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Chapter 4

The Use of Rice in Brewing

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http://dx.doi.org/10.5772/66450

Abstract

Rice could be a useful raw material for the production of a gluten-free beer-like beverage. In today's beer brewing industry, rice is primarily used as an adjunct in combination with barley malt. But, recently, there is some information about rice malt for brewing an all-rice malt beer. The use of rice as an adjunct in brewing is described highlighting the quality attributes of the final beer. The rice grain quality attributes of different samples are reported in order to evaluate their attitude to malting and brewing and also considering their enzymatic activity. Then, the different brewing processes to produce all-rice malt beers will be described and the final gluten-free rice beers is evaluated and compared to a barley malt beer. Finally, the levels of major aroma-active components of an all-rice malt beer and the results of the sensory analysis assessing the beer-like character of the rice beverage are reported. The obtained beer samples show a content of volatile compounds comparable with a barley malt beer. The sensory profile of the rice malt beer is similar to a barley malt beer in aroma, taste and mouthfeel.

Keywords: rice, rice malt, gluten-free beer, adjunct

1. Introduction

Rice is a staple food for nearly 50% of the world's population. According to the Food and Agriculture Organization (FAO) of the United Nations, global paddy rice production in 2015 was of 738.2 million tons (490.3 million tons, milled basis) [1]. Rice does not contain gluten-like proteins, so it is particularly suitable for consumption by individuals with celiac disease [2]. Thus, rice could be a useful raw material for the production of a gluten-free beer-like beverage. Beer is an alcoholic beverage obtained from water, barley malt, hops and fermented by yeast but other cereals can be used as raw materials or adjunct. In today's beer brewing industry, rice is primarily used as an adjunct in combination with barley malt. As a brewing

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adjunct, rice has a very neutral flavor and aroma, and when properly converted in the brewhouse, it yields a light clean-tasting beer. Recently, there is a growing interest about the use of rice malt for brewing an all-rice malt beer. Malt is the product obtained from steeping, germination and drying of cereals, generally barley. The aim of malting is to develop enzymes needed for the brewing process. Some rice varieties showed good aptitude to be malted due to their good germinative energy and protein content. Rice malt beer can be produced by obtaining a gluten-free beverage comparable to conventional beer. The beverage represents a good alternative in the diet of individuals who suffer from celiac disease.

2. Rice varieties for brewing

Rice (*Oryza*), like barley, wheat and millet, belongs to the Poaceae or Graminae family. The two main species successfully cultivated are the African species *O. glaberrima* L. and the Asian species *O. sativa* L., of which 120,000 varieties are known. During its long history of cultivation, *O. sativa L.* Asian rice has undergone considerable differentiation, and thousands of cultivars have evolved as a response to the wide range of environmental condition into which it has been introduced. They fall into three groups, with different features:

(a) short-grained "japonica" or "sinica" forms, adapted to a relatively cool climate;
(b) long-grained "indica" and
(c) broad-grained "javanica" forms, which thrive under more tropical condition [3].

Short grain has the highest starch content, makes the stickiest rice, whereas long grain is lighter and tends to remain separate when cooked. The qualities of medium grain fall between the other two types [4]. These groups also show a different gelatinization temperature, namely the temperature at which the intermolecular bonds of starch molecules break down in the presence of water, that is, a key feature for brewing. In particular, the gelatinization temperature is about 65–68°C for short-grain rice and about 71–74°C for long-grain rice, which is also extremely viscous prior to liquefaction. For this reason, short-grain varieties are usually preferred [5]. In fact, the Californian short-grain varieties, such as Pearl, Mochi, Somi and Cahose, liquefy better than the medium-grain variety Nato [6]. Moreover, other quality parameters are important for the evaluation of suitability of rice variety for malting and brewing, such as thousand kernels weight, germinative energy, water sensitivity and total protein. Mayer et al. [7] analyzed 10 Italian rice varieties (8 short grain: Creso, Selenio, Kernak, Arborio, Vialone nano, Centauro, Crono and Balilla; 2 long grain: Sirio and Libero) for these parameters without finding significant differences between japonica and indica varieties, but finally only the varieties Centauro and Balilla were able to saccharify. In conclusion, not all the variety is suitable for brewing and the careful selection of the right varieties is important.

3. The rice grains quality attributes for brewing

The rice composition makes this cereal particularly suitable for human nutrition. The chemical composition of grains varies widely, depending on environment, soil and variety. The dry matter consists of about 70% starch, 5–8% protein, 0.2–2.2% oil and small amounts of

inorganic substances. The chemical composition of rice, especially the high starch content, makes this cereal also perfectly suitable for brewing [5].

Usually, brewer's rice is a byproduct of the edible rice milling industry. Hulls are removed from paddy rice, and this hulled rice is then dry milled to remove the bran, aleurone layers and germ. The objective of rice milling is to completely remove these fractions with a minimal amount of damage to the starchy endosperm, resulting in whole kernels for domestic consumption. The broken pieces are considered esthetically undesirable for domestic use and sold to brewers at a low price. Rice is preferred by some brewers as adjuncts because of its lower oil content compared to corn grits. It has a very neutral aroma and flavor, and when properly converted in the brewhouse it results in a light, dry, clean-tasting and drinkable beer. The quality of brewer's rice can be judged by several factors: cleanliness, gelatinization temperature, mash viscosity, mash aroma, moisture, oil, ash and protein content. Rice grains contain more starch on a percentage dry weight basis than barley or wheat and they contain lower levels of fiber, lipid and protein, thus possessing some inherently useful properties for the brewer. The starch structure of rice is more granular than that of barley or wheat. Being small grained, rice is low yielding, in terms of brewer's extract [4].

Concerning proteins, their content range from 6.6% to 7.3% for brown rice, 6.2% to 6.9% for milled rice and 8.2 to 8.4% for basmati rice [8]. The average amount of proteins in rice 6–9% is lower than both barley (about 11.5%) and barley malt (about 10.5%). Quantitatively, the major proteins of barley are the prolamin storage proteins, which are endosperm specific. Uniquely, in rice, glutelin-type storage proteins, with a globulin-type amino acid sequence, are the major proteins. There is also some evidence that the endosperm storage proteins of cooked rice are very resistant to hydrolysis [9].

Moreover, just a little part of this nitrogen amount goes into solution during malting, and consequently the free amino nitrogen (FAN) needed for the yeast must be supplied by the malt. For this reason, the employment of high-yielding FAN malt may be important to balance this difference. Protein is most abundant in the subaleurone layers but is also present in aleurone cells [10].

Concerning lipids, their content is about 2.2%, a little bit higher than barley (1.8%). Cereal lipids are a chemically diverse group: neutral lipids, glycolipids and phospholipids. The ratio of these lipids classes does not differ between japonica and indica rice, but their distribution within the grain is not uniform and the endosperm lipids contain a higher proportion of polar lipids [11]. The lipids or oil content of rice is concentrated in the bran fraction, where it can contribute up to 20% by mass (dry basis), specifically as lipids bodies or spherosomes about 0.1–1 μm size in the aleurone layer and bran. The crude oil content in brown rice is about 2.9%, of which 51% was found in the germ, 32% in the polish and only 17% in the endosperm [8]. A high lipid content can cause increased yeast growth and reduced ester formation during fermentation, reduced foam stability, flavor problem and gelatinization difficulties. Brewer's rice should therefore contain less than 1.5% lipid. In such concentration, lipids do not affect beer quality unless they become rancid. On the other hand, rice grain polishing and repeated washing can decrease the fat content. This results in a decrease of the fat-derived metabolites γ-nonalactone and 1-hexanol. Both are specific flavor components, which become perceptible only after fermentation [12].

Concerning starch, the granules are evenly distributed in amyloplasts packed in the endosperm cells [10]. The two outermost cell layers (the subaleurone layer) are rich in protein and lipid and have smaller amyloplasts and compound starch granules than the inner endosperm. Rice endosperm cell walls seem to be different from barley, although arabinoxylans and β-glucans account for the major proportion (~47 to 49%) of endosperm cell wall, there are also substantial proportions of cellulose (~23 to 28%) and pectic substances containing polygalacturonides (~27%) and variable amounts of glucomannans. It does not, however, seem that these pectic substances have an adverse effect on wort filtration when rice is used as an adjunct [9]. Rice starch granules are the smallest produced by plants, with an average size of 3–8 μm and a polygonal but irregular shape. Compound granules having diameters up to 150 μm form clusters containing 20 and 60 individual granules and fill most of the central space within the endosperm cells. However, in waxy varieties, which are essentially 100% amylopectin (0% amylose), the endosperm is opaque because of air spaces between the starch granules [8].

The starch granules are accumulations of numerous starch molecules that can be fractionated into essentially linear chain amylose and the highly branched amylopectin. The main variation in composition of rice starch is caused by the relative proportions of these two fractions in the starch granules. Amylose content varies greatly between varieties, from a low of 0–2% in waxy rice (milled rice and dry mass basis) to a high of greater than 25% in non-waxy rice. The starch content, and the relative proportions of amylose and amylopectin, together with the chain length distribution and the frequency and spacing of branch points within the amylopectin molecule, has a profound influence on the physicochemical properties of starch, such as the gelatinization temperature, which is mainly important for brewing [13].

3.1. Gelatinization temperature of rice

Gelatinization describes the irreversible collapse (disruption) of molecular order within a starch granule when heated in excess water. This feature is particularly important for brewing because if the starch granules swell and lose their structure, then they become susceptible to rapid enzyme attack during mashing. Rice has a relatively broad gelatinization temperature range (65–85°C) but, even considering this great variation, the gelatinization temperature of rice is generally higher than the barley malt (64–67°C), probably because of the smaller starch granules. Consequently, rice need to be gelatinized or pre-cooked before brewing, otherwise malt enzymes will be rapidly inactivated at the elevated temperatures, which is needed to gelatinize the rice starch granules. In fact, for brewing, it is necessary that starch gelatinization happens in a temperature range where the amylolytic enzymes are still active, otherwise they cannot degrade the starch to fermentable sugars and dextrins. Starches with higher gelatinization temperature require longer cooking time than those with lower gelatinization temperature. Gelatinization is affected by several factors including water content of the gel, amylose content, degree of crystallinity in the amylopectin fraction and amylopectin chain length. Other factors that influence gelatinization include placement and content of starch granule-associated protein and lipids. As already illustrated, the short-grain varieties have a lower gelatinization temperature than the long-grain varieties. Thus, the careful selection of

varieties that liquefy well is important [5–14]. The selection of suitable grades is also important, rice liquefies more easily the fine the particle grist is and particles less than 2 mm are considered adequate [6]. Moreover, even if the gelatinization temperature is quite high for unmalted cereals, it can be lowered up to 20°C in the presence of enzymes. It depends on the malting conditions. So the high gelatinization temperature of rice (65–85°C) should also be lowered after malting. But there is no knowledge about the real optimal temperature range of the amylolytic enzymes of rice malt, which can differ from that of barley malt. Moreover the starch granules are already attacked by enzymes during germination, and therefore the starch can be also hydrolyzed below the gelatinization temperature [7].

4. Malting

Malting is a process involving steeping, germination and drying of cereal seed to obtain the malt. Generally, malt production from barley is the first step in beer production but it is possible to obtain malt from other cereals such as rye, sorghum, wheat, quinoa, amaranth or rice [15]. The aims of malting are to produce enzymes in the kernel and modify its chemical constituents. In stored kernel, the enzymes that are important for the malting process are inactive. The first step in malting is the steeping where the kernel absorbs the water, until about 40%, for germination. As a result, the enzyme synthesis is induced and the germination begins. The germination takes place in large tanks or chamber where the temperature and the humidity are controlled. During germination, the formation of enzymes is one of the main requirements of malting because these enzymes are absolutely essential, subsequently, for the breakdown processes that occur during mashing in the brewhouse transforming insoluble substances in the soluble form. The final step is the kilning at high temperature to dry the malt. The temperature of the kilning depends on the type of malt produced and it ranges from about 82°C for a pilsner malt to about 220°C for chocolate malt. During the kilning, the water content is lowered from 40% to about 5%, the germination is stopped but the enzymes are preserved and the color and flavor compounds are formed.

Rice does not contain gluten-like proteins, so it is particularly suitable for consumption by individuals with celiac disease [7, 16]. Thus, rice could be a useful raw material for the production of a gluten-free beer-like beverage in a traditional way, saccharifying completely the wort without the addition of exogenous enzymes. Since rice and barley are physiologically and chemically different, the malting process commonly used for barley is not suitable for rice (**Table 1**) [9].

There are many enzymes involved in the germination process but among these enzymes the amylases have an important role. They breakdown the starch into fermentable sugars. In barley malt, an important attribute for the activity of starch-degrading enzymes is the diastatic power, which measures the combined activity of α- and β-amylases, and for this reason it is always taken into account for the evaluation of malt. Rice malt, however, shows lower diastatic power values, and for this it seems less suitable for brewing [17]. But it contains other amylolytic enzymes that can act synergistically with α- and β-amylases [9, 18, 19]. One of these amylolytic enzymes is limit dextrinase, a debranching enzyme, which

Enzyme	Rice malt	Barley malt
α-Amylase	120 IU/mg protein	206 IU/mg protein
	28–42 DU	44 DU
		365 IU/g
β-Amylase	23–175 IU/g	1017 IU/g
		234 IU/mg protein
α-Glucosidase	0.22–0.30 IU	1.8 IU
Limit dextrinase	2.2–6.0 EU/g	0.2–0.4 EU/g
Endo-β-(1,3)(1,4)-glucanase	0.0–0.1 U/g	100–135 U/g

IU (international unit), amount of enzyme that releases 1 μmol of p-nitrophenol from the substrate per minute at the defined pH and temperature. DU (dextrinizing unit), quantity of α-amylase that dextrinizes soluble starch in the presence of an excess of β-amylase at the rate of 1 g/h at 30°C. EU (enzyme activity unit), amount of enzyme that releases 1 μmol of glucose reducing sugar equivalent per minute at 40°C and pH 5.0 or 5.5.

Table 1. Activity of enzymes important in lager brewing in barley and rice malts.

catalyzes the hydrolysis of the α-1,6-glucosidic linkages in starch and related oligosaccharides and exhibits activity levels in rice several fold higher than in barley malt [20]. Another enzyme, α-glucosidase, shows high activity in rice malt and an optimum temperature of 55°C, whereas in barley malt its activity is low and the optimum temperature is 35–40°C. Above 50°C in barley malt, the enzyme is inactivated very rapidly [21]. Evidently, the same enzyme can have different features in different cereals. With the notable exception of β-amylase, it appears that rice malt has all enzymes required to produce a well-fermentable wort. Nevertheless some authors [9, 22] suggested that supplementation with exogenous cell wall-degrading enzymes, namely, β-1,3–1,4 -d-glucanase, would benefit brewing because rice malt contains low amounts of these enzymes compared to barley malt. Degradation of cell walls in the rice malt endosperm is an important step during the malting and mashing process, because it exposes starch granules to amylolytic enzymes. This behavior is different from rice barley malt. The cell walls of the endosperm of rice, unlikely barley, contain mainly pectin and xyloglucan. So the addition of (1−3,1−4)-β-D-glucanase, which were found in rice malt only in a negligible amount, is not necessary. Pectin might simply be washed out at higher temperatures [23].

Some authors have studied the optimization of the malting condition for rice improving the steeping, the germination and the kilning steps (**Table 2**). Steeping is a critical stage in malting because the enzymes production in grains depends on the steeping period. The steeping time and temperature influence the water uptake and the warmer the steeping water the faster the water is taken up, and vice versa [27]. Some authors performed a short steeping because increasing the steeping period directly increases the steeping losses and the mold development. The optimum steeping period for rice grains should be a balance between time, temperature and losses [17]. However in Ref. [7], it was decided to perform a long an unusual steeping period to increase the water uptake and solubilize any inhibitor for

Grain	Steeping	Germination	Kilning	Rice malt characteristics
Ofada rice [24]	24–48 h	6–7 days	48–60°C	Moisture 11.01%; cold water extract 1.001
Rice [25]	Wet-steep: 20°C for 42 h (20+22); air rest: 4 h	5 days at 20°C	50°C for 24 h	Hot water extract 352 Ldeg/kg; total soluble nitrogen 0.46%; free amino nitrogen 133 mg/l
Italian rice varieties [16]	Wet-steep: 18–20°C for 39 h (24+15); 8 h air rest: 9 h (8+1)	7 days at 20°C	From 45°C to 58°C within 8 h, 4 h at 58°C, from 58°C to 63°C within 4 h, 6 h at 63°C	Final moisture 4.0–5.2%; extract 64.3–73.5% d.m.; saccharification time > 60 min, Kolbach index 15.1–25.7%, viscosity 1.53–1.94 mPas
Jasmine 85 rice [17]	28°C for 48 h	12 days	Not reported	Steeping degree about 36%; diastase activity 668 U/dry malt
6 *Oryza sativa* L. Indica cultivars [26]	30°C for 24 h	4–5 days at 30°C	24 h at 50°C	Steeping degree about 30%; high enzyme activity and satisfactory modification of the rice endosperm
Non-waxy and waxy Black rice [20]	Wet-steep: 25°C for 5 h; air rest: at 95% RH until 44% moisture	8 days at 30°C	24 h at 50°C	Extract 59.3–62% d.m.; Kolbach index 20–23%; viscosity 1.33–1.37 mPas
10 paddy rice varieties of *Oryza sativa* L. japonica and indica [7]	Wet step: 25–23°C 40 h (8×5); air rest: 25–23°C 32 h (8×4)	24 h at 22°C, 24 h at 21°C, 72 h at 20°C	Withering: 12 h at 45°C, 12 h at 50°C, 13.5 h at 55°C. Curing: 6 h, 70°C	Steeping degree about 42%; final moisture <5%; diastatic power 42 WK; fine extract >70% d.m.; saccharification time 50 min, Kolbach index 28.5–40%, viscosity 1.48 mPas

RH: air relative humidity %.

Table 2. Comparative studies on the optimization of the rice malting process.

germination. The longer steeping time was compensated for the lower water temperature of 23–25°C. In this condition no mold was developed and a steeping degree of about 42% was reached, which is necessary for good rice modification. The germination step has a duration of about 4–8 days and it was performed at 20°C or 30°C. In Ref. [20], it was reported that the optimal germination conditions for black rice varieties were at a temperature of 30°C for 8 days obtaining an extract content of 60% (w/w) and a good enzymatic activity related to limit dextrinase and α-glucosidase, which compensate the low activity of β-amylase. Other authors obtained good rice malts performed the germination for 5–7 days at 20°C. In fact the germination temperature affects the extract level and some authors [25] demonstrated that they obtained the highest level of extract at the lowest germination temperature (20°C). As reported in literature, good extract values for barley malt are greater than 82%

and poor values lower than 79% but highest rice malt extract is generally around 70% [7, 16]. Furthermore the European Brewing Congress (EBC) official analytical method to determine the extract is set for barley malt but it was shown that the amount of the endogenous rice malt enzymes is high enough to saccharify the rice malt starch. Anyway, the optimal temperature and pH conditions of rice malt enzymes are different from those of barley malt. So the method to obtain the conventional Congress mash must be slightly changed. With different temperature rests and the addition of $CaCl_2$ and lactic acid, a complete saccharification of the rice malt starch is achieved [7]. The conditions of this new standardized mashing program are 30 min at 45°C, 30 min at 64°C and 30 min at 74°C. The increase of the temperature of the final rest is due to the fact that the temperature at 70°C did not permit the complete gelatinization. The kilning step is important to stop the germination and have a moisture content of about 5%. The kilning step influences the aroma and the color of the rice malt. Generally, the kilning temperature for rice malt is not higher than 70°C, as reported in **Table 1**, to preserve the endogenous rice enzymes. Therefore the color of the rice malts is around 2 EBC units, derived from absorbance at 430 nm. The rice malts are paler than pilsner malt (2.5–4.5 EBC units).

Table 3 reports the quality attributes of rice malt [7]. The fine extracts showed very good results considering the fact that the hull accounts for up to 20% of the kernel's mass and contributes less to the extract. The soluble nitrogen content was low if compared to barley malt. The FAN values were surprisingly high compared to barley malt wort in relation to the soluble nitrogen content. Normally in a good brewing malt, the FAN content is around 22%

Attributes	
Moisture	4.3
Fine extract (% d.m.)	71.7–72.7
Saccharification time (min)	50
pH	5.76–5.96
Color (EBC-U)	1.7–2
Total nitrogen (g/(100 g of d.m.))	1.34–1.43
Soluble nitrogen (mg/l at 8.6°P)	450–506
Kolbach index (%)	29.5–27.4
Viscosity (mPa S at 8.6°P)	1.40–1.48
Free amino nitrogen (FAN) (mg/l at 8.6°P)	148–166
Fermentability (%)	71.2–73.2
Diastatic power (WK)	42

°P, Plato degree; d.m., dry matter; WK, Windish Kolbach.

Table 3. Quality attributes of a rice malt.

of the soluble nitrogen. This could be an overestimation that depends on the method for FAN determination, which is a color reaction with ninhydrin.

5. Brewing

Brewing process consists of mashing, the mix of grinded malt with water to obtain conversion of starch in sugar (wort); lautering, filtration of wort through the grain bed for the clarification and recover of sugar; boiling of the wort for the inactivation of enzymes, concentration and formation of color and flavor and fermentation of the wort by the yeast to produce alcohol. The resulting beers can vary depending on raw materials, temperatures and times used for the production of the worts, type of yeast and temperatures of the fermentation. In most conventional breweries, the malted grains are primarily barley and wheat. Other grains are used as adjuncts to provide a carbohydrate source for alcohol production, to add body or foaming characters to the final product and also to attenuate the negative aspects of malt that may be more evident in lighter style beers. There are breeding efforts to produce dual food and brewing varieties of rice, but worldwide, it is malting barley that breeders focus on to produce a cereal specifically adapted for use in brewing [14].

5.1. The rice as adjunct

Rice is one of the most important cereals used as adjunct in brewing. There are several advantages of using adjunct in brewing. It has lower cost compared to malt, in case of suboptimal malting facilities and malting conditions, adjunct material can be used to supplement the sugar content of barley and wheat malt [28]. A lower production tax in some countries, for example, in Kenya and Japan, beer made from high percentage of adjunct is less taxed than beer made from malted grain [29, 30]. An improvement in the quality and a characterization of the product can also be obtained using adjunct. Rice indeed has a decisive impact on the flavor, color and colloidal stability of an American pale lager. As brewing adjunct, rice has a very neutral flavor and aroma, and when properly converted in the brewhouse it yields to a light clean-tasting beer. Rice for brewing is a by-product of the edible rice milling industry, any kernels that may get fractured during the milling process (~30%) are considered undesirable are therefore sold to the brewing industry at a cheaper price. The main rice adjunct types currently available to the international brewing industry are: gritz, flaked, extrusion cooked and flour/starch. The physicochemical properties of that adjunct will dictate its addition rates to a grist recipe, its time of addition and how it will be processed. The quality of rice can be judged by several factors. A high lipid content can cause reduced foam stability, flavor problems and gelatinization difficulties. Rice should therefore contain less than 1.5% lipid. Rice supplies little free amino nitrogen, and this deficiency should be balanced. Extract yield differences depend greatly on the rice cultivar. It is important that rice is finely milled before brewing, otherwise gelatinization problems will occur. Not all varieties of rice are acceptable brewing varieties. As already stated (see Section 3.1.), short-grain rice is preferred because medium- and long-grain varieties can lead to viscosity problems [31]. The rice starch swells greatly during the gelatinization, and this can lead to the sticking of the pasta to the hot surfaces

of the plant and cause burns. It is therefore necessary to find a compromise so that the malt α-amylases are able to liquefy the viscous paste and make it less viscous. The α-amylases are, however, rapidly inactivated at temperatures of about 80°C and are no longer able to liquefy the starch. As described, is it clear that the use of unmalted rice in brewing is not very easy. There are different solution for the use of rice in mashing [5, 14, 27]:

(1) An adjunct cooker is preferably used. This is a closed kettle in which the rice mash is gelatinized under pressure (i.e. at a temperature above 100°C).

(2) The rice grist is mashed with 10–20% of the malt mash and held at 78°C. Thereby almost all the starch is gelatinized and liquefied.

(3) There are rice varieties that do not gelatinize below 80°C. The rice mash must therefore, to be certain, be heated to 85–90°C, gelatinized at that temperature and then cooled again to 70–75°C in order to be saccharified in a shorter time by the addition of a malt mash.

(4) Another possibility is to heat the rice mash with 10–20% of the malt mash slowly to above 80°C to liquefy the gelatinizing starch by the still active α-amylase in the malt.

(5) A very reliable method is to add commercial, heat-resistant bacterial α-amylase, which is still active at temperatures above 80°C and consequently liquefies the rice mash.

(6) A double-mashing system was developed in North America, to deal with grist containing large proportions of rice. The adjunct mash containing a small proportion of enzyme-rich malt or bacterial amylase is mashed with different temperature steps and is brought to 85±100°C standing until the starch is gelatinized. Meanwhile, the malt mash has been mashed in at 35°C and then mixed together.

(7) Flaked rice has the advantage of being pre-gelatinized.

5.2. The all rice malt beer

5.2.1. Wort production

Once the malt grain is milled, it is added to a large vessel called the mash tun and mixed with hot water to form the mash. The heat from the water activates the enzymes in the malt. These enzymes then convert the starch of the grains into sugars. There are several different types of enzymes within malt, which work at specific temperatures (see Section 4). The mashing process can be carried out by infusion or decoction procedure. In the mashing decoction method, a part of the mash is separated and brought to high temperatures to gelatinize the starch and re-added to the main vessel, thus increasing the temperature of the mash. This process can be repeated several times (one, two or three mash procedure). This procedure could be useful when brewing rice malt because of its high gelatinization temperature. Some authors performed a three mash decoction procedure to obtain an all rice malt beer [32]. Grinded rice malt and water are mixed and mashed at 50°C for 30 min. The mash is decanted and the supernatant rich in enzymes is separated. The bottom part of the mash is heated to 88°C to completely gelatinize the starch and then collected with supernatant reaching thus 62°C. Two further decoction steps are then

performed increasing the temperature of the mash to 67°C and 70°C. Finally, the mash temperature is raised to 74°C. Otherwise, a one mash decoction procedure can be used to obtain an all rice malt beer [33]. Rice malt and water are mixed at 35–37°C for 10 min, one-third of the mash is transferred to a pot and then heated to the boiling point and re-added. Then, the mash is rested to different temperatures to allow different enzymes work properly; 10 min at 50–53°C for proteolytic enzymes, 15 min at 63–65°C for amylolytic enzymes and 60min at 71–73°C, 20 min at 75°C and 5 min at 77°C. Concerning infusion process is simpler than decoction because the entire mash is always kept together. The total mash is heated with rests being used at temperatures determined by the enzyme properties [27]. Nevertheless having rice malt different enzymatic pool from barley malt, an adapted mashing step temperatures in the infusion method need to be used. Some authors reported the infusion mashing program for rice malt in a pilot scale [33]. Rice malt and water were mashed at about 40°C. The mash was allowed to rest at 50°C for 10 min, then at 62°C for 50 min and finally at 72°C for 90 min. During the last rest, the conversion of starch in fermentable sugars was tested by the iodine test and it resulted incomplete. At the end of the process, the mash was heated at 77°C. The pH of the mash was adjusted to a value of 5.5–5.6. Otherwise rice malt can be mashed in a pilot scale brewery by the following procedure [34]. The pH is adjusted with lactic acid to 5.3, and the brewing water is added with CaCl. The infusion mash program is the following: 30 min at 45°C, 45 min at 65°C, 60 min at 74°C and 10 min at 78°C. The used pH value enhances the activity of the most part of hydrolytic enzymes in the starch and cell wall degradation except for α-amylase whose optimum pH is 5.6–5.8. Whereas limit dextrinase (optimum pH value 5.4–5.5) in rice malt is 10-fold higher than in barley malt, the adequate temperature rests at 65°C for limit dextrinase and β-amylase and 74°C for α-amylase, lead to complete saccharification 1 h after reaching 74°C. After the mashing step, the lautering process is carried out in a filtering system (mash tun) for the separation of the spent grains from the wort. The wort passes through a "bed" of spent grains to allow the recovery of the sugar and the clarification. It is a critical step because a slowdown of the wort flow, or even a stop can occur if the bed is not suitable. Barley husks play an important role in the lautering bed allowing the correct flow. Also rice husks are suitable for this process. Lautering problems occur with rice malt if the saccharification result is incomplete and the starch forms a sticky paste [33]. On the contrary, no lautering problems are reported when complete saccharification occurred [34]. Boiling of the wort is a step for the concentration of the wort to the desired sugar content and the formation of aroma and can be 60–90 min time long.

5.2.2. Wort quality

Typical quality attributes for rice malt worts are shown in **Table 4**. pH values are quite similar to worts produced from barley malt (5.2–5.6). The lowest color of the boiled wort is 3.5 EBC units and the highest is 9.6 EBC units. A very clear color of the wort is a consequence of the low color of the malt. Rice malt kilning temperature is usually lower than in barley malt. Thus the rice malt is paler. Also the composition of the grain influence the color, in particular the low rice malt nitrogen content lead to low soluble nitrogen in the wort. Indeed, less Maillard products are produced that are responsible for the wort color and are produced by the interaction of sugar nitrogen and heating. Anyway a caramelization of wort sugars can occur because of direct-fired vessel used in some boiling system causing highest color in the wort.

	Decoction [33]	Infusion [33]	[34]
Original gravity (°P)	10.34–12.20	11.85–12.30	12.65–12.78
pH	5.20–5.98	5.12–5.91	5.20–5.41
Color (EBC)	3.5–9.9	3.7–9.6	5.4–6.9
Brewhouse yield (%)	42.4–63.3	49.2–65.4	64–66
Saccharification (min)	Incomplete	Incomplete	Complete

Table 4. Comparison of the quality attributes of the different rice malt worts obtained by different production process and rice varieties.

The brewhouse yield indicates what percentage of the grist charge is available as extract content in the cast wort. The brewhouse yield is therefore an important internal brewery measure of the efficiency of the brewhouse operations. This percentage (brewhouse yield) is usually between 75% and 80%. The brewhouse yields obtained for rice malt beer are lower than those usually obtained with barley malt. This can be due to an incomplete saccharification, which is sometimes further reduced by a more difficult filtration process. However, it is to be noted that also when the starch is completely converted a bad filtration process adversely affects the brewhouse yield. Complete saccharification, ascertained with the iodine test, is achieved by the optimized mashing program with the starting temperature of 45°C for 30 min and the correction of the pH to 5.3 that improved protein degradation. This is in fact a prerequisite for complete saccharification of the starch.

Sugar profile of rice malt wort is the result of the enzymatic pool that worked during mash steps. Successful fermentation also depends on the wort sugar composition. **Table 5** shows the different sugar profiles of the rice malt worts compared to barley malt wort.

	Decoction [33]	Infusion [33]	[34]	Barley malt wort [35]
Fructose			1.0–1.1	2.1±0.3
Glucose	17–20	16–23	33.8–36.9	13.8±2.1
Sucrose			1.1–1.6	3.0±0.7
Maltose	27–40	34–45	22.6–38.3	73.5±5.4
Maltotriose	9–12	9–10	15.5–15.8	19.6±2.2
Maltotetraose	4–6	4–6	12.3	5.0±1.2
Maltopentaose			4.3–5.9	1.6±0.2
Maltohexaose			12.7–13.7	1.8±0.3
Maltoheptaose			0.5	1.5±0.2

Table 5. Sugar profile of different rice malt worts (g/L) from different production process and rice varieties.

All worts contained an acceptable sugar composition and besides glucose and maltose, maltotriose and maltotetraose were also present but in lower amounts. In the barley malt wort, the most abundant fermentable sugar is maltose. By using an infusion program that lead to a complete saccharification, the obtained rice malt worts show a maltose content in the same range of glucose and there are higher levels of maltotetraose, maltopentaose and maltohexaose. This is an indication of the different amylolytic enzymes working in the rice malts. Moreover, the sum of the fermentation onset stage sugars glucose, fructose and sucrose are between 42% and 49% of the total content of the fermentable sugars. This value should not exceed 25%, because maltose and maltotriose utilization could be delayed causing a slow primary fermentation [34]. On the contrary, some authors find maltose as main sugar, ranging between 27 and 45 g/L, followed by glucose in the range 16–23 g/L. Anyway, with the mashing programs used in these studies, both decoction and infusion method, a complete saccharification was not achieved [33].

5.2.3. Wort fermentation

In the fermentation of the wort, the fermentable sugars are converted into alcohol and carbon dioxide by the yeast (*Saccharomyces cerevisiae* or *Saccharomyces pastorianus*). Fermentation can be conducted at high (18–24°C) or low temperatures (8–13°C), giving top fermented or bottom fermented beer, respectively. Rice beer worts are fermented at low temperatures.

5.2.4. Beer quality

Typical quality attributes for rice malt beer are shown in **Table 6**. The sugars in the wort are not totally converted by the yeast, depending on the wort suitability in terms of sugars and nitrogen composition. The attenuation limit is the highest apparent degree of attenuation, which can be reached by fermentation of all fermentable materials in the extract. It is predetermined by the action of starch-degrading enzymes in the brewhouse. In the rice malt beer, attenuation limit values calculated according to original and final gravity is acceptable, even if in barley malt wort, higher values can be found (80–84%) [27]. In some beers because of problems encountered during fermentation, the attenuation results low (e.g. 50–60%). Problems in the fermentation can occur because of incomplete saccharification and also because of the low content of nitrogen. The rice beer has an alcoholic content of about 3.5–5.1% vol., that is, a usual value for a barley malt beer. The beers have a color very similar to the worts from

	Decoction		**Infusion**	
	[32]	**[33]**	**[33]**	**[34]**
Attenuation (%)	79–81	50–73	59–70	69–76
Alcohol wt/wt (%)-% vol	3.9–4.2	3.7–4.5	3.6–4.5	4.6–5.1
Original gravity (°P)	10.8–11.9	10.3–12.20	11.85–12.30	12.5
pH	4.3–4.4	4.23–4.81	4.35–4.84	4.21–4.24
Color (EBC)	7.2–8.0	3.3–9.6	3.5–9.41	4.3–5.0
Foam stability (s)	30–40.5	not detected	not detected	157–169

Table 6. Quality attributes of rice malt beers from different production process and rice varieties.

which they are produced. The pH is comparable to that of a barley malt beer. Foam as color is a hedonistic aspect of the beer that is very appreciated by the consumer in most of the case. It is formed by the interaction of medium molecular weight proteins and carbon dioxide. Rice malt wort in most case have a sub optimal content of nitrogen that lead to a low foam stability. In a barley beer, good values of foam are higher than 200 s.

Flavor of beer is characterized of typical volatile compound profile affected principally by the yeast metabolism. The low amount of free amino nitrogen present in rice malt wort promotes an overproduction of fermentation by-products like higher alcohols. Indeed, higher alcohols are present in great amounts in the rice malt beers (**Table 7**) but they do not exceed

	Rice malt beer	**Literature value of barley malt bottom-fermented beer**	**Threshold limit in barley malt beer**[**]
Higher alcohols			
1-propanol (mg/L)	16.2–17.6	5–20[*]	800
2-Methyl-1-propanol (mg/L)	34.1–37.4	5–20[*]	200
3-Methyl-1-butanol (mg/L)	58.8–60.1	30–70[*]	65
2-Methyl-1-butanol (mg/L)	26.4–28.8	8–30[*]	70
2-Phenylethanol (mg/L)	23.0–30.4	8–40[*]	125
2-Furanmethanol (mg/L)	0.5–0.6	–	3
Esters			
Ethyl acetate (mg/L)	9.9–23.0	10–40[*]	33
Ethyl butanoate (mg/L)	0.1–12.0	0.05–0.15[*]	0.4
3-Methylbutyl-1-ethanoate (mg/L)	0.1–0.6	0.5–3[*]	(1.2) 1.6
Ethyl hexanoate (mg/L)	0.1–0.3	0.05–0.3[*]	0.23
Aldehydes			
Ethanal (mg/L)	19.1–41.9	2–10[*]	10
2-Methyl-1-butanal (μg/L)	7.6–12.3	60[**]	1250
3-Methyl-1-butanal (μg/L)	24.2–46.0	20[**]	600
Hexanal (μg/L)	19.1–21.8	4.5[**]	300
Furfural (μg/L)	41.7–66.6	40[**]	150,000
Methional (μg/L)	15.4–25.1	–	250
Phenylacetaldehyde (μg/L)	15.7–57.8	45[**]	1600
Trans-2-nonenal (μg/L)	not detected	–	0.3
Sulfur compounds			
Dimethylsulfide (μg/L)	65.5–72.9	<100[**]	100

Ref. [36].
Ref. [27].

Table 7. Volatile compounds in rice malt beer.

the threshold limit. The aroma-active esters, other fermentation by-products that are highly desired in beer because of their fruity, were present in small amounts [37]. Aldehydes are generally off-flavors in beer, and they are produced by oxidation of the corresponding alcohols or are derived from fatty acids and lipids present in the malt and formed during the various stages along the malting and brewing process [38]. Anyway no particular off-flavor was revealed even though ethanal exceeded the perception threshold limit of 10–25 mg/L. The concentrations of volatile compounds in the rice malt beers are in the range of a barley malt beer [27]. The dimethyl sulfide content is an off-flavor derived from malt whose content is below the threshold limit in rice malt beer.

The sensory analysis conducted on the beers shows a pale yellow color and a white coarse foam which rapidly collapsed. Rice malt beer has a relatively flat character. From a sensory test, Vanillin flavor is revealed. The sensory profile of the rice malt beer was similar to a barley malt beer in aroma, taste and mouthfeel, but more flat.

Nowadays, the advancement in research about the use of rice as raw material to produce malt and rice malt beer shows encouraging results. The rice is a suitable grain despite the believed low enzymes content for use in brewing. Rice malt beer can be produced in a traditional way leading to well-fermented beers with no off-flavor comparable to barley malt bottom-fermented beer.

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