

NONTRADITIONAL GRAIN SOURCES IN BREWING AND EFFECTS ON WORT AND
BEER

by

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ABSTRACT

Brewing of beer has a long history and has evolved over time as tastes, markets and science have progressed. Traditionally malted barley is the grain source used in brewing. Malt provides a multitude of benefits including: fermentable carbohydrates, nitrogen for yeast metabolism, color compounds, flavor compounds and minor constituents that provide for various qualities in beer such as foam and colloidal stability. There is, however, interest from brewers and drinkers alike for a variety of beer styles. Because of this and other reasons, brewers have worked with adjuncts such as oats, sorghum, wheat, rice, and maize. These grains can be used in unmalted or malted forms, but the incorporation of these grains affects the brewing process and final beer qualities. A review of literature reveals the use of grains other than malted barley reduce the nitrogen contribution and alter the amino acid profile available for yeast metabolism, leading to slower fermentations and variations in the fermentation products resulting in changes to beer flavor. Exceptions include sorghum and oats, which provide a more beneficial amino acid profile than barley despite lower levels of nitrogen when compared to barley. Extract is found to increase when using maize and rice, while oats and sorghum reduce the amount of extract. Wheat has comparable extract to barley. Grains that contribute B-glucans and arabinoxylans will increase viscosity, while grains without these components will reduce viscosity if fermentation is complete. Additionally, most grains will reduce the foam stability due to altered nitrogen and protein contributions; wheat being the lone exception that improves foam stability. This review will discuss the above mentioned attributes and more to explore the changes to be expected when brewing with unmalted and malted grains other than barley.

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INTRODUCTION & HISTORY OF BREWING

The production of beer and related beverages has a long history dating back thousands of years. While there is debate among historians as to the exact timing of the invention of beer, artifacts that have survived over time show evidence of brewing around 6000 to 7000 years ago in Mesopotamia (Priest, 2006). It is assumed that malting was a part of the beer making process during that time, but there appears to be no clear record detailing this process.

It is also well-known that beer was a part of Egyptian life due to their depiction of such activities in pictographs, dating back to 3300-3100 BC (Esslinger, 2009). Additional evidence comes by references in the Bible in 1 Samuel and Proverbs 20, which date back to roughly 1000 BC.

Regardless of exact origins, beer has become a part of life in many cultures and the processes that developed over the millennia are not much different today, although many refinements in equipment, knowledge of science, agriculture and biology have certainly evolved to benefit us in the form of better tasting and more consistent beers.

Malting, as it relates to brewing, also has a long history although it was most likely discovered by accident (as are many products of the modern age) and has no distinctly documented origin that can be found. According to probrewer.com malting was an intentional practice in ancient Egypt as part of the production of beer, but no dates are given for reference. It notes that the Egyptians would steep the grain in baskets that were lowered into open wells. As the malting process proceeded, the basket was raised or lowered to control temperature or add moisture to the grain.

A better documented account of malt is found in the ancient poem 'Hymn to Ninkasi' where ingredients and processes involved in brewing, including a malted grain called *munu*, and *titah*, a mash

resulting from the malted grain, are described (Esslinger, 2009). It is estimated that this poem dates to 1800 BC giving an idea just how long mankind has been malting grain (Esslinger, 2009).

In modern times the desire for new, unique or more efficient processes are of great interest and have led to many advances in brewing technology. No industry sector has been left untouched by the desire to make improvements, usually for efficiency in time, money or process.

Malting is no different. In relatively recent times, the desire to find ways to produce beer without malted grain has been examined. Esslinger (2009) provides three reasons for using material other than malted barley for brewing: cost incentives, desirable color and flavor attributes imparted to the beer and regional availability or lack of availability of barley. Bamforth (2006) adds quality to this list, in that the adjunct may provide for some desired benefit to the product (flavor, color, foam, etc.).

In some parts of the world, notably Africa and other tropical regions, barley is less available and therefore other grains (i.e. sorghum) are used in brewing. This lack of availability in combination with the cost of importing the malt, currency conversion rates and trade restrictions makes other cereal grains more attractive (Ugboaja et al., 1991). Additionally, barley will not grow in tropical climates where sorghum, rice and maize thrive (Taylor et al., 2013). The Nigerian government began prohibiting the importation of barley malt into the country in 1988, forcing producers to make use of sorghum. This practice has since ended, but it required locals to develop methods for brewing with sorghum.

Historically, in many parts of the world tax was levied on the malt used. This drove an interest in reducing the amount of malt consumed in the process. One example of this is the production of Happoshu, a type of low barley malt beer produced in Japan, which gained significant market share due to the greater taxation of beer using higher levels of barley (Taylor et al., 2013). Uganda's taxation on cereal grains favored the use of locally grown sorghum over other grains (Taylor et al., 2013).

Additionally, the cost of malt itself is high in comparison to adjunct, so a cost savings is typically expected when using unmalted grains (Poreda et al., 2014). However, the use of cereals other than barley may require investment in a cereal cooker if the desired grains have a gelatinization temperature above that of barley (Poreda et al., 2014).

This review aims to look at the use of grain sources other than malted barley in the brewing process and discuss the effect these have in the brewing process as well as the finished beer. While the Food and Agriculture Organization (FAO) of the United Nations lists 11 cereals which have importance in brewing, this paper will examine only the most common cereals used (Esslinger, 2009).

THE BREWING PROCESS

Historically the brewing process involved only 4 ingredients: water, yeast, malt and hops. Today, with the surge of interest in beer and the influence of many micro-breweries, additional ingredients are being added to beer at various stages. Regardless of the new and unique added ingredients, the processing steps remain much the same (Figure 1).

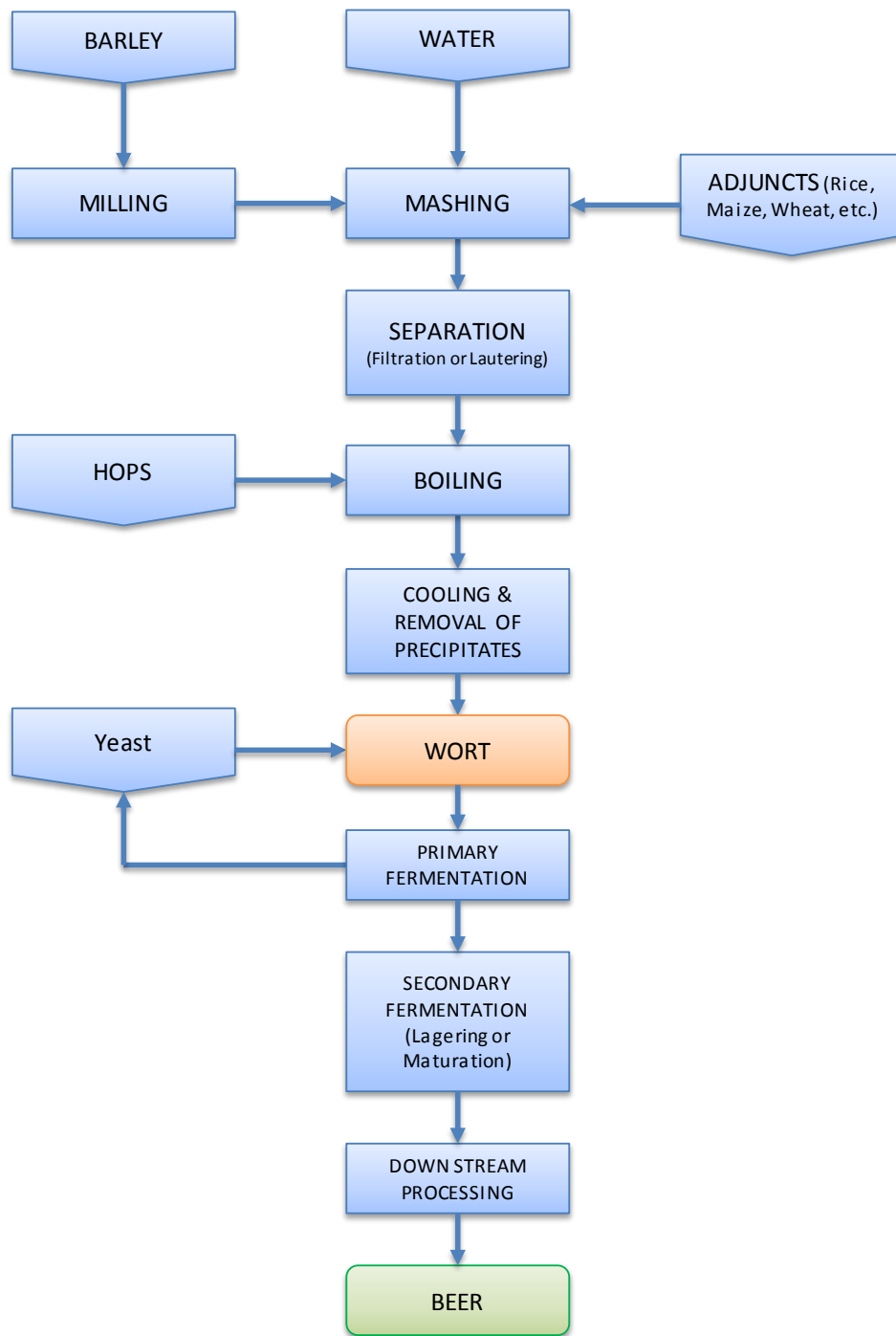


Figure 1: Brewing Process (adapted from Linko et al. 1998)

Milling

To begin the process, barley malt, usually purchased as a whole grain, is milled to the proper specification at the brewery. This can be accomplished through either dry or wet milling and can use a variety of mill types (Delcour and Hosenev, 2010). While it is quite possible for the brewery to malt their own barley, the added capital expense and square footage needed to do so is not in the beer maker's best interest as malt producers can provide brewers with consistent product quality and can also provide any variation of malt desired. The process of malting will be discussed in detail later. The milled malt, in combination with any other grain being milled, produces what is known as the grist.

Once the malted barley is milled, other grains that may be used in the process may be added at this point as well if they are not already milled. Adjuncts such as corn, rice, wheat, unmalted barley, or sorghum are all options available to the brewer. However, if the starch in the adjunct has a gelatinization temperature (Table 1) that is greater than the optimal activity temperature of β -amylase of about 62° C, as is the case for corn, rice and sorghum, it must first be gelatinized and will be boiled separately from the mash in a cereal cooker (Delcour and Hosenev, 2010). If the adjunct is in a form that does not require milling, such as pregelatinized flakes or syrup, it will be added at a subsequent step in the process.

Mashing

The grist is then mixed with hot water to activate enzymes, breaking down proteins and converting starch into fermentable sugars to be used by the yeast during fermentation (Priest, 2006). The mashing process yields wort and spent grains. Mashing can be carried out in multiple ways. Three main mashing methods are used: infusion mashing, decoction mashing and double mashing. It is during

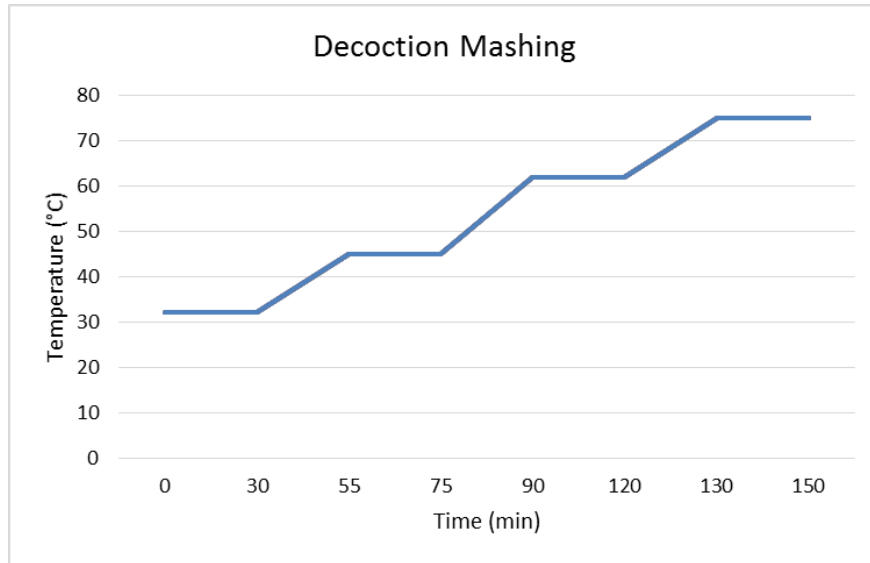


Figure 2: Example of Decoction Mash Process (Hosney and Delcour, 2010)

mashing that the enzymes contributed by barley malt are highly active on starch and proteins, and where the use of unmalted grains will affect the times and temperatures used for mashing.

Infusion mashing is the method classically used by British beer makers (Priest, 2006). It is carried out at a single temperature without any agitation and uses a single vessel, which also serves as the separation vessel once the wort is produced (Priest, 2006). This method of mashing requires that the malt be well-germinated.

Decoction mashing (Figure 1) is typical of European brewers and is more complicated than infusion mashing both in the processing steps and the equipment used. However, unlike infusion mashing it does not require the barley to be as well-malted (Priest, 2006). This is due to the fact that the different temperatures used are optimized for multiple enzymes and therefore require a lower level of those enzymes. The mash is held at specific temperatures for specific periods of time (stands) with each temperature being optimum for a particular enzyme. The temperature is raised by extracting (decocting) a portion of the mash, boiling that portion, then adding it back to the mash (Priest, 2006). This is done

repeatedly at varying temperatures to provide for hydration of the malt, proteolytic stand (40-50° C), β -amylase stand (starch hydrolysis) (54°-65° C), and α -amylase stand (70° C) (Delcour and Hoseneý, 2010).

Source	Gelatinization Temperature (°C)
Barley	61-62
Corn	70-80
Oats	55-60
Rice	70-80
Rye	60-65
Sorghum	70-80
Wheat	52-54

Table 1: Gelatinization Temperatures of Various Cereal Starches (Bamforth 2006)

Double mashing is used primarily by American brewers to produce lighter, less satiating beers popular in this part of the world (Delcour and Hoseneý, 2010). With this system of mashing, two mashes are prepared: a cereal mash and a malt mash. An example of a cereal mash program is shown in Figure 3. As noted above,

this is done to gelatinize the starches of the cereal adjuncts prior to addition to the malt mash. Without pregelatinizing the starches, the malt enzymes would be ineffective at converting the starch to sugar for fermentation. Some of the barley malt may also be added to the cereal cooker to help modify the viscosity of the cereal mash (Priest, 2006). Similar to decoction mashing, the cereal mash is heated in a stepwise fashion (Delcour and Hoseneý, 2010). This allows for the adjustment of pH, hydration of the grain, an α -amylase stand for thinning of the starch in the mash and finally heating to sterilize the mash and denature the amylases (Delcour and Hoseneý, 2010). Once complete, the cereal mash may be cooled before being

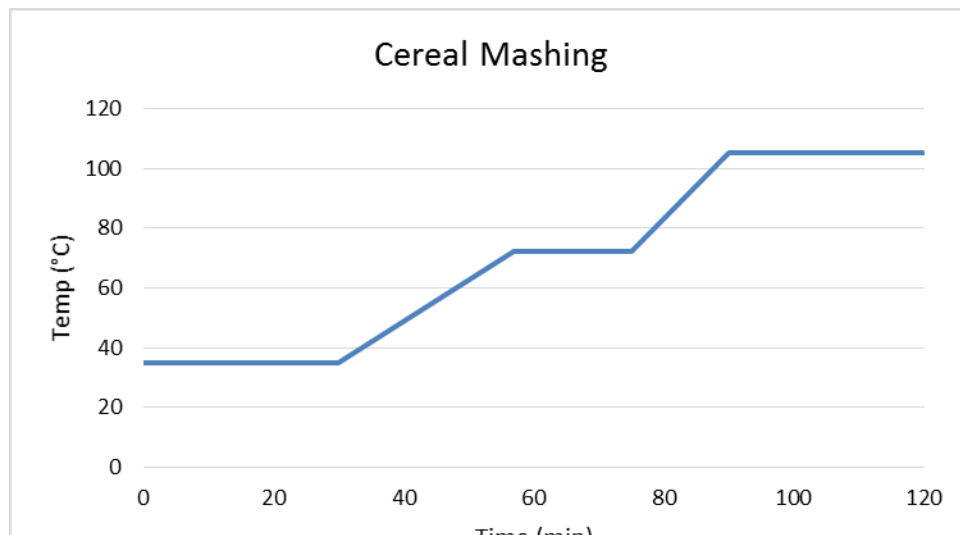


Figure 3: Example of Cereal Mash Process (Hoseneý and Delcour 2010)

added to the mash tun containing the malt mash or it may be transferred to the mash tun without cooling to raise the temperature of the malt mash.

During the mash process the pH is maintained at about 5.5 to allow for optimum amylase activity. The control of pH during mashing will play a critical role in the mashing time and conversion of the grain and must be monitored when using unmalted grains.

Once the mashing process is complete, the solids and liquids must be separated. In the case of the decoction process this can be accomplished through the use of a lauter tun, a large vessel with a screened bottom (a process called lautering), or a mash filter (Priest, 2006). Alternatively this is done by allowing the solids to settle from the sweet wort that has just been produced and form a filter bed, as in the infusion method of mashing. The husks from the malted barley make up an important part of the filter bed allowing for the liquid to drain through the filter bed properly. The filtration process can be greatly affected when using unmalted grains due to the presence of undegraded materials such as cell wall material as well as the lack of husk in certain cereals.

Boiling

Wort is boiled after separation from spent grains for a period of 1.5 to 2 hours to accomplish several goals. First, it sterilizes the wort to prevent unwanted microbial growth at later stages that could cause off-flavors. A portion of the hops are added at the beginning of boiling to contribute their bitter compounds. The remainder are usually added toward the end of boiling to preserve the volatile compounds that would otherwise be lost during the process. Additionally, boiling coagulates proteins and protein-tannin compounds to allow for them to be separated (called the “hot break”). Removal of these proteins is important for stability of the beer and the foam (Priest, 2006). Boiling also darkens the color of the wort due to Maillard reactions and oxidation reactions while also developing flavor in the wort (Delcour and Hosenev, 2010). Lastly, boiling removes any unwanted volatiles, such as dimethyl

sulfide and concentrates sugars through evaporation of the water (Priest, 2006). After boiling is complete, the wort is allowed to settle so that the hot break can be removed.

Wort Cooling

Cooling of the wort to approximately 12° C allows for additional proteins and protein-complexes to precipitate out of the wort (known as the “cold break”) (Delcour and Hosenev, 2010). During the cooling process it is common to add sterilized and filtered air to the wort to increase the cooling rate as well as to oxygenate the wort prior to fermentation.

Fermentation

As the hopped wort is added to the fermentation vessel, “pitching” yeast into the wort is done at a relative rate of 7.5 grams of yeast per US gallon of wort (Delcour and Hosenev, 2010). This equates to 15 to 20 million yeast cells per milliliter of wort (Esslinger, 2009). Priest (2006), gives a wider range of yeast incorporation varying from 5 to 20 million yeast cells per milliliter of wort. In many cases this is an inline process, with yeast added at the heat exchanger prior to the fermentation vessel. It can also be added directly to the fermentation vessel (Priest, 2006). Oxygen can be added at the heat exchanger or during cooling as mentioned above and reduces the time the yeast spend in the lag phase of the growth curve.

Wort fermentation produces not only major components of carbon dioxide and ethanol, but also minor components that contribute to beer flavor such as higher alcohols, organic and fatty acids, esters, carbonyls, and sulphur compounds (Kordialik-Bogacka et al. 2014). Two groups of higher alcohols represent the majority fraction that determine the aroma of beer: aliphatic and aromatic alcohols (Esslinger, 2009). The aliphatic alcohols of beer include 1-propanol, 2-methyl-1propanol, 2-methyl-1-butanol and 3-methyl-1-butanol (Esslinger, 2009). The aromatic alcohols of beer are mainly 2-phenyl-1-

ethanol (Esslinger, 2009). These compounds are formed by yeast metabolism in the first 2-3 days of fermentation (Esslinger, 2009). Their concentrations should not exceed 100 mg/L or they will unfavorably influence both flavor and quality of beer (Esslinger, 2009). Esters contribute flavor to beer and produce fruity tones at quite low detection thresholds (Esslinger, 2009). They are produced through enzymatic catalysis of organic acids, ethanol and higher alcohols. Up to 50 different esters can be present in beer, however, only 6 strongly contribute to flavor character (Esslinger, 2009). Both the higher alcohols and esters are important contributors to beer quality, and once those esters are formed, they remain in the beer through the remainder of the brewing process (Esslinger, 2009)

At this point there are some differences in processing depending on the type of beer being made. Ales use a top fermenting yeast, *Saccharomyces cerevisiae*, while lagers use a bottom fermenting yeast, *Saccharomyces carlsbergensis*. The temperature at which fermentation proceeds also differs depending on whether an ale or lager is being produced. While these differences exist, they will not be discussed in detail in this paper as the use of unmalted grains has similar effects in either fermentation process.

Characteristics of importance in the wort are nitrogen content (total soluble nitrogen, TSN) and composition (free amino nitrogen, FAN), pH, and concentration and composition of fermentable sugars – all of which are developed in mashing and impact fermentation. All of these attributes are affected by the use of unmalted grains.

Secondary Fermentation (Lagering or Maturing)

Primary fermentation is a complex and very active process producing carbon dioxide, a variety of alcohols, esters and other compounds. It also produces some compounds that are not appealing in the finished beer, which is why aging (also known as lagering or maturing) is a necessary step. Diacetyl, as shown in Figure 4, is one compound that is produced during primary

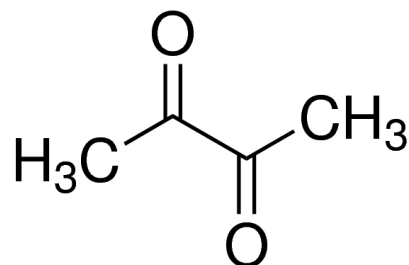


Figure 4: Diacetyl

Source: www.sigmaaldrich.com

fermentation that, if it remained in the beer, would result in a rancid butter or butterscotch type flavor (Priest, 2006). This can be diminished to below detectable levels through maturation.

Additional benefits of aging, also known as cold conditioning or cold storage, are: removal of compounds causing chill haze, clarification, maturation of flavor and aroma, and carbonation to a minor extent (Priest, 2006). The presence of excessive amounts of protein or other compounds, due to the use of unmalted grains, will increase the likelihood of a permanent or chill haze developing.

By holding the beer at temperatures around 0° C, flocs of polypeptides and polyphenols will form and fall out of the beer (Priest, 2006). These compounds can cause a haze in the finished beer when chilled due to a lack of solubility at reduced temperatures. Once formed, these compounds, along with residual yeast and other insoluble materials, are filtered out. Removal of the polyphenol material will reduce the bitter flavors imparted by these compounds, improving the overall drinkability of the beer (Priest, 2006).

During cold storage yeast activity is low, therefore, so is carbon dioxide production. CO₂ is therefore added to the beer by holding it under a counter pressure of carbon dioxide to allow dissolution into the beer (Delcour and Hoskeney, 2010).

Further Processing

Once the beer has been aged and filtered, it is ready for consumption. Depending on the end use of the beer, however, it may still require additional processing in the form of filtering, pasteurization or packaging.

THE MALTING PROCESS

While any cereal grain can be malted, this discussion focuses on the malting of barley as it is the grain most widely used for malting. Some differences in malting of other grains will be discussed later.

Malting of grain provides a variety of benefits to the brewing process. The malt contains the only source of enzymes used to convert carbohydrates into sugar for yeast to use during fermentation. The malt imparts flavor complexes to the brew as well as color, both of which can be varied through the degree of kilning.

The malting process begins with whole, intact barley (in traditional malting) and is comprised of 4 steps – cleaning, steeping, germination and kilning. Through these steps the barley is allowed to germinate under controlled conditions to a pre-determined point at which the germination process is halted by raising the temperature to stop enzymatic and other biological activities of the grain.

Cleaning removes any foreign material from the grain, but also provides an opportunity to sort the grain by size. If the size of the grain varies too widely, the milling process will be more difficult and result in a much less uniform product. Also, because moisture migration in the kernel during steeping is carried out via diffusion, the variance in grain size will also affect the amount of time the kernel needs to fully hydrate.

Once the grain is cleaned sufficiently it is steeped, i.e. soaked, in water to increase the moisture content of the grain to the point where metabolic processes are triggered and germination begins. For barley, this is at 42-44% moisture content (Delcour and Hosney, 2010). To prevent anaerobic conditions which would promote microbial growth and choke out the barley, the water may be aerated or changed repeatedly during steeping.

Germination takes place in beds where the grain is kept at depths of roughly 2 meters. Cool, moist air is pumped through the germination beds to create conditions beneficial for the grain to germinate. The primary purpose at this stage is to achieve maximum endosperm conversion with as little vegetative growth as possible (Delcour and Hosney, 2010). During endosperm conversion, or endosperm modification as it is known, changes take place in the endosperm via enzymatic degradation where endosperm cell walls are degraded and the starch granules are freed (Gupta et al., 2010). During this process enzyme (α -amylase) synthesis will occur, as will activation of other enzymes such as β -amylase; both of these enzymes will be of importance during the brewing process (Delcour and Hosney, 2010). The germination period will vary based on the moisture content of the grain, temperature, and enzyme activity of the grain, but will generally take four to six days to complete.

The final step in malting is kilning through which moisture content is decreased significantly and flavor and color may be developed through higher temperature drying. Enzymes in the green undried malt are highly sensitive to temperature at high moisture levels. Gentle heating to reduce the moisture content without inactivating the enzymes is needed for a high quality malt. As the moisture content decreases, temperature increases more rapidly developing color through Maillard reactions and concurrently developing flavor characteristics of the malt. The Maillard reaction results in melanoidins, complex compounds that have a major influence on color in wort and beer (Bamforth, 2006).

GRAIN MODIFICATIONS DURING MALTING

Several attributes of malt affect the finished beer and are directly related to the raw material or the malting process. The malt should provide high extract yields after mashing. It should possess a sufficient level and activity of various enzymes, such as α -amylase, β -amylase, proteases and β -glucanase, needed during mashing (Linko et al. 1998). The grain should also provide a reasonable amount of nitrogen to the wort for yeast metabolism during fermentation.

BREWING WITH UNMALTED GRAIN

While the reasons for incorporating unmalted grains in beer may be straightforward, the resulting changes to the mash, wort and final beer add complexity for the brewer. The following properties are changed when unmalted grains are incorporated into the brewing process:

- Changes in the wort composition such as viscosity and β -glucan content affect the filtration rate. β -glucan content affects foam stability (Sadosky et al 2002).
- Altered mash pH affecting the rate of enzymatic processes as well as the flavor, foam stability, color, rate of fermentation and final beer stability
- Increased haze
- Reduced nitrogen content and modified nitrogen composition, slowing the rate of fermentation

Many benefits come with the use of unmalted grains as adjuncts as well. Incorporation of adjuncts can increase brewhouse capacity by allowing for shorter brewing cycles as well as providing for consistent wort quality (O'Rourke, 1999). Other positive attributes associated with the use of adjuncts are: they are easy to handle and use, produce cleaner fermentations with better yeast heads, better hot

and cold breaks and reduced maturation time (O'Rourke, 1999). Liquid adjuncts can have benefits beyond those listed here.

Viscosity

Wort viscosity can alter the filtration time during lautering. This decreases the efficiency of the brewhouse, but can improve the final beer through improved body and foam retention by slowing the liquid from exiting the foam (Schnitzenbaumer et al. 2012). In addition, high viscosities affect processes such as pumping, mixing, stirring, boiling, cooling, clarification, and filtration (Schnitzenbaumer et al. 2012).

β -glucans are noted for their ability to bind large amounts of water (even to the point of forming gels in some instances). This will increase the mash viscosity. In wheat, the total β -glucan content is between 0.5 and 1 percent, as compared to between 3 and 11 percent in barley and 4 to 6 percent in oats (Delcour and Hosoney, 2010). Other causes of high viscosity are related to undegraded starch and cell wall material, including β -glucan and arabinoxylans (Goode et al., 2002).

pH

Mash, wort and beer pH are critical quality attributes that need to be monitored and controlled. Proper wort pH will guarantee maximum activity of yeast during fermentation as well as malt enzymes during mashing (Kordialik-Bogacka et al. 2014). The solubility and extractability of other compounds are also affected by pH (Bamforth, 2006). Caution must be practiced when determining the "optimum pH" of a particular product during mashing as it will depend on the composition of the grist as well as the mashing protocol followed (Bamforth, 2006). pH is also temperature dependent requiring measurements to be taken at a consistent product temperature.

A mash pH of 5.4 to 5.6 results in higher attenuation, improved lautering times, reduced viscosity and reduced color production during boiling, but also results in higher activity of phosphatases increasing the buffering capacity through production of phosphate ions and affecting acidification during fermentation (Priest, 2006). Therefore, according to Priest (2006), it is recommended to reduce the mash pH to 5.1 to 5.2 to provide better yield, quicker lautering, improved taste and foam stability as well as reduced color production during boiling. Bamforth (2006) suggests that maximum yield and fermentability are achieved at pH 5.3-5.8, but maximum soluble nitrogen and FAN are achieved at pH 4.7-5.2. Esslinger (2009) simply states, “mash pH must be in the range 5.4-5.8.”

Other characteristics affected by changes in pH are beer flavor, foam stability, colloidal (haze) stability and microbiological stability (Schnitzenbaumer et al. 2012). Contributing factors to pH are the pH of the grist material and the water used for brewing (Schnitzenbaumer et al. 2012). It has also been reported that lautering time is affected by pH, where a lower pH is beneficial to the filter cake permeability; however, grist particle size distribution is likely a larger contributor to lautering time (Schnitzenbaumer et al. 2012).

Colloidal Stability

Colloidal stability in beer manifests itself, as it does in other mixtures, through turbidity in the form of haze, both permanent and temporary. Chill haze is a temporary reversible haze that can appear as beer is chilled to 0° C or below and will disappear as beer reaches 20° C (Esslinger, 2009). Chill haze is a precursor to permanent haze in beer if it is stored at ambient conditions for extended periods of time (Esslinger, 2009). This conversion from temporary to permanent haze can be prevented in the brewhouse by cold conditioning (Bamforth, 2006).

The particles that contribute to permanent haze are larger than those that cause chill haze (Esslinger, 2009). An example of how these particles form to cause haze in beer is shown in Figure 5.

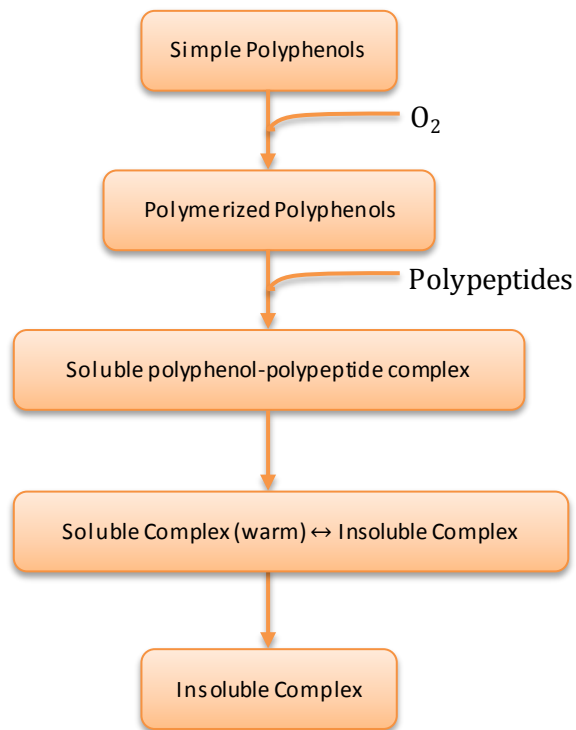


Figure 5: Haze Formation in Beer (Esslinger 2010)

These particles are composed of a wide range of compounds, but are principally polypeptides, polyphenols, and polysaccharides (Esslinger, 2009). These polymers are primarily from malt, but haze-inducing components can come from other sources like hop resins, melanoidins, and lignin (Esslinger, 2009). In addition to these compounds, there are additives that will contribute to haze such as foam stabilizers, preservatives and detergents (Esslinger 2009). Mineral content and composition, especially iron and copper, of brewing water can also

contribute to haze leading to oxidation reactions causing turbidity (Esslinger, 2009). Bamforth (2006) lists additional sources of haze-causing compounds such as dead bacteria from malt, incomplete broken down starch, oxalate from calcium-deficient wort, carbohydrate, and protein from damaged yeast. As it relates to the use of unmalted grains, the addition of polyphenol compounds and tannins which complex with protein causing haze will be of importance.

Nitrogen Content and Sources

Proper fermentation depends on adequate levels of nitrogen sources in wort and their composition will ultimately determine many of the final beer's qualities. However, not all source of nitrogen will be used by yeast, but only assimilable nitrogen, that is yeast-usable nitrogen (O'Conner-Cox and Ingledew 1989). Amino acids and ammonium ion provide the main sources of nitrogen that are

assimilable by yeast (O’Conner-Cox and Ingledew 1989). Di- and tri-peptides are also used by yeast, but to a lesser extent as amino acids and ammonium ions (O’Conner-Cox and Ingledew 1989).

One of malt’s major functional contributions is to provide nitrogen to the wort for yeast fermentation (O’Conner-Cox and Ingledew 1989). Adjuncts, such as unmalted grains, serve to dilute the nitrogenous content of wort, while providing greater fermentable extract (O’Conner-Cox and Ingledew 1989). Therefore, additions of unmalted grains must be carefully calculated to ensure enough nitrogen is present for complete fermentation and so as to not negatively affect quality attributes of beer. O’Conner-Cox and Ingledew (1989) report 15 g/kg of nitrogen as typical in wort and indicates that higher concentrations can cause haze.

Koszyk and Lewis (1977) found that some unmalted grains can deliver equivalent amounts of diastatic power and protease activity. According to Kordialik-Bogacka et al (2014) the amount of nitrogen needed in barley wort is 700-800 mg/L, where the free amino nitrogen (FAN) should be 200-250 mg/L. Schnitzenbaumer et al. (2012), however, gives a larger range of total soluble nitrogen (TSN) ranging from 900 to 1200 mg/L. When an adjunct is used, a lower FAN of 140-150 mg/L is recommended (Kordialik-Bogacka et al. 2014). FAN is likely the most critical element of wort in determining its effectiveness in fermentation (Kordialik-Bogacka et al. 2014). It is regulated by the degree of malt modification and the level of usage of the malt (as opposed to replacement by adjunct) (Kordialik-Bogacka et al. 2014). Lower levels of FAN result in slower fermentation and beer with low attenuation (Kordialik-Bogacka et al. 2014).

Oats

Mainly grown in the USA, Canada and Russia, oats are produced at a much smaller volume per annum relative to other cereal grains, accounting for only 23.9 million metric tons harvested worldwide in 2013 (Figure 6) as compared to 715.9 million metric tons of wheat and 1,018.1 million metric tons of

corn (Kordialik-Bogacka et al. 2014 and www.statistica.com). Despite the low cultivation of the crop, oats have several positive health benefits.

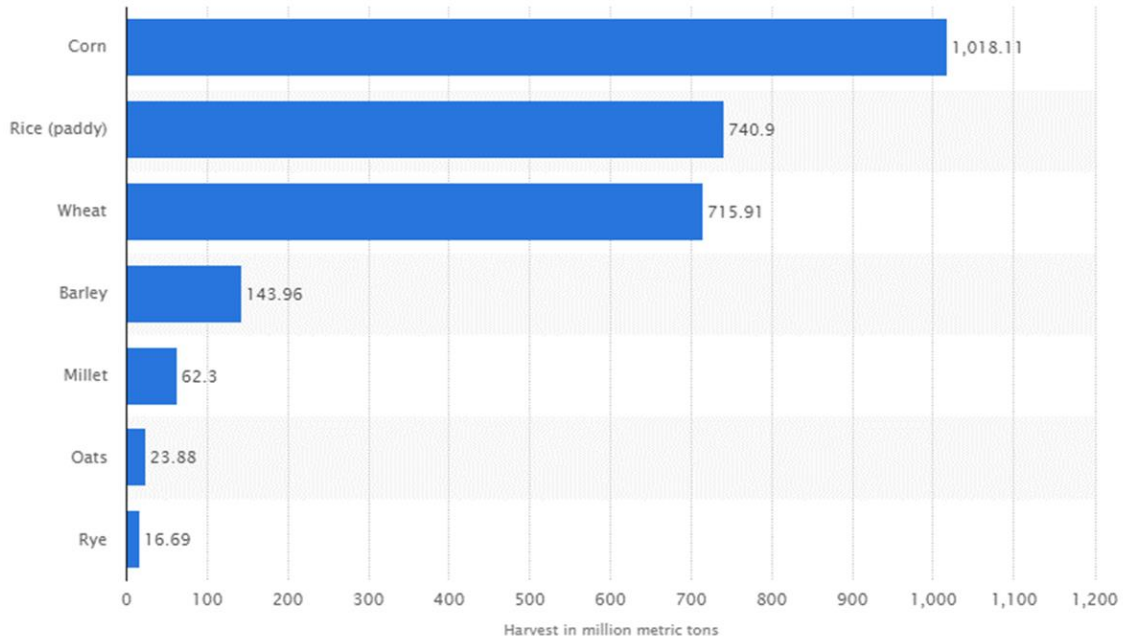


Figure 6: Worldwide Production of Grain in 2013
(<http://www.statista.com/statistics/263977/world-grain-production-by-type/>)

Oats provide folate, magnesium, vitamin B6, and vitamin E as well as some antioxidants, all of which are beneficial in reducing the risk of cardiovascular diseases (Kordialik-Bogacka et al. 2014). They are relatively high in protein, fat and fiber (primarily β -glucan) compared to other cereals (Table 2); the fat being mainly comprised of unsaturated fatty acids such as oleic, palmitic and linoleic acid that have protective functions for the blood and nervous systems (Kordialik-Bogacka et al. 2014). Near 80% of the total protein in oats is globulin, a superior protein from a nutritional standpoint (Kordialik-Bogacka et al. 2014). Oats also have significant levels of micro and macro nutrients such as iron, iodine, zinc and phosphorus. Aside from their health benefits, oats have a high proportion of husk and a low carbohydrate content reducing their extract potential in brewing (Schnitzenbaumer et al. 2012).

Historically oats were used to produce beer of inferior quality during the Middle Ages. Today they are used mainly as an adjunct at relatively low inclusion levels in stouts, ales and lagers— roughly at 10-

	Wheat	Rye	Corn	Barley	Oats	Rice
Moisture	12.6	13.6	11.3	12.1	13.1	13.0
Protein (Nx6.25)	11.3	9.4	8.8	11.1	10.8	7.7
Lipids	1.8	1.7	3.8	2.1	7.2	2.2
Available Carbohydrates	59.4	60.3	65.0	62.7	56.2	73.7
Fiber	13.2	13.1	9.8	9.7	9.8	2.2
Minerals	1.7	1.9	1.3	2.3	2.9	1.2

Table 2: Average Composition of Cereal Grains (Gobbetti and Gänzle 2013)

15% grain usage rate – adding a toasted flavor and aroma as well as a creamy mouthfeel (Schnitzenbaumer et al. 2012). Despite the health advantages of the oat composition, some oat attributes are detrimental to beer processing and quality.

Nitrogen content and composition

Malted oats produce a low wort extract from mashing, and although this can be improved upon through modification in milling, it will remain low as compared to barley (Taylor, 1999/2000). Malt from oats also produces very low amounts of nitrogen, reducing the total soluble nitrogen (Taylor, 1999/2000). Schnitzenbaumer et al. (2012) found a decrease in TSN from 940 mg/L with 0% oats to 817 mg/L with 40% oat inclusion and a FAN decrease from 177 mg/L with 0% oats to 131 mg/L with 40% oats in cooled worts. The amino acid profile from unmalted oats, however, has been shown to be more beneficial to yeast (*Saccharomyces pastorianus*) than that from malted barley alone, being more readily absorbed (Schnitzenbaumer et al. 2012).

Viscosity

Schnitzenbaumer et al. (2012) found that as the amount of oats in the grist increased, so did the viscosity of the wort prior to boiling. The same study determined a positive correlation between the β -glucan content and the viscosity of the mashes and worts because the unmodified β -glucan and protein became solubilized from the cell walls of oats in the mashing and lautering processes. This caused

increased viscosity as oat levels increased from zero to 40%. This also affected lautering time for oat levels at and above 20% (Schnitzenbaumer et al. 2012).

pH

Schnitzenbaumer et al. (2012) found as the level of oat adjunct increased, pH also increased in the mash and resulted in a higher pH once mashing was complete – 5.65 for 40% oats as compared to 5.52 for the reference product. Interestingly, Schnitzenbaumer et al. (2012) further notes that the pH in the final beer remained unaffected where the reference beer (0% oats) had a pH of 4.43 and the 40% oat beer had a pH of 4.41 and that usage of oats at 10% had no effect on mash and wort pH, but usage at 20% and above negatively affected the pH of mash and wort.

Wort produced from oats tends to be darker than wort produced from malted barley. This relates to the higher pH due to better extractability of the color compounds at this pH (Kordialik-Bogacka et al. 2014). Cereal grains, malted and unmalted, contain compounds in the husk that contribute to color (Kordialik-Bogacka et al. 2014). The high contribution of husk material relative to the rest of the grain of oats affects the color of the wort when used at high levels (Kordialik-Bogacka et al. 2014).

Haze/Aroma/Flavor/Color

The high protein and fiber (especially β -glucan) levels in oats contribute to other quality factors. Haze is one result of excessive levels of materials being suspended, dissolved or in colloidal dispersion (Esslinger, 2009). It can be removed by sedimentation, filtration or through enzymatic means (Esslinger, 2009). While a low protein content can affect flavor, high protein can contribute to haze, as was shown by mashes containing both unmalted and malted oats (Kordialik-Bogacka et al. 2014). Bitter off flavor compounds from long-chain hydroxy fatty acids and rancidity compounds from volatile aldehydes, ketones and alcohols are common in beers produced primarily from oats (Kordialik-Bogacka et al. 2014).

Foam Stability

Schnitzenbaumer et al. (2012) found that the foam stability of beers made with 20% or more unmalted oats was lower, decreasing from 295 seconds to 223 seconds for 0% oats and 40% oats, respectively. At the lowest level tested (10%), the change in stability was not significant. It is believed that the reduced foam stability is due to the low level of TSN and a reduction in high-molecular-weight-proteins (Taylor, 1999/2000) when using oat malt. Taylor and Humphrey (2008) confirm a reduction in head retention values in malted oats adding that it is not attributable to the higher lipid content of the oats, as the majority of lipids are lost to the spent grain and that flavor stability over 12 months did not deteriorate at a greater rate than other beers.

Sorghum

Interest in Western lagers led to much research during the 1970's and 1980's to create similar beer from sorghum (Goode et al., 2002). Sorghum grows in the semi-arid climates of the world, of which there are select areas on every continent, with the exception of Antarctica. Sorghum can be of a range of colors including white, red, bronze, yellow or brown (Delcour and Hosenev, 2010). It loses its hull when threshed (Delcour and Hosenev, 2010). It is a hardy plant which can grow in many soil types and across a wide soil pH ranging from 5.0 to 8.5 and grows at altitudes up to 9800 feet (Smith and Frederiksen, 2000).

Sorghum has been used for the production of beverages in various parts of Africa and it has been used as a brewing adjunct in Mexico and Latin America (Goode et al., 2002). Malted sorghum is used in large quantities specifically in Zimbabwe and South Africa to produce a traditional African dark sorghum beer, while Nigerian brewers are using unmalted sorghum and maize in lager beer production (Goode et

al., 2002). A cloudy beer known as Kaffir, made from malted sorghum, is also popular in Africa (O'Rourke, 1999).

While Goode et al. (2002) note that it is possible to brew lager beers with sorghum as either a malt or unmalted grain using grits or whole grain, they list several reasons why the use of unmalted sorghum in combination with enzymes is more advantageous than using malted sorghum, including poor diastatic (starch degrading) development during malting, minimal protein modification requiring addition of exogenous enzymes, high variability in the raw material, high losses in malting, and high cost of malting.

That said, Ugboaja et al. (1991), found that beer produced with up to 25% sorghum was at parity in quality to those made with 100% barley malt. Ratnavathi et al. (2000) state that sorghum can be well suited in its unmalted form as a brewing adjunct.

Nitrogen content and composition

As noted previously, nitrogen composition is an important attribute, directly affecting yeast metabolism as well as the flavor and aroma of the final beer (Goode et al., 2002).

As the amino acid profile affects the fermentation process and quality of beer produced, it is interesting to note that malted sorghum has high concentrations of free α -amino nitrogen and has a superior FAN quality to that of malted barley (Ratnavathi et al., 2000). This higher concentration was in spite of the fact that the average protein level of the sorghum used was 9.9%, significantly lower than the average protein level of barley, as given above. In fact, Ratnavathi et al. (2000) found that the high starch cultivars had higher concentrations of free α -amino nitrogen. The amount of FAN was also found to be adversely affected by decorticating the sorghum, where intact sorghum had a reduced range of FAN (one-third) (Ratnavathi et al., 2000). Agu (2002) remarked it is known that unmalted cereals, when used as adjuncts, reduce wort protein concentration and thereby decrease the amount of free α -amino nitrogen

available for fermentation. Seventy percent of the amyloglucosidase α -amino nitrogen is generated during malting, so displacement of malted grains with unmalted ones will undoubtedly affect the fermentation rate and final beer quality (Agu, 2002). The results of Ratnavathi et al. (2000) differ significantly from what Goode et al. (2002) determined when *unmalted sorghum* was used, noting that all of the individual amino acids decrease in value as sorghum increases. This is believed to be attributable to the lack (or resistance) of sorghum protein degradation during mashing.

Despite the quality of the malted sorghum, Goode et al. (2002) found that nitrogen, in all forms (soluble nitrogen, high-molecular weight nitrogen, and FAN), decreased at a rapid rate as the usage of

Group A	Group B	Group C	Group D
Aspartic Acid (1)	Histidine (3)	Glycine	Proline
Glutamic Acid (1)	Valine/Methionine (2)	Alanine (2)	
Asparagine	Isoleucine (2)	Tyrosine (2)	
Serine (1)	Leucine (3)	Tryptophan (2)	
Glutamine (1)		Phenylalanine	
Threonine (1)			
Arginine (3)			

Table 3: Amino Acid Groups (Class), Goode, Halbert and Arendt (2002)

unmalted sorghum increased. Reduced soluble nitrogen will likely result in longer fermentation times and will affect the flavor and aroma characteristics of the beer

(Goode et al., 2002). Agu (2002) determined that even at low levels of sorghum addition (5-20%), a significant decrease in extract recovery, soluble nitrogen, and FAN production occurred despite the fact that sorghum was found to release greater amounts of peptides than that of barley and maize.

Goode et al. (2002) note that Jones and Pierce (1964) had classified amino acids into four groups based upon their rate of uptake by yeast (Table 3). This classification is also found elsewhere in literature. Group A amino acids are metabolized nearly immediately. Group B are metabolized more slowly throughout fermentation, and Group C are only metabolized once Group A have been consumed. Group D, which contains only proline, is metabolized only under anaerobic conditions, and then only to a small degree. Amino acids have also been divided into three classes based upon their importance to yeast metabolism. Class 1 amino acids are not critical to yeast as their carbon backbone can be synthesized by

yeast (Goode et al., 2002). Class 2 amino acids are of more importance since yeast can only partially synthesize their components and if their initial concentration is not in balance, the final beer quality may be affected (Goode et al., 2002). Lastly, Class 3 amino acids are critical to yeast metabolism as they cannot be synthesized by yeast and therefore need to be provided; their absence will greatly affect the fermentation process and final beer quality (Goode et al., 2002).

Goode et al. (2002) compared worts prepared from unmalted sorghum to a typical malted barley wort and found that the sorghum wort was lacking in serine (A,1), glutamine (A,1), tyrosine (C,2), valine/methionine (B,2), tryptophan (C,2), isoleucine/phenylalanine (B2,C2) and leucine (B,3). Sufficient levels of aspartic acid (A,1), glutamic acid (A,1), asparagine (A), alanine (C,2) and arginine/aminobutyric acids (A,3) were present (Goode et al., 2002).

As noted previously, the presence of high-molecular weight nitrogen (HMWN) compounds is a factor in foam stability. With decreased levels of HMWN, the foam stability of beers produced with sorghum is expected to be reduced, but some improvement can be seen by addition of foam stabilizing ingredients or through addition of gelatinized sorghum grist late in the process (Goode et al., 2002). Values of 200-240 mg/L of HMWN are regarded as the proper range for good foam stability. The beers produced in this study using sorghum ranged from 136 mg/L to 210 mg/L of HMWN with the aid of various enzymes at up to 60% sorghum (Goode et al., 2002). Above 60% sorghum usage, HMWN declined sharply. While a decrease in foam stability is expected with the addition of unmalted sorghum, Goode et al. (2002) did not measure this attribute specifically.

FAN levels for the sorghum-containing beers ranged from 90 mg/L to 266 mg/L (up to 60% usage of sorghum), but were only in the acceptable range of 130-150 mg/L for beers using 20% or less sorghum (Goode et al., 2002). This shows that levels above 20% of sorghum extend fermentation times, or require modification of the process through the use of enzymes to improve throughput.

Viscosity and Filtration

Wort viscosity affects filtration both of the wort and the final beer. As viscosity increases, so does the amount of time needed to filter the wort or beer, causing inefficiencies in the brewing process. One factor in filtration, β -glucan, can have a large effect on wort viscosity and therefore filterability. Goode et al. (2002) cite studies showing β -glucan levels in sorghum malt were quite low as compared to barley malt (unlike oats). Consequently, the viscosity of sorghum worts and beers was found to be lower than that of those brewed with barley malt. Goode et al. (2002) also reported a decrease in viscosity as the level of sorghum increased.

Despite the lower viscosity, Goode et al. (2002) discovered that for sorghum levels under 20%, and without supplementing with commercial enzymes, “filterability was not possible.” The addition of enzymes significantly improved filterability, but it was still significantly below that of barley malt wort. Because the authors used a modified mashing program, incorporating a 40 minute stand at 95° C, it is assumed that the sorghum starch was effectively pasted to allow for hydrolysis by the added enzymes. The authors were able to achieve filtration rates equivalent to that of mashes produced from 100% barley in mashes using high sorghum levels through the use of heat stable α -amylase.

The husk of barley plays an important role in wort filtration, and the lack of husk when using sorghum is an issue. This can be solved in processes that make use of a malt filter, although when sorghum levels are high, the amount of glucans and arabinoxylan may complicate filtration due to water binding of these components in the spent grain and therefore slowing filtration rates (Goode et al., 2002). Furthermore, Goode et al. (2002) found that extract from worts produced using unmalted sorghum decreased sharply as sorghum content increased. A surprisingly large improvement in extract was achieved using enzyme treatments at levels of sorghum 40% and higher, but none of the mashes provided an equivalent amount of extract to that of 100% barley.

pH

Goode et al. (2002) found that as sorghum content increased, the pH of the wort increased. This was the inverse of what was previously reported in literature. It was noted that the referenced study used a different variety of sorghum and the authors concluded that the direction of pH change is dependent on variety.

Color/Flavor/Aroma

Increasing levels of sorghum were found to lead to decreased color in worts (Goode et al., 2002) when a white sorghum was used. In studies cited by Goode et al. (2002), the opposite was reported when a red sorghum was used, as would be expected. When a combination of particular commercial enzymes was used (Bioprotease and Hitempase), it was found that the color increased, a possible result of higher quantities of solubilized protein creating a greater quantity of melanoidin during mashing (Goode et al., 2002). Due to the lower concentrations of soluble nitrogen when using sorghum, changes to flavor and aroma characteristics are noted (as expected) (Goode et al., 2002).

Attenuation

Attenuation is an attribute of beer which is affected by yeast activity and produces beers of different densities, alcohol levels and body (Esslinger, 2009). Attenuation is a measure of the degree of conversion of sugars to alcohol by yeast (Delcour and Hosenev, 2010). As unmalted sorghum content increased, attenuation decreased, resulting in beer with low conversion of sugar to alcohol (Goode et al., 2002). The authors suggest that to produce beer with an acceptable attenuation, the addition of an amyloglucosidase is needed when brewing with 100% unmalted sorghum to assist in conversion of starches to glucose. O'Rourke (1999) holds that both enzymes and yeast nutrients are a necessity when producing beer with unmalted sorghum, especially when it is the sole grain used.

Wheat

Food use of wheat in the Near-East and Middle Asia can be found as far back as 7800 BC, when agriculture was at its first stages (Esslinger, 2009). Today wheat has more land mass committed to its cultivation than any other food crop (Delcour and Hosenev, 2010). This is certainly due to its hardiness, which allows for it to be grown in many climates and soil conditions, as well as the abundant number and types of the products that can be made from wheat flour (Delcour and Hosenev, 2010).

Wheat can be classified by a variety of characteristics including overall protein content, spring or winter growth, endosperm texture, and bran color (Depraetere et al., 2004).

For brewing purposes, wheat is a popular choice as it brings a characteristic wheat flavor and can impart a dryness to the beer (O'Rourke, 1999). When used at higher levels of inclusion, definite citrusy or tangy notes are present. Weissbier, produced from malted wheat, is common in Europe and North America, but is most well known in Bavaria, Germany. When malted, the loosely adhered husk is lost and therefore it is important to turn the green malt carefully as to not damage the acrospire (Taylor, 1999/2000). Malted wheat provides a higher protein level than does barley, but results in lower FAN levels with poorer modification than barley, and a higher enzymatic activity which provides greater extract (Taylor, 1999/2000).

Unmalted wheat also has a long history of use, especially in Belgium where wheat beers (witbier or bière blanche) use up to 50% raw wheat in their production (Esslinger, 2009). Even bread flour or pre-gelatinized forms can be used as a source of adjunct to improve wort extract according to Esslinger (2009). There appear to be varying opinions as Depraetere et al. (2004) note that it is typical to use soft wheat for brewing due to the "mealy or floury endosperm" character.

Nitrogen content and composition

Some wheats examined by Koszyk and Lewis (1977) possessed diastatic power equal to or greater than barley malt with protease of similar or greater activity. Amino nitrogen contained in the wort was found to be less than the all-malt products, which is consistent with other findings (Koszyk and Lewis, 1977). Despite the lower levels of nitrogen, the composition was determined to be proportionate to all-malt wort (Koszyk and Lewis, 1977). Wheat was also found to produce less free amino acids than other unmalted cereals examined (triticale, rye, oats, barley, maize, rice and barley malt).

Results from Depraetere et al. (2004) agree with those above, in that protein analysis showed a reduced nitrogen content of wheat beers, but that total protein content of the wheat positively affected the nitrogen content of the beer. In fact, Depraetere et al. (2004) showed that nitrogen content increased linearly as total wheat protein increased. Depraetere et al. (2004) also found a decrease in α -amino nitrogen with the addition of wheat, ascribed to poor wheat protein hydrolysis by malt proteolytic enzymes. The effect of this lower α -amino nitrogen level is the reduction of wort fermentability.

Viscosity /pH

Koszyk and Lewis (1977) state that worts with unmalted wheat were similar to all barley malt in viscosity, but had higher pH at 40% usage. Conversely, Depraetere et al. (2004) described the wheat beers made with 40% wheat as being higher in viscosity with a lower pH than that of the barley malt beer. They attributed the lower pH to a lower buffering potential of wheat as compared to barley.

Haze

	EBC	ASBC	NTU
Brilliant	< 0.5	< 35	< 2
Almost brilliant	0.5 - 1.0	35 - 70	2 - 4
Very Slightly Hazy	1.0 - 2.0	70 - 140	4 - 8
Slightly Hazy	2.0 - 4.0	140 - 280	8 - 16
Hazy	> 4.0	> 280	> 16

Table 4: Haze Scales
EBC – European Brewing Convention
ASBC – American Society of Brewing Chemists
NTU – Nephelometric Turbidity Units
(Bamforth 2006)

In almost any other type of beer, a haze, or lack of clarity, would be considered an egregious quality defect. In wheat beers, however, this is a common and desired characteristic. Greater amounts of stable haze are common in wheat beers due to the level of protein, specifically the gluten content, in the final beer (Depraetere et al., 2004). This is dependent on the amount of wheat used as well as the total protein content of the wheat used (Depraetere et al., 2004). This would agree with the brewers who choose hard wheat varieties in brewing due to their belief that hard wheat contains more haze active high-molecular-weight-proteins (Depraetere et al., 2004). This would be reasonable since hard wheat contains higher levels of protein, and therefore, more gluten. Interestingly the literature reveals that a wide range of haze values can be achieved through the use of wheat, even to the point of great clarity, as if no wheat were used. Three commonly used scales used for classifying haze are shown in Table 4.

Depraetere et al. (2004) concluded that wheat gluten complexes with polyphenols causing haze, although at high usage rates of wheat, the complexes become so large they settle out of the beer and, in fact, reduce haze intensity, a phenomenon well-known in the literature. These complexes can then easily be filtered out of the beer to provide for better clarity. It is therefore assumed that as the protein contributed via wheat inclusion increases, more complexes form and create an overall reduction in haze due to their presence and subsequent settling (Depraetere et al., 2004). Delvaux et al. (2003) showed that addition of gluten to the brewing process at low concentrations drastically increased the haze readings, but at higher levels, the haze intensity was lower than that of the control sample. Interestingly,

a greater haze was produced by low levels of wheat flour than with higher levels of wheat gluten (Delvaux et al., 2003). This would seem to show that there are compounds in wheat flour, beyond just gluten, that influence haze. It was also found that wheat variety has an effect on haze at low wheat levels, but to a smaller extent than usage rate (Delvaux et al., 2003).

In addition to overall protein level, Depraetere et al. (2004) comments that improved colloidal stability may be due in part to the reduction in soluble nitrogenous compounds and a reduction in polyphenols when malt is reduced due to the addition of wheat. Because malt contributes about 80% of the phenolic compounds found in beer, with the balance from hops, it would be expected that a large decrease in overall polyphenols is associated with a decrease in malt content (Gupta et al., 2010). If malt is contributing more nitrogen than is needed for fermentation, excess nitrogen could contribute to haze. Depraetere et al. (2004) measured polyphenols by centrifugation of the beers produced and found negative correlation between polyphenol level of wheat beer and the total protein content of the wheat.

The all-malt beer used for reference by Depraetere et al. (2004) possessed a haze of 28 EBC units (on a 100 point EBC-Analytica scale). When 40% wheat was used to produce the beers, the haze intensity value declined to 1 EBC unit, irrespective of the protein level in the wheat (Depraetere et al., 2004). When the level of wheat used was reduced to 20%, the haze levels rose significantly, but these values were dependent upon the amount of modification in the barley malt as well (Depraetere et al., 2004). Where a normal modified malt was used, there was greater proteolytic activity that degraded the wheat proteins into smaller particles, causing greater haze since these particles will tend to stay suspended (Depraetere et al., 2004). For malts that were highly modified, the reduction in proteolytic activity was manifested through less impact of wheat level on haze intensity (Depraetere et al., 2004).

Delvaux et al. (2003) found that high levels of unmalted wheat use (40%) caused a decrease in haze intensity, which they attribute to the contribution of wheat gluten, specifically the gliadin fraction

being responsible for the negative effect of haze in wheat beer. In previous work, Delvaux (2003) described that researchers, through the use of a model system, have determined gliadin has a strong affinity for proanthocyanidins, producing haze forming particles.

Koszyk and Lewis (1977) rated the beers made from wheat in their study as having a “very slight haze” to “slight haze”, depending on the variety of wheat used. This would equate to a 1 to 4 rating on the EBC scale for haze. The usage level of wheat and other adjuncts in their study was 40%. Wheat beers produced by Depraetere et al. (2004) were lighter in color than their all-malt counterparts which they reasoned was due to the lack of a kilning process for the raw grain as would be commonplace if it were malted.

Foam Stability

The effect on foam stability when using unmalted wheat is not as conclusive as when reviewing other cereals. Depraetere et al. (2004) concludes that while the prevailing theory is that wheat improves foam stability, the literature to confirm this is minimal. It is suspected that wheat has foam active compounds and their functionality is related to the degree of modification in malt (Depraetere et al., 2004). While wheat does not necessarily have more protein than barley, wheat appears to contribute more high-molecular-weight-proteins to the wort, specifically wheat glycoproteins, which have been shown to provide for greater foam stability (Depraetere et al., 2004). Wheat also contains other high molecular weight compounds, such as the polysaccharides β -glucan and arabinoxylan, known for increasing viscosity and thereby reducing liquid drainage from foam, improving overall foam stability (Depraetere et al., 2004).

Taylor and Humphrey (2008) found when using malted wheat that head retention values increased by 50 seconds over that of a 100% barley malt beer. They attributed this to the higher protein

content of wheat. The authors noted this agrees with past results. Priest (2006) states, “Wheat malt gives beer outstandingly good head retention”, but does not substantiate this claim with any figures.

When an under-modified or normally modified malt is used in combination with wheat, a loss of between 2 and 10% foam stability occurs (Depraetere et al., 2004). However, when over-modified malt is used with wheat, the foam stability improves by 9% (Depraetere et al., 2004). Depraetere et al. (2004) do note that the over modified malts were not within a typical brewer’s quality range.

Using two methods common to industry, NIBEM and Rudin, Depraetere et al. (2004) analyzed the foam stability of the beers they produced. From previous studies the authors reviewed, they note that the use of CO₂ using the Rudin method showed foam stability improvement, while the use of N₂ produced similar results with wheat beers equaling or surpassing that of the all-malt control beer head retention value (HRV). The authors were not surprised that wheat shows an improved foam stability with the Rudin test, as it measures the liquid drainage rate from the foam. As noted, wheat produces a higher viscosity beer than malt and also has a smaller bubble size. Both attributes possessed by wheat suggest a reduction in the amount of liquid drainage from the foam, improving the foam stability (Depraetere et al., 2004). However, they found improvement only in the Rudin method using N₂ and a slight reduction in HRV when using CO₂, only partially confirming results of earlier studies. From the NIBEM method, where the time was measured for the foam to collapse by 3 cm, the results varied from 236 seconds per 3 cm to 261 seconds per 3 cm for 40% wheat beers as compared to 222 seconds per 3 cm to 261 seconds per 3 cm for all-malt (Depraetere et al., 2004). The authors note that replication of the Rudin results were difficult compared to the NIBEM method.

Maize

Of the cereal grains, maize is the largest, weighing an average of 350 mg per kernel (Delcour and Hosenev, 2010). It is also the largest in plant height of all grains and the main producers of maize are the United States, China, and Brazil (Esslinger, 2009). Like sorghum (and the other cereals), maize can be of a variety of colors including white, yellow, red, blue, purple or dark brown (Delcour and Hosenev, 2010). However, in brewing yellow corn is most widely used as it is also the most widely available (Ugboaja et al., 1991). Flakes or grits are common forms when used as a solid, but maize can also be used as a liquid syrup with a range of sugars depending on the level of hydrolysis (O'Rourke, 1999).

Historical use of maize dates back to 5000 BC. Today it is used in brewing but not as a whole kernel due to the large amount of oil contained in the germ, which must be removed prior to use in brewing (Esslinger, 2009). Being one of the less expensive cereals available, it has use in many European beers and reportedly up to 50 percent usage in American beers (O'Rourke, 1999 and Ugboaja et al., 1991). When added as an unmalted adjunct, maize provides for a fuller flavored beer (O'Rourke, 1999).

Extract & Nitrogen Content and Composition

When incorporated as an adjunct, in similarity to wheat, maize is found to provide greater extract than malted barley alone (Ugboaja et al., 1991). While this appears to be a common belief, the research does not appear to consistently support this view. Poreda et al. (2014) cited previous work showing that extract recovery of barley was higher than extract recovery of barley with 20% adjunct.

Maize is low in protein, so it would be expected to have a lower contribution of nitrogen to wort and beer than other grains. This is why Ugboaja et al. (1991) reason that the amount of maize used in brewing must be limited. They note that the desired range of protein for grains should be between 9 and 11%. The protein level of the maize used in their study was 8.5%. Agu (2002) reported a lower extract

using maize compared to barley malt, despite the common belief that maize has a higher extract potential. Similarly, Poreda et al. (2014) also reported a lower non-fermentable extract using maize at 10 and 20% of the grist compared to an all-barley malt control sample. One explanation for this is that the proteins contributed to the wort by maize are more difficult to hydrolyze while concurrently reducing proteolytic enzyme contribution from barley thereby reducing their extractability (Poreda et al., 2014). It should be noted that the study conducted by Poreda et al. (2014) was done on commercial scale, which may add variation due to uncontrolled conditions as compared to a laboratory study. The benefit, however, of a commercial scale study is that the results have been tried and found true in a practical application setting.

Briggs et al. (1986) comment that extruded maize flakes at 30% usage produced “poor extract recovery”; however, the data presented appears to be comparable to other extruded cereals and a 100% lager malt control where the all-malt product produced 291 and 285.7 l/kg of extract with and without commercial enzymes, respectively and the maize flakes yielded 292.9 and 285.2 l/kg extract with and without enzymes, respectively. From their review, Poreda et al. (2014) summarize that the lower non-fermentable extract is a benefit because the carbohydrate profile of the wort has improved oxidative stability owing to the fact that non-fermentable extract has a higher reduction potential than fermentable extract.

In some studies maize was found to possess higher fermentable extract potential than barley. Ugboaja et al. (1991) found an extract increase when using maize at 25%, but not at 10%. Maize at 25% provided 13.5% extract versus maize at 10% yielding an extract of 12.6%, comparable to the barley control sample (Ugboaja et al., 1991). Additionally, beers made with increasing levels of maize had more alcohol (about 0.4% greater) than all-malt beer and a higher attenuation by 4 to 5% over the all-malt beer (Poreda et al., 2014).

Poreda et al. (2014) found as maize levels increased from 0 to 20%, the FAN level decreased, as would be expected due to the lower protein content in the maize. This is despite the use of a proteolytic stand of the adjunct of 15 min at 50° C (Poreda et al., 2014). However, unlike some other grains reviewed, this did not result in an unacceptable level of FAN. Adjunct containing samples fell between 220-240 mg/L of nitrogen (Poreda et al., 2014).

Viscosity

As regards to the effect of maize on the wort and beer viscosity, no data was found in the literature. It might be assumed that with lower protein levels, no contribution of β -glucan, and high conversion of carbohydrate viscosity would be minimally affected or even lowered relative to that of a malt-based beer.

pH

With the use of 10 and 20% maize it was notable that the pH remained the same for all samples (Poreda et al., 2014). This is an especially positive trait, indicating that there should be little change in fermentation times when maize is used at these levels, although the reduction in nitrogen contribution may negatively affect fermentability. Likewise, Ugboaja et al. (1991) found no differences in pH compared to control for beer made with 10 or 25% maize.

Haze/Aroma/Flavor/Color

Ugboaja et al. (1991) used maize at 25% together with 75% barley malt and found that the attenuation of the product was high, indicating to the authors that the maize grit was more easily hydrolyzed. This is interesting considering that at a lower level of 15% maize grits, there was no appreciable difference in the attenuation, which also agrees with the amount of extract recorded for maize at this level.

Using 10 and 20% maize with barley malt, Poreda et al. (2014) found a decrease in wort color. This is reasonable considering the overall reduction of protein available for Maillard reactions. Ugboaja et al. (1991) experienced similar results, finding lower color values as the use of maize grits increased.

Dimethyl sulfide (DMS) is a volatile compound which produces an unpleasant flavor and aroma similar to cabbage at levels as low as 30 µg/L (Poreda et al., 2014). DMS precursors are contributed to the process from malt and produced through the breakdown of malt compounds during wort boiling (Poreda et al., 2014). It was found that addition of maize reduced the DMS in wort (Poreda et al., 2014). One of two possible reasons for this decrease is that barley malt is the primary contributor of DMS precursors, and therefore, any decrease in malt would reduce the overall DMS load (Poreda et al., 2014). While this seems perfectly logical, the authors also noted that maize has levels of DMS precursors similar to those of barley malt, but that the maize precursors are broken down during wort boiling and are not carried forward in the process like barley DMS (Poreda et al., 2014).

As discussed, higher levels of protein play a role in haze formation and longer filtration. In the case of Poreda et al. (2014), all beers produced (including control) were considered 'brilliant' according to the EBC haze scale, not exceeding 0.5 EBC units. It was also found that there was no significant change in filtration when maize was added (Poreda et al., 2014).

Foam Stability

Of the literature reviewed, very little data was found regarding head retention values for beers made with maize. One study (Briggs et al., 1986) found reduced HRV when using extruded maize flakes at 30%. Using the Rudin method, they found maize flakes had an HRV of 96 seconds as compared to extruded barley and wheat flour pellet beers (also at 30% levels) producing results from 124-128 seconds. This is a striking difference showing the effect of maize on foam stability, although it is only one example found in literature.

Rice

Dating back 7,000 years ago, evidence suggests cultivation of rice in Southern China (Esslinger, 2009). Today, over half of the world's production of rice comes from only three countries: China, India and Indonesia (Esslinger, 2009). Of the 25 species of rice, only two continue to be cultivated today: *Oryza glaberrima* and *Oryza sativa* (Esslinger, 2009). *Oryza glaberrima* is found in Africa, while *Oryza sativa* is of Asian origin and contains 120,000 known subspecies (Esslinger, 2009).

Overtaking Germany in 1993, China became the second largest beer producer in the world (ewe). In China rice is used as the primary adjunct (Jin, Gu and Rogers, 2000). Large amounts of production in China make rice especially available and provides for easy access by brewers. It has been used at high grist levels of 30-50% in certain countries where it is used to lower costs, improve stability (through the lack of polyphenol and protein content) and intentionally provide for flavor differentiation from other beers (Le Van et al., 2001).

Little research has been conducted on rice in brewing. This may be due to its relatively minor use in brewing, aside from giant brewer Budweiser, likely the largest user of rice in beer. This could also be due to the higher gelatinization temperature of rice starch, requiring separate gelatinization from that of malt. Considering that this is a situation shared with other grains such as maize and sorghum, it seems this could be easily overcome. Another possible reason is the difficulty in handling or processing rice after cooking as it can produce a very viscous mash if long grain rice is used (Taylor et al., 2013). This viscous mash may cause filtration problems as well as complicate cleaning and sanitizing operations.

Nitrogen content and composition

There should be no surprise that the inclusion of rice, as is the case with other adjuncts, lowers the overall nitrogen content. Rice has a lower level of protein than other cereals at approximately 7-8% as compared to barley at 8-15%, reducing the overall ability to contribute nitrogen to the wort (Taylor et al., 2013). Buch and O'Donnell (1985) used pregelatinized rice flour in the production of beers which gave a lower FAN than that of an equivalent beer brewed with wheat flour. However, when a protease enzyme was included the FAN content was equal to or exceeded the acceptable range previously specified of 140-150 mg/L. Taste panels found these beers to be acceptable despite their low FAN level.

Le Van et al. (2001) found that high usage of rice (40% grist) resulted in sharp declines in both the ammonium nitrogen and the free amino nitrogen in wort. At this usage rate, Le Van et al. (2001) found that fermentation time doubled as compared to a 100% malt mash. The consequence of low nitrogen compounds in wort is not only increased fermentation time, but also fermentation will be incomplete and become "stuck" as the yeast growth ends prematurely. Le Van et al. (2001) found that the nitrogen composition could be significantly improved with the addition of microbial protease or through the use of yeast extract. The addition of protease in mashing provided for improvements in total nitrogen, and the use of yeast extract resulted in higher FAN levels (Le Van et al., 2001). Furthermore, Le Van et al. (2001) found that yeast extract reduced fermentation times more than did the addition of protease. The effect from this study is that the final beer quality, from an organoleptic perspective, was significantly changed when rice was used at 40% (with and without protease or yeast extract treatment) as compared to 100% malt beer.

Viscosity

As noted above, Taylor et al. (2013) note that long grain rice is not used in brewing due to the resulting viscous mash. Aside from this comment, no other literature was found to discuss changes in viscosity of mash, wort or beer when rice is used as an adjunct.

pH

Of the literature reviewed, no sources described changes to pH due to the addition of rice. This either means that there is little or no impact to pH when mashing with rice, or that no studies have been conducted to verify the effect mashing with rice has on pH.

Haze/Flavor

One of the main reasons to use adjuncts is to produce more mild flavored beers. Rice is certainly no different, providing for lighter color and a clean flavor. As for beer clarity, Esslinger (2010) notes that higher rates of usage of rice as an adjunct provide for better colloidal stability. This is likely due to the low protein content of rice, reducing the opportunity for protein-anthocyanin interactions. It is also suspected that rice proteins are less subjected to proteolysis of malt enzymes and therefore have less effect on flavor than do other grains (Jin et al. 2000).

Foam Stability

Presumably foam stability when using rice is adversely affected. Due to low contribution of protein an increase in rice would dilute the protein and nitrogen provided by malt, but virtually no literature reviewed discussed this important beer quality. Fumi et al. (2009) notes that nitrogen compounds not only affect fermentation, colloidal stability and formation of flavor compounds, but specifically contribute to beer foam strength, stability and lacing.

Le Van et al. (2001) found improvement in nitrogen composition with the use of protease. It is likely that foam stability can be formulated to be equivalent to malt beers with close attention to usage level of adjunct and addition of commercial enzymes.

Barley

Barley may be the grain with the oldest examples of use found at the upper Euphrates valley dating back to 10,000 and 7,000 BC (Esslinger, 2009). It is able to grow in a variety of climate regions from sub-Arctic to sub-tropical (Gupta et al., 2010). Due to its adaptability, it has found use in the diets of those in many parts of the world especially the Middle East, North Africa, Eastern Europe and Asia (Gupta et al., 2010). Remarkably, only 2% of barley produced is used for human consumption (Gupta et al., 2010).

Barley provides an excellent source of fiber, both soluble and insoluble, the majority contributed by β -glucan, which possesses blood cholesterol lowering powers (Gupta et al., 2010). It is also a rich source of B-vitamins, vitamin E, minerals and phenolic compounds (Gupta et al., 2010). The majority of phenolic compounds in beer, roughly 80%, are contributed by barley malt (Gupta et al., 2010).

Use of barley malt in brewing is due to its unique characteristics of being able to provide sufficient sources of starch and protein, various classes of enzyme including amylolytic, proteolytic and cytolytic, as well as its husk providing a natural mash filter (Goode et al., 2005). It also contributes flavor and color compounds delivered from the malting process (Goode et al., 2005).

One might expect that unmalted barley would be the perfect substitute for barley malt, due to its uniqueness in delivering all the qualities needed to produce good beer. Some of the properties of unmalted barley are well-suited to the replacement of malt. For instance, it maintains the same starch gelatinization temperature as malt, which allows for easy incorporation into mashing programs (Goode et al., 2005). Other benefits unmalted barley has over other cereal grains is the retention of the husk, so that filtration is minimally affected when using a lauter tun (Goode et al., 2005). Additionally, raw barley contains enough β -amylase to provide for maltose production in mashing (Goode et al., 2005). Barley, however, lacks α -amylase, proteases and glucanases in its unmodified form with the endosperm being

relatively difficult to access. This limits its use to 20% or less of total grain unless the use of commercial enzymes are applied (Goode et al., 2005).

Nitrogen content and composition

It should be of no surprise that with increasing levels of unmalted barley, as is the case with other raw cereals the level of TSN and FAN also decreased. Goode et al. (2005) found that TSN dropped from 927 mg/L for the all-malt wort to 579 mg/L for a 100% unmalted barley wort with no enzymes added. The TSN remained in the recommended range of 700-800 mg/L by Kordialik-Bogacka et al (2014) up to 60% unmalted barley. FAN, however, was only in the recommended range of 140-150mg/L (recommended range when using adjunct) up to 20% unmalted barley. Not surprisingly, as malted barley increased so did the assimilable nitrogen content (Goode et al., 2005).

In order to show that brewing with 100% unmalted barley is viable, Goode et al. (2005) prepared mash and wort samples using all barley with various enzyme treatments. Through the use of a commercial enzyme cocktail, they were able to show exponential increases in TSN, FAN and high-molecular-weight protein. While many attributes of the wort were studied, there was no discussion as to the properties or organoleptic analysis of the final beers, leaving curiosity as to the acceptability of the beer produced with 100% barley.

Viscosity

Barley contains high levels of β -glucan as compared to other cereal grains (Gupta et al., 2010). This higher concentration can lead to reduced extract, produce viscous worts, cause filtration troubles and chill haze (Gupta et al., 2010).

A modest increase in wort viscosity was found by Goode et al. (2005) as unmalted barley increased, related to a greater increase in β -glucan level in the worts. Once enzymes were included, they

found that there was a decrease in wort viscosity, with the prediction that this is due to greater hydrolysis of starch amylase, dextrins and β -glucan as enzyme concentrations increased.

pH

Goode et al. (2005) found a slight change in pH going from an all-malt mash ranging from 6.01 to 6.09 in all barley with a range across all samples of 5.92 to 6.09. The authors did not discuss this attribute and it is assumed that these changes are insignificant, although they are outside of the recommended ranges found in literature for conventional worts as discussed earlier. Based on this, it would be presumed that the beer from these mashes would suffer from unfavorable flavor, aroma and color changes.

Haze/Aroma/Flavor/Color

Color of worts prepared with unmalted barley decreased as the level of barley increased (Goode et al., 2005). Similar results have been shown with other cereals, but here it was found to be counteracted by the use of exogenous enzymes (Goode et al., 2005). The use of enzymes produced similar color results as malted barley when either a cocktail containing α -amylase, β -glucanase, or protease was used (Goode et al., 2005). The same results were found using these enzymes individually (Goode et al., 2005). The authors note that their work agrees with previous research showing that enzyme addition improves color through added proteolysis and amylolysis activity.

Foam Stability

From the literature reviewed, no discussion was found in changes to foam stability when using unmalted barley. As unmalted barley would presumably contribute similar levels and composition of protein to the beer, it is logical that only minor changes in foam stability would be measured as unmalted barley content increases. It is also possible that various factors affect foam stability differently and therefore negate one another. The fact that nitrogen content decreases as unmalted barley increases

would suggest that foam stability would be affected negatively. However, unlike other grains, the higher levels of β -glucan may offset the effect of lower nitrogen, potentially improving foam stability.

Extract

Small changes in the amount of extract recovered from mashing were seen as increased levels of unmalted barley resulted in lower extract. The largest difference seen was between 80% and 100% unmalted barley where a decline of 22% in extract was witnessed (Goode et al., 2005). Despite only a small change in extract recovery between 0% to 80% unmalted barley the fermentability (measured as apparent extract) was impacted more severely. Additionally, Goode et al. (2005) found differences in the composition of the extract sugars as well. Increasing levels of malt provide for higher concentrations of α -amylase, which has greater activity levels than β -amylase (β -amylase levels are essentially equivalent in raw and malted barley) (Goode et al., 2005). Therefore, greater concentrations of α -amylase resulted in higher production of glucose and maltotriose than maltose; in typical worts, maltose comprises 50-60% of total fermentable sugar (Goode et al., 2005). Additions of unmalted barley can reduce the total available fermentable sugars through lack of enzymatic conversation and therefore reduce the extract. Malting of barley provides not only preformed sugars and other soluble substances, but makes the carbohydrate substrate more available to enzymatic action (Goode et al., 2005).

CONCLUSION

The amount of research and understanding of beer processing today is truly astonishing. A beverage that has been enjoyed around the world for thousands of years has become a mature industry with great insights into the science of every unit operation.

From the research conducted, it is apparent that there is a great desire to produce beer from sources other than traditional malt. These reasons are quite varied, but the displacement of malt by

unmalted or even other malted cereal grains other than barley presents a number of challenges to the brewer of today. Not long ago it would seem that limitations to the use of alternative grains would be limited to incorporation of 10 to 20%, but with the enzyme technology developed in recent years, it is plausible to believe that levels approaching 100% are possible with some grains. Additionally, changes to processing, such as mashing with adjuncts in combination with barley and possibly the addition of exogenous enzymes appears to be one solution to allow incorporation of higher levels of adjuncts. More than one source noted that adjuncts are routinely used at levels of 40 to 50% of the grist. There is no doubt from the research reviewed that this is not a simple process and that additional care in processing and formulation must be taken in order to ensure the beer is of acceptable quality to consumers.

Since sorghum has found popularity in parts of the world for several decades, it would appear that much is known as to how to incorporate it into regional beers. By contrast, little research has been found regarding the use and effect of rice and maize on wort and beer. Perhaps this is due to a deep industry knowledge and good experience with these grains. It seems likely that due to their use in many American macro-breweries that they are well understood and easy to incorporate. However, broad knowledge across academia and in smaller operations may be limited, only being proliferated by those who are devoted to the trade of brewing or through informal, non-scientific media. Due to this fact, there would be great benefit for additional research on the use and function of maize and rice in brewing to build upon the already wide base knowledge provided in literature for other grains.

	Oats	Sorghum	Maize	Wheat	Rice
Nitrogen Content	Decreases	Decreases	Decreases	Decreases	Decreases
Amino Acid Profile	Improved	Improved	-	Comparable	-
Viscosity	Increases	Decreases	Decreases	Comparable	Decreases
pH	Increases	Varies	-	Decreases	-
Haze	Increases	-	Decreases	Varied	Decreases
Flavor	Toasted	Varies	Mild	Fruity/Citrusy	Mild
Color	Darker	Varies	Lighter	Lighter	Lighter

Table 5: Summary of Grains and their Effect on Wort or Beer

Similar to sorghum, oats and wheat have found favor in the literature, wheat more so than oats. The challenges associated with using oats at levels higher than 20% appear to be of significant challenge today; however, based upon the progress that has been made in this industry over the last few decades, solutions may be close at hand that would allow for oats to be used at up to 40-50%, much like maize or rice. Many properties of oats appear to prevent it from being used exclusively, including high fat content, high viscosity, and low extract. New technologies in enzymology may be able to improve beers using high levels of oats and offer even more varieties of product. As wheat has a long history of use in particular cultures, there appears to be a good understanding of its use over a wide range of grist levels.

It is clear that all of the cereals examined, sorghum, maize, oats, wheat and rice, have a place in brewing. Their effects in wort and beer are summarized in Table 5. The modifications they can provide to beer flavor, color and added efficiencies in the brewhouse have found acceptance around the world. It is likely that much more can be discovered as more research is conducted to allow for better use of these grains and produce higher quality beers.

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