremely viscous solution especially before liquefaction. Thus, short-grain varieties are mostly preferred for brewing (Marconi, 2017). Paddy rice processing involves pre-cleaning, dehusking and dry milling (polishing), which removes husk, bran and germs, leading to a reduction in lipid content, while preserving the starch endosperm as much as possible. Rice intended for brewing purposes usually contains 0.6% lipids (Stewart, 2016a). The morphology of rice starch granules is unique and does not appear in any other cereal. The rice starch forms very small granules of irregular shape 3–5 μm diameter, which are clustered into larger formations (Taylor et al., 2013).

Rice can be attractive for breweries due to its higher starch content compared to barley or wheat, lower levels of fibre, lipids and proteins (Marconi, 2017). Another advantage of the rice adjunct is easy handling, because even fine grist contains little dust and, unlike corn or wheat starch, can easily flow through a regular hopper bottom as well as conveying equipment (Stewart, 2016a). Recent studies on technological issues arising from rice incorporation into beer production or on monitoring the effect of rice on the organoleptic properties of beer are given in Table 6. On the contrary, rice needs the highest range of gelatinisation temperature of all cereal substitutes (Hertrich, 2013; Stewart, 2016a). Its extremely viscous solutions have been already mentioned. In case of poor liquefication, the obstacles with pumping of this immensely viscous liquid may occur (Stewart, 2016a).

Although, rice is particularly employed in unmalted form in combination with barley malt, there are also several studies examining rice malt and its use for whole-rice malt beer. Similar to corn, rice is used in the Chinese novelty "Three High", which corresponds to the high wort gravity, high proportion of rice and high ratio of material to water in the liquefaction phase (Zhu et al., 2015).

Forms. The usual forms of rice used in brewing and its specifics:

- common husked rice grain;
- damaged rice grain from processing in the food industry is more economically advantageous, as it is a by-product;
- grist or refined grist such as flakes, flour or extruded product;
- malted rice (Marconi, 2017; Stewart, 2016a).

Milling. Fixed-roller mills used in wheat flour milling or hammer mills are recommended for fine rice milling that is advisable to facilitate gelatinisation and liquefication. Brewery malt mills are insufficient for rice milling (Hertrich, 2013).

Pre-gelatinisation. A separate cooker is essential for pre-gelatinisation because of the above-mentioned high gelatinisation temperatures. They can reach more than 80°C, therefore temperatures of 85–100°C is recommended for proper gelatinisation (Adebowale et al., 2010; Briggs et al., 2004). Without installation of a special cooking vessel there would be unacceptable time delays required to cool rice mash before mixing it with barley mash (Hertrich, 2013). Malt enzymes (10–15%) may be added to the cereal cooker to help liquefaction and to facilitate pumping the rice mash. Gelatinisation is reached at atmospheric or pressure boiling (112°C)(Briggs et al., 2004). The gelatinisation process depends mainly on water content of the gel, amount of amyloses, degree of crystallinity in the amylopectin fraction and branching and length of amylopectin chain (Marconi, 2017).

Fox et al. (2019) compared the effect of the rice pre-gelatinisation on viscosity and total maltose in mash. The results confirmed that mashing the pre-treated unmalted rice significantly reduced the mash viscosity, reached a higher extract and at the same time it provided a higher amount of maltose as a main fermentable carbohydrate affecting the proper fermentation.

Mashing. The pre-gelatinised rice is mixed with 10–20% of mash and kept at 78°C, which enables to complete gelatinisation and liquification. When brewery is not equipped with a separate cooker, then the chosen rice variety should have a lower gelatinisation temperature range and prolonged time, since economic demands on the batch must be taken into account. In this case, rice with 10–20% of mash is either slowly heated up to the gelatinisation temperature while the activity of α-amylase is maintained, or bacterial thermostable α-amylase is added to the mash, which maintain activity even at 80°C (Adebowale et al., 2010; Briggs et al., 2004).

Lautering. Zhu et al. (2015) dealt with the permeability of the spent grain layer when a high proportion of rice was employed as an adjunct. They found that large and irregular rice particles, unlike corn starch granules, can increase the porosity and thus the permeability of the spent grain layer.

Wort and beer. Lower levels of soluble nitrogen as well as FAN are typical for rice wort. These values are even lower compared to corn adjunct (Maia et al., 2021; Stewart, 2016a; Yorke et al., 2021). Yorke et al. (2021) evaluated beers prepared from 30% and 60% of unmalted rice and found that no negative features were detected in beers made from 30% rice. Only a very slightly sweet malty and fruity character was noticed. When using 60% rice, beers were rated much worse because of defects caused by fermentation in an extremely low level of nitrogen. This resulted in excessive higher alcohols and acetaldehyde and an absence of sweet malty character.

Malted rice. Rice malting is gaining prominence mainly due to the gluten-free potential in the food and beverage industry. Although rice malt has a lower enzymatic power than barley malt, several studies have agreed that rice is sufficiently equipped with all the necessary enzymes to produce well-fermentable wort (Marconi, 2017; Taylor et al., 2013). Specifically, the activity of α-amylase is rated as adequate and β-amylase is relatively good (Taylor et al., 2013). However, these diastatic enzymes are supplemented with higher levels of other amylolytic enzymes including debranching limit dextrinase.

The mashing process can be supported by exogenous enzymes, for example the cell wall-degrading β-1,3–1,4 -d-glucanase would considerably help with cytolytic degradation (Marconi, 2017).

Compared to different chemical and physiological properties of barley, rice is not suitable for the classic malting method. In general, it is appropriate to prolong steeping, while water should have higher temperatures. Nevertheless, this method supports development of mould and increases losses. Also low kilning temperatures of up to 70°C necessary to maintain enzymatic activity are a typical feature of rice malting. This mild kilning results in a very pale colour of around 2 EBC units (Marconi, 2017). An overview of different malting conditions and rice malting parameters collected from various studies can be found in several tables by Marconi (2017). The disadvantage of rice malt in brewing is a relatively low extract, generally reaching only around 70%.

Table 6 *Literature overview on brewing with rice as an adjunct*

Proportion and form of grist	The aim of study	Applied enzymes	Brewing Scale	References
10 and 20% rice flour	compensation of technological properties of six-row barley	barley malt enzymes	600 ml	Han et al. (2016)
10; 20; 30; 40; 50; 60; 70% medium grain rice	wort separation performance in high adjunct ratio brewing	thermostable α-amylase	laboratory	Zhu et al. (2015)
10.5; 11.7;15% rice grist	the relationship between the starch structure and the amount of maltose in mash	barley malt enzymes	laboratory	Fox et al. (2019)
12.5; 25;37.5;50 %long white rice	impact on flavour stability	β–glucanases, xylanases	400 ml	Maia et al. (2021)
15; 30; 45 and 100% long shaped rice	monitoring of organic acids formed during fermentation	barley malt enzymes	laboratory	Li and Liu (2015)
30 and 60% torrefied rice	sensory and analytical profiles of lager beer	barley malt enzymes	25 l	Yorke et al. (2021)
35 % medium shape rice	optimal ingredient proportions	Ondea Pro®	laboratory	Cooper et al. (2016)
43% rice flakes + 57 % oat malt	quality parameters of beer	oat malt enzymes	laboratory (~20 l)	Orhotohwo et al. (2021)
40% raw or extruded rice	comparison of raw and extruded rice impact on beer quality	barley malt enzymes	~100 l	Zhang et al. (2017)

4 Conclusion

Malt substitutes are extensively used in the brewing industry due to their high economic benefits, better availability in certain countries, improved colloidal stability of beer or the possibility to optimise organoleptic properties. Industrial production of exogenous enzymes made it possible to use substrates with insufficient enzymatic apparatus such as unmalted barley, corn, rice, etc. Today's trend is to examine higher shares of unmalted cereal adjuncts to better understand the factors and processes that have so far prevented the incorporation of a higher percentage of unmalted cereals in beer recipes. Studies focused on partial brewing operations show the need to adapt all individual brewing steps from the grain milling, over enzyme types and their dosage, adjustment of mash schedule up to fermentation a stabilization processes.

In the coming years, a further increase in the use of malt substitutes can be expected due to climate change rising energy costs, increasing number of people who suffer from celiac disease or the constant growth of human population leading to a search for alternative crops with high adaptability to external conditions. Another and simpler reason may be just the increasing demand for special beers with a different sensory character.

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