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Parboiled Rice: Understanding from a Materials Science Approach

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Abstract

The material properties like glass transition temperature, diffusion, microstructures of rice kernels and gelatinization and retrogradation of the rice starch are reviewed to understand the nature and quality of the parboiled rice. Details of the diffusion related material properties of rice kernels such as the rate of diffusion, different models of diffusion, diffusion in glassy and rubbery state and diffusion in the gelatinized starch are discussed. The influences of hydrothermal treatment on the properties of the rice kernel are also highlighted to understand the overall quality of parboiled rice.

Highlights

- Parboiling of rice increases its nutritional and milling quality
- Improvement in colour and texture are needed to make parboiled rice more preferred.
- The rice kernel undergoes significant material change during parboiling process.
- The diffusion is the key parameter that affects the material property change.
- Understanding of material change process can be used to tailor the final quality.

Keywords: Parboiled Rice; Hydration; Dehydration; Diffusion; Gelatinisation; Glass Transition Temperature; Retrogradation
1 Introduction

Rice (*Oryza sativa* L.) is an important staple food for nearly one-half of the world’s population, contributing 21% of the global human per capita energy and 15% of per capita protein. More than a billion households of Asia, Africa and South America are dependent on rice for their main source of income and employment. Rice fields cover more than 9% of total earth’s arable land (Maclean et al., 2002).

The forms that rice is consumed include whole grains (brown, milled or parboiled), flour and fermented products. Parboiled rice is prepared by soaking, cooking and drying of paddy (or brown rice) before milling.

The preference for parboiled over milled rice is based on the ‘traditional taste’ preference of consumers, with some areas in South Asia preferring parboiled rice because it is typically less sticky than non-parboiled rice (Kato et al., 1983; Unnikrishnan & Bhattacharya, 1987). In addition, it is also preferred by health sensitive consumers due to its better nutritional properties compared to non-parboiled rice. Agronomic conditions during harvesting also promote the need to parboil rice because almost all the rice harvested during rainy season and rice that has experienced flooding during harvesting show excessive breakage during milling (Bhattacharya, 2011). To counteract this, the paddy is parboiled to improve the Head Rice Yield (HRY).

The type of rice chosen (e.g. amylose content, grain length) and parboiling method varies between countries and depending on its intended final use (Juliano, 1993). This literature review aims to provide a critical assessment of research behind the physical and chemical processes that impact on grain quality to better understand the choice of variety and methods used.

2 Parboiling Processes

There are many variations in traditional methods of parboiling depending on the place and scale of operation (Araullo et al., 1976), but the basic production steps are hydration of the paddy (to a moisture level ~24-30% wb), thermal treatment to achieve complete gelatinisation and dehydration to a moisture content appropriate for milling. In large scale commercial parboiling processes, variation in the processes is done to make it efficient, economical and to improve the end product quality (Bhattacharya, 2004).
Different variations of the parboiling process yield rice with different material properties, and so may challenge consumer preference for the product. For example, the hot soaking process gives a more discoloured product than cold soaking process, while pressure parboiled rice is even more discoloured. Furthermore, the cold water soaking method taints the paddy with off flavours. The dry parboiled rice has the faster dehydration and puffing characteristics than others. A brief comparison of commercial parboiling processes is given in Table 1.

In addition to the more common parboiling processes, there are other methods such as combination soaking (Igathinathane et al., 2005), ultrasonic soaking (Wambura et al., 2008), and soaking in alkali or acid solutions (Bello et al. 2004) but these are not widely used.

3 Diffusion, Gelatinisation and Retrogradation in Parboiled Rice

The key factors in controlling the material change due to changes in chemical and physical properties of the rice grain during parboiling process are:

- Diffusion of water and other compounds into and out of the rice grain during hydration (rice soaking), dehydration (drying) and re-hydration (cooking prior to consumption) of rice grains
- Starch gelatinisation and protein denaturation during heating as affected by moisture content, temperature and time
- Starch retrogradation after heat treatment process

Here, a review of the phenomena encountered, and the opportunities that exist to tailor the final quality of parboiled rice to consumer demand will be presented.

3.1 Diffusion

Diffusion is common to all steps of parboiling. The diffusion properties of rice depend on a number of factors including grain structure, composition, post-harvest processing, temperature and moisture content. The following section will examine how rice grain structure, microstructure, composition and glass transition dictate diffusion during hydration and dehydration processes.

3.1.1 Glass Transition and Diffusivity

Starch below the glass transition temperature (Tg) is in glassy state with low expansion coefficients, specific volume and diffusivity. In comparison, starch above the Tg is rubbery
with a higher expansion coefficient, specific volume and diffusivity. This physical change is influenced by the moisture content of the grain, with increased moisture content decreasing the glass transition temperature (Perdon et al., 2000; Slade & Levine, 1995; Slade et al., 1991). The glass transition that starch undergoes during drying plays an important role in determining the Head Rice Yield (HRY) (Ondier et al., 2012; Perdon et al., 2000). It has been reported that the annealing of starch that happens above glass transition also reduces the kernel breakage (Truong et al., 2012).

During soaking, the hydration rate increases with an increase in soak water temperature. When the temperature exceeds the gelatinisation temperature, the water absorption increases significantly (Bakshi & Singh, 1980; Bello et al., 2007; Suzuki et al., 1977). This phenomenon may also be true for other water soluble components such as inward and outward diffusion of pigments and micronutrients. The glass transition temperature of parboiled paddy is around 20°C (Siebenmorgen et al., 2004), or even lower due to the thermal breakdown of starch into lower molecular weight compounds (Fery, 1980; Slade & Levine, 1995). Drying of parboiled paddy above its Tg would be faster because it would have the starch with greater free volume where the water is more mobile (Slade et al., 1991) creating the higher diffusion rate.

When the starch in the rice kernel is below the Tg, the granules are compact and the water is relatively immobile, resulting in long drying times to reach the final product moisture content (Cnossen et al., 2002). Drying above Tg (in the rubbery state) will be faster because the starch have a greater free volume and the water in starch is more mobile (Slade et al., 1991) creating a higher diffusion rate.

### 3.1.2 Diffusion Models

Water movement into paddy dictates the rate of hydration during the soaking step of parboiling and can be described by Fickian diffusion where the rate of water diffusion (flux) in the direction of flow is proportional to the concentration gradient. The diffusion coefficient is dependent on factors such as temperature, initial moisture content and internal composition of the grain (Bakshi & Singh, 1980; Bello et al., 2007; Suzuki et al., 1977). In rice, the major factor controlling hydration is temperature.
The moisture migration into and out of the grain involves a number of transport phenomena, such as capillary motion, molecular diffusion, liquid diffusion, vapour diffusion and Knudsen flow (Brennan et al., 1990; Senadeera et al., 2003; Zogzas & Maroulis, 1996). During soaking or drying, the moisture migration in/out the grains is generally considered to be governed by the diffusion caused by the moisture gradient between the surface and the centre (Becker, 1960; Engles et al., 1986; Sayar et al., 2001). Hence, Fick’s second law of diffusion has been widely used to model the water sorption and desorption behaviour in grains during soaking and drying.

Researchers have applied semi-theoretical models to the water uptake kinetics of food in the same manner as drying. These models are also based on Fick’s second law of diffusion which are derived by simplifying the general series and hence these offer a compromise between theory and ease of use (Table 2).

Singh et al. (2010) applied Peleg’s model to the sorption data of paddy, brown rice and milled rice. They compared the experimental and predicted values of water absorption and reported that Peleg’s model works well for predicting the hydration behaviour of paddy, brown and milled rice. However, the predicted values reported were lower than the experimental values. Page, Modified Page, Henderson & Pabis and Two Term Exponential Model were used to predict the hydration behaviour of brown rice (Cheevitsopon & Noomhorm, 2011) and milled rice (Kashaninejad et al., 2007). Both research groups reported that the Page model gave better predictions than others and satisfactorily described the experimental soaking characteristics of brown as well as milled rice. Akal et al. (2007) and Hacihafizoglu et al. (2008) compared twelve different semi-empirical models (Table 2) during thin-layer dehydration of paddy and reported that Midilli et al. model was the best in explaining the drying characteristics of rough rice whereas the geometric model appeared to give the worst fit.

3.2 Hydration

Hydration barriers originate from the morphology of the rice grain and the composition of the endosperm. This section discusses each.
3.2.1 Grain Structure

3.2.1.1 Grain dimensions

Paddy grain has variable length and breadth depending on the variety and even within a variety. Milled rice is classified on the basis of grain length which can range from 4.0 mm for a short grain to 7.7 mm for a long grain. Across these classifications, width and breadth of milled grain can range between 1.71-2.85 mm respectively (Bhattacharya, 2011). As the rate of diffusion is directly proportional to the surface area, varietal differences based on grain dimension will influence the mass water diffusion. Even within the same variety, the size of the grains differs and hence the diffusion rate.

3.2.1.2 Husk layer

Paddy grain is a multi-layered material consisting of husk (cellulose, outer layer), bran (aleurone; middle layer) and starch (inner layer). These three different layers have different material properties and hence differ in the rate of water diffusion.

The characteristics of the husk (e.g. thickness, tightness of lemma and plea, pore-size and concentration of the silica) may be important factors in water diffusivity (Bhattacharya, 2004). An earlier study suggested that if the husk of the paddy could be slightly opened, the diffusion rate would be much faster than the paddy with intact husk (Swamy et al., 1971). The water diffusion coefficient of the dehusked brown rice is at least two times greater than that of paddy (Table 3) which suggests that the husk as one of the major barrier for water diffusion (Bello et al., 2004; Thakur & Gupta, 2006). However the diffusion coefficient also varies depending on the temperature and variety (Shittu et al., 2012).

Some paddy varieties have hairy husks and awn which further impose a barrier for diffusion. The varieties that have tighter interlocking between lemma and plea are more resistant to hydration than the varieties that have loose interlocking (Bhattacharya, 2011).

Additionally, the hydration of rice grain can be affected by its position in the panicle. The grains in the primary panicles as well as those in the top of the panicles attained complete hydration (and hence parboiling) faster than the grains in lower positions (Pillaiyar et al., 1998). This was found to be a result of variation in the material properties among the grains within the same panicle due to their relative maturity.
3.2.1.3 Bran layer

Studies have shown that the brown rice kernel absorbs less water than milled rice during cooking (Figure 1) (Billiris et al., 2012; Desikachar et al., 1965). This has been attributed to the bran which is composed of hydrophobic waxy cuticle (Champagne et al., 2004) high in lipid content that offers the physical barrier for water diffusion into the kernel. The bran is also rich in protein and this also limits the starch hydration (Martin & Fitzgerald, 2002). In totality, the bran cuticle containing the high surface lipids and surface proteins collectively act as the barrier to diffusion.

3.2.2 Kernel microstructure

The microstructure of the rice kernel such as the granular arrangements of starch, pores and cracks present in the endosperm affect the diffusion process. The water diffusion in a polymeric system is related to the availability of molecular-sized holes (pores) in the polymer structure and polymer-water affinity. The number of holes depends on the microstructure of starch polymer, its morphology and crosslink density (Diamant et al., 1981).

In addition to pores, rice kernels have cracks in the kernel that also contribute to the free volume in the kernel. The cracks are created due to the moisture stress during pre-harvest or post-harvest stage (Kunze & Calderwood, 2004). Together; these pores and cracks act as the water channels which affect the rate of diffusion.

For many polymer systems, the free volume created within the materials (due to presence of pores and cracks) tends to dominate the diffusion process (Diamant et al., 1981; Johncock & Tudgey, 1986) because the change in volume of the polymer due to moisture-induced swelling is significantly less than the volume of moisture absorbed (Adamson, 1980; Wong & Broutman, 1985). This indicates that a large portion of the absorbed water resides in the free volume created by the pores and cracks. In rice kernels, the true density of the kernel increased with the increase in soaking temperature up to 40°C but it decreased when the soaking temperature was 70°C (Kashaninejad et al., 2007). It can be inferred from this result that the true density of kernel increases below the gelatinisation temperature because it gains mass but does not expand much in volume. During hydration of a polymer in the glassy phase, the water first fills the pores and cracks before causing an expansion in kernel volume. A larger number of pores and cracks will facilitate the higher water mass diffusion. When the temperature passes the glass transition temperature (Tg), the starch granules swell and the
volume increases significantly than the mass thereby decreasing the kernel density (Kashaninejad et al., 2007). Hence, it can be said that for the starch polymer in rice also, the free volume present due to the cracks and microstructure of the starch plays a dominant role in water diffusion before starch gelatinisation occurs.

### 3.2.3 Composition

#### 3.2.3.1 Lipids

Lipids in rice are classified into two types: non-starch and starch lipids. The non-starch lipid content in brown rice is 2.9-3.4% (db) whereas the starch lipid is 0.66-0.76% (db). Rice bran is mainly composed of the aleurone layer and embryo, and contains 60% of non-starch lipids that are the major lipids present in bran layer as spherosomes (Godber & Juliano, 2004). Starch lipids are present at relatively low concentrations and primarily in complex with amylose. Non-waxy rice, having a higher content of amylose, contains more starch lipids and less non-starch lipids than waxy milled rice (Choudhury & Juliano, 1980).

The hydrophobic nature of lipids offers a barrier for the mass water diffusion. Billiris et al. (2012) reported that the hydration of brown rice was much slower than the milled rice. Kaur et al. (2011) did a study on cereal bran (wheat, rice, barley and oat) and found that the defatted bran had higher water absorption than full fat bran. They reasoned that the hydrophobic nature of fat, which might have contributed to the reduced water absorption of full-fat bran, while the hydrophilic nature of crude fibre might have contributed to the increased water absorption in the defatted bran samples. Confirmation of this could be achieved if an appropriate method for lipid removal from whole kernel without affecting its composition and micro-structure could be developed.

#### 3.2.3.2 Proteins

Proteins are most concentrated on the outer surface of rice kernel and in the bran (Champagne et al., 2004). Surface proteins may have the role in regulating the water diffusion into the starch granule and control the granule swelling during gelatinisation because glass transition of protein is slightly lower than that of starch (Matveev et al., 2000) and hence it will have higher water absorption capacity than starch. Despite their presence at a lower concentration than starch in the rice, proteins have been identified as the major water absorbers (Derycke et al., 2005b; Martin & Fitzgerald, 2002). It has been reported that high protein rice requires more water and longer time to cook (Husain et al., 1981). The faster
hydration of protein than starch leads to the general conclusion that protein has a higher water diffusion coefficient than starch.

3.2.3.3 Starch

Starch has a multi-scale structural model where the granules are made from the alternating growth rings of amorphous and crystalline structure. This gives three different dynamic components in the starch, namely a highly crystalline region formed from amylopectin double helices; a more mobile, rubber-like amorphous region associated with amylopectin branch points and solid-like regions formed from lipid inclusion complexes of amylose (Morgan et al., 1995). However, the distinction between crystalline and amorphous states in starch is not absolutely clear in terms of molecular order.

Starch granules contain pores on the surface that extend to the centre of the granules. Based on the X-ray diffraction pattern, native rice starch is classified as type A-crystalline. These types of structures are closely packed with water molecules between each double helical structure, whereas B-types are more open and water molecules are located in the central cavity (Corre et al., 2010). Tang et al. (2000) found there were four water reservoirs in the potato starch (B-types) which were extra-granular water, water in the amorphous growth rings, water in the semi-crystalline lamellae and channel water located in the hexagonal pores of amylopectin crystals. However, they did not find the “channel water” in A-type crystals that are prevalent in non-parboiled rice starch.

The amorphous regions of starch are considered to be susceptible to chemical reaction because this region swells the most upon hydration. The distribution of crystalline and amorphous regions of starch could be the determining factor for water diffusion within the starch granules. The crystallinity of the rice starch is 38-51% (Corre et al., 2010) which is greatly influenced by the moisture content and the amylopectin content. But amylose content has little effect on crystallinity for A-type starches. The higher gelatinisation temperature for the increasing level of crystallinity suggest that less water diffusion and swelling occurs in such rice kernels (Metcalf & Lund, 1985).

3.3 Dehydration

The final stage of the parboiling process after the starch in kernel is gelatinized during the soaking and heating steps of parboiling, is to dry the kernel to a safe moisture level (~12% wb) in order to render it suitable for further processing or storage conditions. The drying
pattern of the kernels that has gelatinized starch will be different from the non-gelatinized counterpart because of the change in material properties. Gelatinized starch is irreversibly swollen whereby water occupies the internal kernel void spaces including channels and bound to starch chains. Upon drying at a fast rate, the vacated water leaves behind fissures and hollow cavities in the dried grain that further increase diffusivity (Amornsin, 2003) to yield a low Head Rice Yield (Bhattacharya, 2011). Therefore to maintain and preferably improve Head Rice Yield, the final drying step of parboiling is crucial.

The diffusion coefficient of water in the gelatinized starch \( (2 \times 10^{-10} \text{ m}^2/\text{s}) \) is less than the non-gelatinized starch \( (5 \times 10^{-10} \text{ m}^2/\text{s}) \) (Uzman & Ahbaz, 2000), though in the case of paddy, parboiling opens the husk (Bhattacharya, 2011) which might facilitate the rate of moisture removal.

At a molecular level, relative to unprocessed rice, during the final cooling and drying steps of parboiling the starch increases in crystallinity including the formation of crystalline amylose-lipid complexes (Derycke, 2007). These changes to crystallinity are accompanied by a gradual change from a viscous-amorphous state to a glassy state. The change in physical state in turn impacts the diffusion of water out of rice kernel.

### 3.4 Rehydration

An uncooked rice grain (dry) absorbs less water than a parboiled rice grain at the room temperature. At temperatures near to the gelatinisation temperature of the rice, the uncooked rice grain absorbs more water than the parboiled rice (Pillaiyar & Mohandoss, 1981a). This unusual property of the hydration of the rice kernel has been explained from the viewpoint that water diffusion property of the starch is governed by the extent of starch gelatinisation and retrogradation, as well as the level of pores and fissures present in the grain. However a study on the rehydration of freeze dried parboiled rice showed that a higher extent of gelatinisation increased the rate of rehydration (Puspitowati & Driscoll, 2007). This suggests that not only the extent of starch gelatinisation but the microstructure that underlines the gelatinised nature of the kernel affects the rehydration phenomena of parboiled rice.

### 3.5 Starch Gelatinisation and Retrogradation

Parboiled rice is produced by heating starch above the gelatinisation temperature after hydration, or by hydrating in water above the gelatinisation temperature. Gelatinisation and re-crystallization are the major changes in rice starch that occur during parboiling. During re-
crystallization process, the starch exhibits polymorphisms which contribute the final texture of cooked parboiled rice.

During gelatinisation the swollen starch granules melt and the phase transition of starch occurs. As a result, the optical properties such as light polarization or iodine coloration value of the starch change, and some starch within the granules leaches out due to the bursting of granule cell wall. The detailed review of starch gelatinisation can be found in the reviews by Delcour & Hoseney (2010) and Fitzgerald (2004). The fully gelatinized starch turns into a viscous mass which has extremely limited water uptake capacity because diffusion process can no longer overcome the resistance of the highly viscous medium (the gelatinized starch).

Starch gelatinisation also affects on the hydration behaviour of paddy because paddy exhibits two different soaking responses below and above gelatinisation temperature. Below the gelatinisation temperature, the rate of hydration increases with increasing temperature, with a slow increase in moisture content over the time until the equilibrium moisture content is achieved. Above the gelatinisation temperature, the hydration rate is high leading to the rupture of starch granules (Bandyopadhyay & Roy, 1978) and solid loss.

During cooling and drying of parboiled rice the gelatinized starch re-crystallizes into A-and B-types of crystals. Non-parboiled rice predominantly contains A-type crystals whereas in parboiled rice starch A-, B- and V-types coexist (Derycke et al., 2005a). If the starch recrystallizes in the presence of a fatty acid or long chain alcohol, the V pattern is obtained. Amylose also gives V-pattern when complexed with n-butanol or lipids due to the amylose-lipid complex formed as a result of parboiling (Buléon et al., 1998). The proportions of these crystal types (A, B or V) depend on the moisture content and the extent of heating during parboiling methods. For example, the temperature required for complete gelatinisation (determined as when A type crystals totally disappear) is 90°C at 60% moisture content which is 145°C at 25% moisture content (Derycke et al., 2005a).

Ong and Blanchard (1995b) reported five polymorphic forms of the starch in parboiled rice: (1) residual unmodified starch (in partially parboiled rice) which gives the A-type of X-ray diffraction pattern and has the crystal melting point \(T_m\) of about 75°C, (2) annealed starch granule, which gives the A-type of X-ray diffraction pattern and a \(T_m\) of about 85°C, (3) re-crystallized or retrograded amylopectin which also gives the A-type X-ray diffraction pattern and has the \(T_m\) of about 50°C, (4) lipid-amylose inclusion complex type I, which gives the V-
type X-ray diffraction pattern and $T_m$ more than 100°C and (5) lipid-amylose inclusion complex type II, which also gives a V-type X-ray diffraction pattern and has the $T_m$ in the range of 105-120°C.

However, the extent of retrogradation and its effect on the organoleptic properties of the cooked parboiled rice is still a subject of interesting research. When starchy foods such as rice grains are boiled, the starch granules at or near the outer surface gelatinize easily but the starch granules near the centre of the kernel are hard to be gelatinized because they are scarce in water. Hence, during the initial period of soaking at higher temperature, the mechanism of starch gelatinisation inside the food body may be governed by rate of gelatinisation in the limited water condition and the diffusion of water. Takeuchi et al. (1997) reported that during initial period of kernel boiling, there is a sharp moisture profile difference between the surface and the centre, which may also be the reason for uneven gelatinisation of starch during short time cooking. Watanabe et al. (2001) described that the diffusion in such a situation is of non-Fickian type and can be explained by the water demand (WD). They have proposed a new mathematical model to describe the features of water diffusion in starchy food during the course of cooking.

4 Physical properties of parboiled rice

Ultimately, it is the acceptability of the physical and chemical attributes of the final product that will promote the acceptance of a parboiled product. During hydrothermal treatment, the paddy undergoes some specific changes due to physical and chemical interactions. The extent of changes within the rice kernel depends on the processing variables applied during processing. Some of the major properties of parboiled rice are discussed in following headings.

4.1 Grain Dimensions

The water diffusion coupled with heat treatment causes the irreversible swelling of starch granules and hence the parboiled rice kernel is thicker and shorter than non-parboiled counterpart (Bhattacharya, 2004). This change was observed in the parboiling under excess water system but not in the limiting water systems such as dry heat and pressure parboiling process (Sowbhagya et al., 1993).
4.2 Chalk

The opaque white patches seen on the belly of the milled rice (chalkiness) is the result of different cellular morphology of starch granules whereby chalky grains are packed loosely leaving some air spaces that scatter light and so look opaque. Chalkiness is a highly undesirable trait in all non-waxy rice varieties except for Arborio and Sake style rice. Due to the loose packing of starch there is more free volume within the kernel that can absorb more water than normal types. The water diffusion and starch gelatinisation process during parboiling removes such air spaces and hence the reduces the chalkiness (Bhattacharya, 2011). In this respect, parboiling increases the consumer appeal of the product.

4.3 Colour

The colour of parboiled rice is different than the non-parboiled rice. Parboiled rice has a shade of amber colour possibly due to the diffusion of husk colour into the endosperm (Lamberts et al., 2006a; Lamberts et al., 2006b). Another cause has been reported to be the presence of an increased level of reducing sugar and free α-amino nitrogen (FAN) and isomerisation of glucose to fructose suggest the likelihood of non-enzymatic Maillard type of browning for colour change in parboiled rice (Lamberts et al., 2008).

The colour change in parboiled rice increases with increasing soak water temperature (Islam et al., 2004; Sareepuang et al., 2008) and increasing steaming duration (Bhattacharya & Subba Rao, 1966; Lamberts et al., 2006a) as well as the increasing steaming pressure of inadequately hydrated grains (Bhattacharya, 2011). The husk colour absorption is also higher at high soaking temperature (Lamberts et al., 2006a) and the absorption of the coloured material (such as in folic acid fortification) from soak water (Kam et al., 2012) also negatively affects the whiteness of the rice kernel.

4.4 Mechanical Properties

The parboiling temperature and duration has the significant influence on the hardness of the kernel. The hardness of the paddy decreases with the increasing soak water temperature (Pillaiyar & Mohandoss, 1981b) and it increases with increasing steaming time (Kar et al., 1999). Parboiling also increases the ultimate tensile strength (by about four to five times) and modulus of elasticity of the rice kernel. These strength values are directly proportional to steaming duration and the degree of starch gelatinisation (Saif et al., 2004). The increase in
strength may be the reasons why there is less breakage when parboiling rice is milled process and has altered texture than non-parboiled rice when cooked.

5 Chemical properties of parboiled rice

The parboiling process was found to impart the increased protein, lipids and ash content of rice kernel (Sareepuang et al., 2008). The chemical composition also differed due to different parboiling processes. For example, parboiled rice produced with high soak water temperature was reported to be less in lipid content (Sareepuang et al., 2008), higher in thiamine content (Chukwu & Oseh, 2009) but experienced higher starch leaching (Han and Lim, 2009). Whereas, the increasing steaming period decreased protein, calcium, iron and sodium but increased the fat, total ash and crude fibre content in parboiled rice (Ibukun, 2008).

The chemical composition at a molecular level significantly influences the characteristics of the cooked parboiled rice that the consumer will ultimately base their preferences on. The following is a review of known changes to the composition and structure that occurs within the kernel.

5.1 Starch

Due to gelatinisation during the heating/cooking process, starch is irreversibly swollen in the parboiled rice. It is also thermally broken down to low molecular weight products depending on the time/temperature combination during processing (Mahanta & Bhattacharya, 1989). The different methods of parboiling, which differ in time/temperature combinations, will have significantly different extent of starch breakdown. The effect of starch breakdown on the cooking and eating quality of parboiled rice has not been reported in detail.

5.1.1 Proteins

The total protein and amino acid content of parboiled rice does not change although the protein bodies in the kernel are ruptured during the steaming process (Bhattacharya, 2011). The protein is hydrolysed leading to increased disulphide bonds which increases the viscosity and hardness in the parboiled rice (Derycke et al., 2005b). If the ageing of rice is connected with the change in protein structure and conformations, a study of this change in double boiling parboiling process could be of significant importance because the rice produced from this method imparts the ‘aged’ characteristics (Bhattacharya, 2004).
5.1.2 Lipids

During parboiling, the lipid bodies or the spherosomes of the non-starch lipids are broken and fat is released from the surface of kernel. This band of lipids are diffused outwards and hence the bran of parboiled rice is more oily (Mahadevappa & Desikachar, 1968) whereas the parboiled rice kernels (after milling) are less in lipid content than brown rice (Sareepuang et al., 2008).

5.1.3 Vitamins and Minerals

The parboiled rice is reported to retain more B-vitamins (thiamine and nicotinic acid) than raw rice. Parboiled rice has more thiamine and nicotinic acid than milled rice (Aykroyd, 1932; Kik, 1946). Despite the fact that these two vitamins are lost during parboiling (leaching loss during soaking, thermal breakdown during steaming) (Ramalingam & Raj, 1996), the parboiled rice is still richer in these vitamins than milled (white) rice because the white rice looses these during polishing (Bhattacharya, 2011). Manful et al (2007) reported that the thiamine content in the parboiled rice increased gradually as parboiling intensity was increased from initial soaking temperature at 30°C and steaming for 4 min to soaking at 70°C and steaming for 12 min. There was a sharp rise in thiamine when the soaking temperature was further increased to 90°C and steamed for 12 min. The gradual increase in thiamine content with the severity of heat treatment (during soaking and steaming) indicates the possibility of the formation of this vitamin during thermal treatment. But this hypothesis can only be concluded after proper investigation. Whereas, the riboflavin level showed a different pattern because it increased with parboiling with increasing temperature of soak water up to 70°C but beyond that it decreased (Manful et al., 2007). The loss of vitamins A and C was also observed after parboiling which was directly related to the severity of temperature (Chukwu & Oseh, 2009).

The reasons behind the increased level of B-vitamins despite some loss has been reported due to the inward diffusion of these vitamins from bran layer to endosperm during the parboiling process (Pauda & Juliano, 1974). But a previous study done by Rao and Bhattacharya (1966) showed that the increase in the level of thiamine did not occur during soaking but it happened after steaming (gelatinisation). It was postulated that the gelatinisation ‘fixes’ this vitamin and that is why the parboiling process strongly prevents the milling loss of these vitamins. The disagreement between the work by Subba Rao and Bhattacharya (1966) and Pauda and Juliano (1974) makes a topic of further research to determine whether the increase in the
level of B-vitamins is due to inward migration during soaking or fixation or both or even the product of thermal degradation.

6 Properties of cooked parboiled rice

6.1 Texture of cooked grain

Texture of the rice grain after cooking is the principal quality attribute dictating the consumer acceptability and palatability which is expressed in terms of hardness or firmness and stickiness or adhesiveness as well as moistness to touch (Ramesh et al., 2000).

The texture of the cooked rice grain is mainly affected by the genetic variability (variety), storage duration (ageing) and parboiling. The major varietal factor that controls the texture of cooked rice is amylose content. The high-amylose rice becomes flaky and dry upon cooking whereas low-amylose rice is sticky and moist (Juliano et al., 1981). The freshly harvested rice cooks sticky and lumpy as compared to the aged samples of the same variety. Cooked parboiled rice is more fluffy, non-sticky and free-flowing than non-parboiled counterpart. The gelatinisation, thermal breakdown of starch and the recrystallization (retrogradation) of the starch with some lipid-amylose inclusion complexes are the major factors that cause the texture change in parboiled rice (Mahanta et al., 1989; Ramesh et al., 1999; Ramesh et al., 2000). The type of starch polymorphs (as discussed formerly) formed during particular parboiling process are important in determining the final texture of cooked parboiled rice (Ong & Blanshard, 1995a).

6.2 Gelatinisation Temperature

Based on the gelatinisation temperature, rice is grouped into three classes: low (55 to 69°C), intermediate (70 to 74°C), or high (75 to 79°C). The gelatinisation temperature of the rice is not variety-specific, and varies due to environmental and other factors (Bhattacharya, 1979). Gelatinisation is related to cooking time and texture of the rice. Knowledge of the gelatinisation temperature prior to parboiling is useful in hot-soak parboiling processes to adjust the temperature of soak water. For example, paddy with high and intermediate gelatinisation temperature can be soaked in hot water of 70°C whereas the paddy with low gelatinisation temperature will be over hydrated at this temperature if soaked for the same period as the paddy with high gelatinisation temperature (Bhattacharya, 2011).
Parboiling process increases the gelatinisation temperature of rice which is proportional with the severity of the heat treatment (Islam et al., 2002).

6.3 Viscosity

Viscosity provides inferences to the final texture of the cooked product. The peak viscosity, breakdown, final viscosity, set back time to peak viscosity and pasting temperature (Figure 2) are typical parameters recorded by rapid visco-analyser (RVA) to assess the pasting properties of cooked rice (Bhattacharya, 2011). The viscosity curves are variable with the moisture, protein, lipid and amylose content of the rice samples (Fitzgerald et al., 2003).

The increase in pasting temperature, reduction of peak viscosity, elevation of final viscosity and the reduction in the breakdown and total setback time are the major changes due to parboiling (Ali & Bhattacharya, 1980; Rao & Juliano, 1970). The high-amylose starches are intensely affected by parboiling than medium-and low-amylose starches (Zavareze et al., 2010).

7 Conclusion

The factors in controlling the material properties of parboiled rice are the diffusion of water and other compounds into and out of the rice grain, starch gelatinisation and retrogradation and the protein denaturation and disulfide linkage.

Diffusion is a key parameter to dictate the final quality of parboiled rice. The diffusion properties of rice depend on a number of factors including grain structure, composition, post-harvest processing, temperature and moisture content. Fick’s second law of diffusion has been widely used to determine the diffusion behaviour in grains during soaking and drying. Researchers have also applied semi-theoretical models to understand the diffusion process in the rice grain.

Gelatinisation and re-crystallization are the major changes in rice starch that occur during parboiling. During gelatinisation the swollen starch granules melt and the phase transition of starch occurs. And in re-crystallization process, the starch exhibits polymorphisms which contribute the final texture of cooked parboiled rice.

The extent of changes within the rice kernel during hydrothermal treatment depends on the processing variables applied during processing. The parboiled rice kernel is thicker and
shorter than non-parboiled counterpart. The opaque white patches seen on the belly of the milled rice (chalkiness) is removed by parboiling. The parboiled rice has a shade of amber colour possibly due to the diffusion of husk colour into the endosperm or non-enzymatic Maillard type of browning. The parboiled rice has higher mechanical strength which makes it less susceptible to breakage during milling. The content of B-vitamins is increased in parboiled rice. The eating properties of parboiled rice are also altered than non-parboiled counterpart because it is less sticky, absorbs less water and takes a bit more time in cooking.

The severity of the time-temperature treatment adopted during different parboiling process affect the final quality of parboiled rice. For example, the colour change increases with increasing soak water temperature and increasing steaming duration as well as the increasing steaming pressure. Whereas, the hardness value decreases with the increasing soak water temperature but increases with increasing steaming time. The parboiled rice produced with high soak water temperature was reported to be less in lipid content, higher in thiamine content (Chukwu & Oseh, 2009) but experienced higher starch leaching. The thiamine content in the parboiled rice increases gradually as soaking temperature and steaming duration is increased. Whereas, the increasing steaming period decreased protein, calcium, iron and sodium but increased the fat, total ash and crude fibre content in parboiled rice. There is loss of vitamins A and C which is directly related to the severity of temperature.

Acknowledgments

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8 References


Page, G. (1949). *Factors influencing the maximum rates of air drying shelled corn in thin layers*. Purdue University, Indiana.


Table 1: Comparative overview of some parboiling methods (Bhattacharya, 2004).

<table>
<thead>
<tr>
<th>Process</th>
<th>Benefits</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Single boiling process</td>
<td>Simple technology</td>
<td>Risk of microbial fermentation</td>
</tr>
<tr>
<td>Soak paddy at ambient temperature for about 72 hr. Drain and steam paddy for a few minutes. Dry.</td>
<td>Easy to implement</td>
<td>Fermentation may cause off-flavour in the product.</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
<td></td>
</tr>
<tr>
<td>2. Double boiling process</td>
<td>Reduced soaking time compared to (1).</td>
<td>Risk of microbial fermentation</td>
</tr>
<tr>
<td>Steam paddy prior to putting in into the soak water (pre-steaming heats the water). Soak at ambient temperature for about 36 h, drain, steam and dry.</td>
<td>Aged rice texture</td>
<td>Fermentation may cause off-flavour in the product.</td>
</tr>
<tr>
<td></td>
<td>Risk of grain bursting</td>
<td></td>
</tr>
<tr>
<td>3. Hot water (or Central Food Technological Research Institute) process</td>
<td>Reduced soaking time</td>
<td>Batch process</td>
</tr>
<tr>
<td>Soak paddy in hot water (about 70°C) for about 3 hr (Water is re-circulated to prevent temperature difference between the top and bottom). Drain, steam and dry.</td>
<td>Complete removal of foul odour in the product</td>
<td>Costly</td>
</tr>
<tr>
<td></td>
<td>Reduced soaking time</td>
<td></td>
</tr>
<tr>
<td>4. Low moisture process</td>
<td>Soaking, steaming and drying can be done sequentially in the same equipment</td>
<td>Risk of uneven hydration</td>
</tr>
<tr>
<td>Soak paddy/brown rice in hot water (~75°C) until reaches ~24% moisture (partial hydration), drain, temper (~4 hr), heat (or steam) and dry.</td>
<td>Low grain moisture reduces drying time and cost</td>
<td></td>
</tr>
<tr>
<td>5. Hot water process (above gelatinisation temperature)</td>
<td>Does not require a separate starch gelatinisation process</td>
<td>Risk of grain bursting or inadequate starch gelatinisation</td>
</tr>
<tr>
<td>Soak paddy in hot water (80-85°C) for 2-3 h, drain and dry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Pressure- parboiling process</td>
<td>Short processing time.</td>
<td>Product is discoloured and very hard</td>
</tr>
<tr>
<td>Soak paddy until it reaches ~24% moisture content, steam under high pressure and dry.</td>
<td>Parboiled grain has low final moisture reducing drying time and cost</td>
<td></td>
</tr>
<tr>
<td>7. Dry-heat process</td>
<td>Steam is not required (hence more economical process).</td>
<td>Cooking time depends upon the final moisture after HTST processing</td>
</tr>
<tr>
<td>Soak paddy in hot water (~75°C to ~30% moisture), drain, high temperature short time heating (125-150°C for ~40-50 s) and dry.</td>
<td>Very short drying time as most of the moisture is removed during high temperature short time (HTST) process</td>
<td>Care should be taken during HTST to reduce the puffing of the rice</td>
</tr>
<tr>
<td>8. Brown-rice process</td>
<td>Very fast hydration, and reduced operation cost</td>
<td>Caking and cracking causes the difficulty in handling. Higher dry matter loss</td>
</tr>
<tr>
<td>Soak brown rice (dehusked paddy) in hot/cold water, heat (steam or dry heat) and dry.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Semi-theoretical models used for paddy, brown and white rice hydration and dehydration.

<table>
<thead>
<tr>
<th>Model &amp; Reference</th>
<th>Description</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewis Model (1921)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} \exp(-k_0 t)$</td>
<td>Hydration of milled rice (Kashaninejad et al., 2007), dehydration of paddy (Abe &amp; Afzal, 1997; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Page Model (Page, 1949)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} \exp(-k_0 t^n)$</td>
<td>Hydration of milled rice (Kashaninejad et al., 2007), dehydration of paddy (Abe &amp; Afzal, 1997; Akal et al., 2007; Basunia &amp; Abe, 2001; Das et al., 2004; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Henderson and Pabis Model (Henderson &amp; Pabis, 1969)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = A_0 \exp(-k_0 t)$</td>
<td>Hydration of milled rice (Kashaninejad et al., 2007), dehydration of paddy (Abe &amp; Afzal, 1997; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Modified Page (Overhults et al., 1973)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = \exp(-k_0 t^n)$</td>
<td>Hydration of milled rice (Kashaninejad et al., 2007), dehydration of paddy (Abe &amp; Afzal, 1997; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Two term exponential model (Sharaf-Elddeen et al., 1980)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = A_0 \exp(-k_0 t) + A_1 \exp(-k_1 t)$</td>
<td>Hydration of milled rice (Kashaninejad et al., 2007), dehydration of paddy (Kashaninejad et al., 2007), dehydration of paddy (Akal et al., 2007; Chen &amp; Tsao, 1994; Hacıhafızıoğlu et al., 2008; Noomhorm &amp; Verma, 1986; Sharma et al., 1982; Verma et al., 1985)</td>
</tr>
<tr>
<td>Diffusion (Becker, 1960; Crank, 1975)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = \frac{6}{\pi^2} \sum^n_{n=1} \frac{1}{n^2} \exp \left[ -\frac{n^2 \pi^2}{r^2} D_{eff} t \right]$</td>
<td>Hydration of rice (Bandyopadhyay &amp; Roy, 1978), dehydration of paddy (Akal et al., 2007; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Peleg’s model (Peleg, 1988)</td>
<td>$M_1 = M_0 \pm \frac{t}{K_1 + K_2 t}$</td>
<td>Hydration of paddy (Singh et al., 2010), milled rice (Kashaninejad et al., 2007; Singh et al., 2010), parboiled rice (Botelho et al., 2010; Singh et al., 2010), freeze dried gelatinized rice (Puspitowati &amp; Driscoll, 2007)</td>
</tr>
<tr>
<td>Geometric model (Chandra &amp; Singh, 1995)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = A_0 t^n$</td>
<td>Dehydration of paddy (Akal et al., 2007; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Wang and Singh model (Wang &amp; Singh, 1978)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = 1 + at + bt^2$</td>
<td>Dehydration of paddy (Akal et al., 2007; Hacıhafızıoğlu et al., 2008)</td>
</tr>
<tr>
<td>Model</td>
<td>Equation</td>
<td>Deposition of paddy (Agrawal &amp; Singh, 1977; Akal et al., 2007; Hacıhafızoğlu et al., 2008)</td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Logarithmic model (Chandra &amp; Singh, 1995)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = A_0 + A_1 \exp(-kt)$</td>
<td>Dehydration of paddy (Agrawal &amp; Singh, 1977; Akal et al., 2007; Hacıhafızoğlu et al., 2008)</td>
</tr>
<tr>
<td>Verma et al. model (Verma et al., 1985)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = A_0 \exp(-k_0t) + (1 - A_0) \exp(-gt)$</td>
<td>Dehydration of paddy (Akal et al., 2007; Hacıhafızoğlu et al., 2008)</td>
</tr>
<tr>
<td>Midilli et al. model (Midilli et al., 2002)</td>
<td>$MR = \frac{M - M_e}{M_0 - M_e} = A_0 \exp(-k_0t^n) + bt$</td>
<td>Dehydration of paddy (Akal et al., 2007; Cihan et al., 2007; Hacıhafızoğlu et al., 2008)</td>
</tr>
</tbody>
</table>

Note: The symbols

MR = Moisture Ratio (dimensionless)

$M_e$, $M_0$ and $M =$ Equilibrium (Saturation), initial and current moisture contents (kg/kg, dry basis) respectively

t = Time (s)

T = Temperature (K)

r = Equivalent radius (radius of the sphere having the same volume as the grain) (m). Rice (sphericity ≤0.5) is assumed as a sphere (Bandyopadhyay & Roy, 1978; Bello et al., 2004, 2007; Shittu et al., 2012; Suzuki et al., 1977)

$D_{eff}$ = Effective diffusivity (m$^2$/s)

$A_0$; $A_1$; $A_2$; $k_0$; $k_1$; $k_2$, $b$, $g$ are empirical coefficients
Table 3: Effective diffusivity of paddy, brown rice and milled rice during hydration and dehydration.

<table>
<thead>
<tr>
<th>Process</th>
<th>Variety</th>
<th>Temperature (°C)</th>
<th>( D_{\text{eff}} ) (m(^2)/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydration</td>
<td>Long grain</td>
<td>25</td>
<td>1.78 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long grain</td>
<td>35</td>
<td>1.78 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long grain</td>
<td>45</td>
<td>2.08 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.24 \times 10^{-11}</td>
<td>(Thakur &amp; Gupta, 2006)</td>
</tr>
<tr>
<td></td>
<td>Long grain</td>
<td>55</td>
<td>2.59 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long grain</td>
<td>60</td>
<td>4.10 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long grain</td>
<td></td>
<td>7.92 \times 10^{-11}</td>
<td>(Thakur &amp; Gupta, 2006)</td>
</tr>
<tr>
<td></td>
<td>Long Grain</td>
<td>65</td>
<td>7.20 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long Grain</td>
<td>75</td>
<td>7.17 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long Grain</td>
<td>80</td>
<td>7.34 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Long Grain</td>
<td>90</td>
<td>9.36 \times 10^{-11}</td>
<td>(Bello et al., 2004)</td>
</tr>
<tr>
<td>Dehydration</td>
<td>Short Grain</td>
<td>43</td>
<td>1.4 \times 10^{-11}</td>
<td>(Steffe &amp; Singh, 1980)</td>
</tr>
<tr>
<td></td>
<td>Long Grain</td>
<td>43</td>
<td>3.2 \times 10^{-11}</td>
<td>(Steffe &amp; Singh, 1982)</td>
</tr>
<tr>
<td></td>
<td>Parboiled Banki</td>
<td>60</td>
<td>2.8 \times 10^{-10}</td>
<td>(Onuoha et al., 2013)</td>
</tr>
<tr>
<td></td>
<td>Parboiled De Gold</td>
<td>60</td>
<td>5.7 \times 10^{-10}</td>
<td>(Onuoha et al., 2013)</td>
</tr>
<tr>
<td></td>
<td>Parboiled Liberia</td>
<td>60</td>
<td>3.8 \times 10^{-10}</td>
<td>(Onuoha et al., 2013)</td>
</tr>
</tbody>
</table>
Figure 1: Hydration characteristics of brown and milled rice (Billiris et al., 2012).
Figure 2: A characteristic viscogram curve (Bhattacharya, 2011).