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Review

Novel food and non-food uses for sorghum and millets ☆

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Abstract

Sorghum and millets have considerable potential in foods and beverages. As they are gluten-free they are suitable for coeliacs. Sorghum is also a potentially important source of nutraceuticals such antioxidant phenolics and cholesterol-lowering waxes. Cakes, cookies, pasta, a parboiled rice-like product and snack foods have been successfully produced from sorghum and, in some cases, millets. Wheat-free sorghum or millet bread remains the main challenge. Additives such as native and pre-gelatinised starches, hydrocolloids, fat, egg and rye pentosans improve bread quality. However, specific volumes are lower than those for wheat bread or gluten-free breads based on pure starches, and in many cases, breads tend to stale faster. Lager and stout beers with sorghum are brewed commercially. Sorghum's high-starch gelatinisation temperature and low *beta*-amylase activity remain problems with regard to complete substitution of barley malt with sorghum malt . The role of the sorghum endosperm matrix protein and cell wall components in limiting extract is a research focus. Brewing with millets is still at an experimental stage. Sorghum could be important for bioethanol and other bio-industrial products. Bioethanol research has focused on improving the economics of the process through cultivar selection, method development for low-quality grain and pre-processing to recover valuable by-products. Potential by-products such as the kafirin prolamin proteins and the pericarp wax have potential as bioplastic films and coatings for foods, primarily due to their hydrophobicity.

Keywords: Sorghum; Millet; Food; Bread; Malting; Brewing; Bioethanol; Gluten-free; Kafirin; Wax

Contents

Abbreviations: DDG, distillers dried grains; DDGS, distillers dried grains with solubles; GAX, glucuronoarabinoxylans; GMS, glycerol monostearate, HDL, high-density lipoprotein, LDL, low-density lipoprotein; SCFX, supercritical-fluid-extrusion; WVP, water vapour permeability

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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1. Introduction

Sorghum and millets are the most drought-tolerant cereal grain crops and require little input during growth, but, as with other crops, yield better with good husbandry (ICRISAT/FAO, 1996). With increasing world population and decreasing water supplies, they represent important crops for future human use. While sorghum and millets are vital food crops for millions of people in parts of Africa and Asia, they are an underutilised resource in most developed countries, with sorghum being primarily used as animal feed and millet little cultivated (ICRISAT/FAO, 1996). Sorghum and millet have considerable further potential to be used as a human food and beverage source. In developing countries the commercial processing of these locally grown grains into value-added food and beverage products is an important driver for economic development (Taylor, 2004). The use of sorghum and millets not only provides farmers with a market for their products but also saves foreign exchange, which would otherwise be required to import cereals. Particularly in the developed countries, there is today a growing demand for gluten-free foods and beverages from people with coeliac disease and other intolerances to wheat who cannot eat products from wheat, barley, or rye.

Sorghum, in particular, could also play an important role in the production of ethanol and other bio-industrial products such as bioplastics, especially in dry areas where other crops are not as easily grown (McLaren et al., 2003).

Several previous reviews have addressed the subject of traditional foods from sorghum and millets in depth, for example McDonough et al. (2000), Murty and Kumar (1995) and Rooney and Serna-Saldivar (2000). This review sets out the state of the art in sorghum and millet science and technology with respect to their novel use in major food and beverage products, including baked goods and lager and stout beer, and the utilisation of sorghum for bio-industrial products such as ethanol, starch, and plastics. Emphasis is placed on how the particular structural and chemical compositional characteristics of the sorghum and millet grains influence their potential applications and the processing technologies required. The review concludes with some comments on further research needs.

2. Sorghum and millets in nutrition and health

Coeliac disease is a syndrome characterised by damage to the mucosa of the small intestine caused by ingestion of certain wheat proteins and related proteins in rye and barley (Fasano and Catassi, 2001). The gliadins (Kagnoff et al., 1982) and glutenins (Van de Wal et al., 1999) of wheat gluten have been shown to contain protein sequences that are not tolerated by coeliacs.

Modern screening studies show that coeliac disease is much more prevalent than previously thought. The average worldwide prevalence has been estimated as high as 1: 266 (Fasano and Catassi, 2001). Estimates place the number of persons with coeliac disease in the USA at roughly 3 million. The cornerstone treatment for coeliac disease is the total lifelong avoidance of gluten ingestion. This means that wheat, rye, and barley have to be avoided, including durum wheat, spelt wheat, kamut, einkorn, and triticale (Kasarda, 2001; Kasarda and D'Ovidio, 1999). Sorghum is often recommended as a safe food for coeliac patients, because it is only distantly related to the Triticeae tribe cereals wheat, rye and barley (Kasarda, 2001), being a member of the Panicoideae sub-family which also includes maize and most millets (Shewry, 2002). Sorghum therefore, provides a good basis for gluten-free breads and other baked products like cakes and cookies (biscuits) and in snacks and pasta. Although the millets have been less investigated for such food uses, they also have potential.

Sorghum and millet grains can contain substantial levels of a wide range of phenolic compounds. Their health-promoting properties, in particular their antioxidant activity, and their use as nutraceuticals and in functional foods are reviewed in the paper by Dykes and Rooney (2006). In addition to the potential health benefits of sorghum and millet phenolics, sorghum wax may also have unique health properties. Sorghum wax, which is concentrated on the surface of the pericarp of the grain, is composed of fatty aldehydes (46%), fatty acids (7.5%), fatty alcohols (41%), hydrocarbons (0.7%), wax and sterol esters (1.4%), and triacylglycerols (1%) (Hwang et al., 2002a). The fatty alcohols in sorghum wax can be classified as policosanols, which are primary long-chained alcohols.

Since sorghum wax contains only a small amount of wax esters, it was suggested that the term "long-chained lipids" might be more appropriate than "wax" (Hwang et al., 2004b). The latter study reported long-chained lipids from different sorghums in the range 37–44% for policosanols, 44(48)–55% for aldehydes and 4–5% for acids, and that long-chained lipids constituted 0.2–0.3% of sorghum kernels. Therefore, the policosanol content of sorghum kernels was approximately 800 ppm. Sorghum-dried distillers grains (DDG), in which non-starch components are concentrated, contained approximately 2500 ppm policosanols (Hwang et al., 2004b). These amounts are high relative to other sources, e.g. brown rice, rice bran, rice germ and wheat germ (Hwang et al., 2004a, b). Octacosanol (28:0) and triacontanol (30:0) comprised more than 80% of the policosanols in sorghum kernels and DDG (Hwang et al., 2004b). It has been suggested that mixed C24–C34 alcohols, including octacosanol and triacontanol, lower the amount of low-density lipoprotein (LDL) cholesterol and raise the amount of high-density lipoprotein (HDL) cholesterol, thus improving the LDL/HDL ratio (Hargrove et al., 2004). These authors also indicated that long-chain fatty alcohols, aldehydes and acids are interconverted in cellular metabolism, so that all three classes might lower cholesterol. Varady et al. (2003) concluded that policosanols are a promising resource for the prevention and therapy of cardiovascular disease. Carr et al. (2005) found that a crude lipid extract from whole kernel sorghum, which comprised a wide range of lipid substances including plant sterols and policosanols, lowered cholesterol absorption and plasma non-HDL cholesterol in hamsters.

3. Novel and non-traditional sorghum foods

The development of white, tan-plant, so-called food-grade, sorghum lines has enabled white, bland-tasting flour to be produced from sorghum grain. This flour is useful in food products because it does not impart unusual colours or strong flavours and it may be desired over maize flour for these reasons (Waniska and Rooney, 2002). Nevertheless, varieties with red or black pericarp and tannin-containing (sometimes referred to as "brown") varieties might have their niches as well. Dark colours from black or tannin-containing sorghum varieties might be advantageous in products for the health market (Rooney and Awika, 2005) or in countries where dark, rye-based bread is common (e.g. Germany or Eastern Europe). In such communities, usually "dark" is associated with "healthy". Brownish colours might also be acceptable in chocolate cakes, cookies and muffins, or molasses cookies. For example, a sorghum line with red pericarp produced an interesting, pinkish-brown bread that might be promoted as specialty bread (Schober et al., 2005). Brannan et al. (2001) found that consumers did accept the colour and appearance of a lighter-coloured sorghum muffin, resembling a plain or maize muffin as well as a dark brown one, resembling a chocolate, pumpernickel or dark bran muffin. The resulting colour of sorghum products, however, cannot be predicted based on the colour of the whole grain. It depends on pericarp and endosperm colours, pigmented or non-pigmented testa, degree of milling and pH of the food (Brannan et al., 2001; Rooney, 1996).

3.1. Gluten-free leavened breads

Traditional flatbreads from sorghum and millets as described by Murty and Kumar (1995) might be regarded as leavened if they are fermented like injera (Ethiopia) or puffed like chapatti/roti (India). Another well-established use of sorghum in leavened baked goods is in wheat–sorghum composite breads (Munck, 1995). While numerous studies have dealt with the above-mentioned products, only a limited number have addressed the issue of wheat-free loaf breads from sorghum, resembling wheat pan breads. Unlike composite breads, wheat-free sorghum breads are suitable for coeliacs (Schober et al., 2005) and might possibly replace wheat breads in developing countries, reducing expensive wheat imports (Satin, 1988). Much of the older research on sorghum bread has been reviewed by Taylor and Dewar (2001). Nevertheless, that which is pertinent will be re-discussed in the present review as a basis for the understanding of newer studies.

3.1.1. Starch breads and additives

Wheat-free breads based on pure starches, yeast, sugar, salt and water plus additives such as soy flour, gums, shortenings, and emulsifiers have been described in the literature for many decades (Ács et al., 1996a, b; Jongh, 1961; Ranhotra et al., 1975). Jongh (1961) used wheat starch, 60% water on a starch basis, salt (NaCl), sugar (sucrose) and yeast for bread production. When $\geqslant$0.05% glyceryl (glycerol) monostearate (GMS) was added, bread quality improved markedly. The author assumed that GMS helped to form junction points between the starch granules. The granules thus aggregated and, in concentrated suspensions, as in a starch bread dough, formed a coherent network through the whole system. In the same study, starch bread was also produced successfully with 5% GMS and 85% water. Ranhotra et al. (1975) developed a bread based on wheat starch with added soy protein isolate (0–40% on a starch basis). Xanthan gum and shortening were added. Soy protein isolate improved loaf volume, crumb grain and texture. Required water levels increased in parallel with the amount of soy, and were generally high (120–139% on a starch + soy basis), and these authors. emphasised that strict adherence to the water requirements of each batter was necessary. Ács et al. (1996a) found that xanthan gum improved quality of bread based on corn (maize) starch. This improving effect was stronger than for guar gum, locust bean gum and tragant (tragacanth). Another important finding was that incorporation of margarine into the corn starch bread with added xanthan

gum had negative effects, including coarse crumb and brittleness.

Starch breads have the obvious disadvantage of lacking dietary fibre, protein and micronutrients (reviewed by Gallagher et al., 2004). Due to the easy digestibility of isolated starches, they can also be expected to cause a distinctly higher glycaemic response than breads using wholemeal cereals or even white wheat breads (Berti et al., 2004; Englyst et al., 1996; Jenkins et al., 1987). Starch breads may, however, reach high specific volumes, e.g. in the work of Ranhotra et al. (1975) 8.03 $in^3/oz \approx 4.6\,cm^3/g$). In contrast, most studies on gluten-free breads using wholemeal cereal flours or partly decorticated sorghum flours, found much lower specific volumes, 1.8–2.5 cm^3/g for rice breads with added rice bran (Kadan et al., 2001), corn starch, brown rice flour, soya flour and buckwheat flour containing mixture (Moore et al., 2004) and sorghum breads (Olatunji et al., 1992a, b; Schober et al., 2005). Reasons for this will be discussed in Section 3.1.2.

3.1.2. Flour breads and additives

Several researchers have specifically addressed production of gluten-free pan bread from sorghum flour. Hart et al. (1970) studied non-wheat breads from sorghum and barley flours. For sorghum, they developed a basic recipe in initial studies and then tested addition of different gums, starches, enzymes, emulsifiers and shortening as well as sourdough fermentation. They found that soft batters (50–60% water based on dough weight, i.e. ≈100–150% on flour weight) rather than firmer "doughs" were required to obtain sufficient rise. Firmer "doughs" lacked elasticity and were brittle. In the batter systems, methylcelluloses improved bread quality by increasing gas retention and prevented loaves from collapsing, and 2% methylcellulose (4000 cP viscosity) produced the best results. Starches improved oven rise and crumb structure when combined with methylcellulose. Different starches (sorghum, modified and waxy sorghum, corn, cassava, arrowroot, potato) produced similar results. *alpha*-amylase, protease and emulsifiers/shortenings weakened crumb structure, but shortenings combined with methylcelluloses softened the loaves. Apart from adding a new flavour, sourdough did not improve bread quality.

Rye pentosans are another additive suggested for wheat-free breads, including breads from sorghum, millet and cassava, alone and in mixtures (Casier et al., 1977). Positive effects of pentosan addition were described in all cases. Besides acceptable volumes, these authors reported that staling was prevented for at least one week in the sorghum bread. Similar results were obtained with pure millet flour. The species of millet was not specified but was probably pearl millet. These findings are in agreement with the common knowledge that in rye breads, the pentosans are structure forming, while the formation of gluten is suppressed (Cauvain, 1998). It has also been described that pentosans decreased staling rate in wheat breads and retarded retrogradation of starch gels (Kim and D'Appolonia, 1977a, b). While sorghum bread containing rye pentosan might be an alternative for wheat bread in developing countries, it seems unlikely that such bread might be appropriate for coeliacs because rye secalins are toxic for them (Murray, 1999). An isolation process that warrants the complete absence of secalins in the pentosans at all times would be required.

Satin (1988) examined sorghum and other crops as an inexpensive alternative to wheat for developing countries. He recommended xanthan gum as an additive, and suggested that this gum could be produced locally in developing countries. Although xanthan gum addition generally produced acceptable breads, he found that applying the right technique for its addition was important. Soaking the xanthan gum in water before adding it to the dough resulted in improved bread quality relative to dry addition. For bread from cassava flour, Satin (1988) also found that pre-gelatinised starch could help to hold gas, while egg white could help in the setting of the bread during baking. Other researchers have also used pre-gelatinised starch and egg in sorghum products. Sorghum breads containing pre-gelatinised cassava starch have been developed by Olatunji et al. (1992b) and Hugo et al. (1997). Egg was used by Keregero and Mtebe (1994) in wheat-sorghum composite bread and deep fat fried buns. These experiments also included tests with 100% sorghum. The pure sorghum breads were reported to be quite unattractive, but the corresponding buns were rated more favourably.

Cauvain (1998) suggested several formulations for sorghum bread. However, they were relatively complicated. They contained either skim milk powder, sodium carboxymethyl cellulose, baking powder and soya flour or 50% corn starch, skim milk powder, sodium carboxymethyl cellulose and dried egg albumen in addition to sorghum flour, yeast, salt, and water (80–100% based on flour + starch). In contrast Olatunji et al. (1992a) used a simple recipe comprising sorghum or millet pearl flour (70%), cassava starch (30%), yeast, salt, sugar, water (80–100%, flour + starch basis) and only small amounts of fat and fungal amylase as additional ingredients. Soft batters were produced and acceptable specific volumes (2.2–2.3 cm^3/g) and an estimated keeping quality of about three days were achieved. The authors reported that pearl millet bread would have been slightly better than sorghum bread, except for the greyish colour of the millet varieties used. In another study, Olatunji et al. (1992b) examined the use of pre-gelatinised cassava starch and also incorporated an emulsifier (monoglycerol palmitate) in the formulation. A total of 100–110% water (flour + starch basis) were used. Best results were achieved with 70/20/10 flour from decorticated sorghum/pre-gelatinised cassava starch/raw cassava starch. This bread was found to be superior to other formulations in extensive sensory testing and reached a specific volume of 2.4 cm^3/g. The authors hypothesised that raw and gelatinised starch complement each other, with the pre-gelatinised cassava starch trapping air bubbles in the batter due to its gummy and sticky properties, while

the raw starch increases the elastic strength of the system during baking, when it becomes gelatinised. They referred to the work of Jongh (1961) with regard to the effect of emulsifier and assumed that it reduces the repulsive forces between the starch granules in the batter and thus causes them to adhere to one another.

Similar to Olatunji et al. (1992a, b), Hugo et al. (1997) developed a simple recipe based on sorghum flour and cassava starch. Pre-gelatinising the cassava starch was an important element. Best results were obtained with the same flour/starch mixture used by Olatunji et al. (1992b). Specific volumes as high as 3.3 cm^3/g were reported. The addition of shortening and emulsifier (succinylated monoglycerides) were also investigated. These had improving effects, although the combination of both produced an off-flavour. Shortening on its own reduced the bread firming over 2-days storage, and the authors suggested that retarded retrogradation due to fat-amylose complexes might have been responsible. Generally, however, the bread had reduced acceptability by the second day.

3.1.3. *Effect of cultivars*

Hugo et al. (1997) investigated three sorghum cultivars with different endosperm types (normal, heterowaxy, and waxy). The normal sorghum produced best results, whereas the waxy type (essentially 100% amylopectin in the starch) resulted in unacceptable bread, with a large hole and a pudding like crumb. The authors concluded that amylose plays a critical role and that possibly retrogradation upon cooling is important for the stabilisation of the crumb structure. Schober et al. (2005) investigated the effect of cultivar, using nine selected sorghum hybrids and a commercial sorghum flour. Similar to wheat dough, where the farinograph may be used to adapt the amount of water to reach a standardised dough consistency, they used an extrusion cell to standardise batter consistency to a constant value. Proofing to height, rather than for a constant time, was another important feature in this study. This was because it was difficult to achieve reproducible proofing of gluten-free bread using a constant time, even when standardising flour and water temperature, environmental conditions, and previously activating the yeast. A simple formulation was used, similar to the one used by Olatunji et al. (1992a), based on sorghum four and maize starch (70/30) plus only water (95–120%, flour + starch basis), salt, sugar and yeast. While bread volume and height were not affected by the hybrid used, considerable differences were found with regard to crumb grain and texture (Fig. 1). The amount of mechanically damaged starch in the flours was identified as a key factor explaining these differences, with higher starch damage resulting in a coarser crumb structure. Higher starch damage resulted from higher kernel hardness. Most likely, damaged starch was more easily degraded by endogenous amylases, resulting in a higher amount of fermentable sugars and at the same time in a weaker starch gel. In the second part of the study, these authors chose the two hybrids with the most different crumb grain and additionally added xanthan gum, skim milk powder and varied the water level, using response surface methodology. They found that the differences in crumb grain were maintained at various combinations of xanthan gum, skim milk powder, and water. However, besides improved crust appearance, the former two ingredients had only negative effects on bread quality and were not recommended for this type of wheat-free bread, Whilst xanthan gum reduced loaf volume, skim

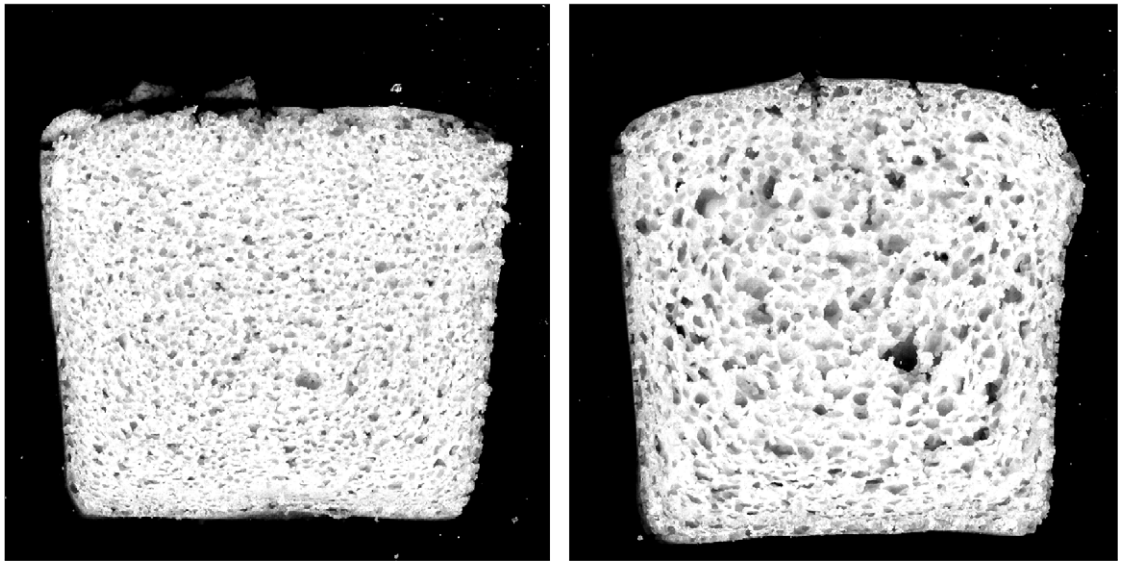

Fig. 1. Sorghum/maize starch breads (70/30) produced from two different sorghum hybrids (Schober et al., 2005). Hybrid line 3 (left) mean cell area (1.3 mm^2), starch damage (13.5% db) and SKCS kernel hardness 87.3. Hybrid line 7 (right) mean cell area (3.3 mm^2), starch damage (16.0% db) and SKCS kernel hardness 95.1. All values are significantly different ($P<0.05$).

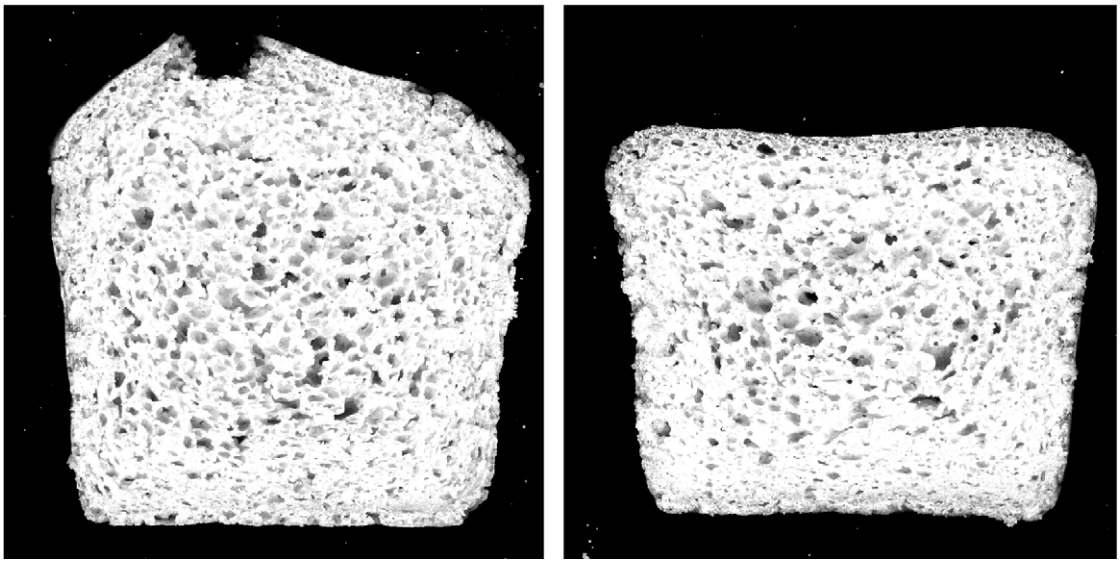

Fig. 2. Sorghum/maize starch breads (70/30) produced from sorghum hybrid line 3 with 0% (left) and 6% (right) skim milk powder on a flour-starch basis (Schober et al., unpublished data). Levels of water (107.5%) and xanthan gum (0.75%) were identical for both breads.

milk powder specifically lowered bread height by causing the centre of the loaves to collapse (Fig. 2). Low viscosity of the batter system, as resulting from increased water levels and reduced levels of xanthan gum, was found to improve bread volume.

3.1.4. Theoretical basis for sorghum functionality in gluten-free breadmaking

Summarising the successful formulations for gluten-free bread, the following observations seem relevant. Water addition levels are generally much higher than those common in wheat dough. High water addition produced liquid, batter-like systems. Lower water addition produced firm "doughs" from sorghum that lacked elasticity, were brittle and rose insufficiently. This indicates that high dilution of all suspended particles (bran, coarse endosperm particles from the hard endosperm) is desirable in the batter. While for successful production of pure starch breads, some type of additive (emulsifier, hydrocolloid, soy protein isolate) was incorporated in all studies, whereas studies on sorghum bread were made with and without such extra ingredients. Although not essential for acceptable sorghum bread, hydrocolloids, especially methylcelluloses, and also xanthan gum and rye pentosan, improve quality. These findings with sorghum batters are in agreement with that described by Gan et al. (1995) for wheat doughs, despite that fact that in gluten-free batters an aggregated protein network is absent. Gas cells in fermenting batters are surrounded by liquid films, which are stabilised by surface active substances, including polar lipids, soluble proteins and soluble pentosans (Gan et al., 1990, 1995; Izydorczyk et al., 1991). Thus, starch bread additives including emulsifiers, hydrocolloids or soy protein isolates may stabilise the liquid films around gas cells. Sorghum bread without additives may also be produced, since such substances, soluble proteins (albumins and globulins), polar lipids and soluble pentosans, are present in sorghum (Chung and Ohm, 2000; Hamaker and Bugusu, 2003; Karim and Rooney, 1972; Schober et al., 2005), although polar lipids are present in rather low concentrations.

Concerning the role of starch, the addition of pure starches, in native or pre-gelatinised form, to sorghum flour also has positive effects on its breadmaking quality. This may be simply a dilution effect, i.e. endosperm and bran particles in the sorghum flour are diluted by the added starch. Any bran or endosperm particles would be expected to disturb the uniformity of the starch gel and interfere with the liquid films around the gas cells (Gan et al., 1995; Moore et al., 2004). It is likely that gluten-free breads containing wholemeal cereals have lower volumes than starch breads for the same reasons. Additionally, several factors appear to limit gelatinisation of starch in sorghum flour, including high-starch gelatinisation temperature (Lineback, 1984), embedding of the starch in hydrophobic matrix proteins (Munck, 1995), and formation of extended, web- or sheet-like structures by sorghum proteins upon heating, with starch embedded (Hamaker and Bugusu, 2003). Thus, added pure starch would be expected to gelatinise more readily and completely. Pre-gelatinised starch might additionally trap air bubbles in sorghum breads due to its hydrocolloid properties (Olatunji et al., 1992b). As heterowaxy and especially waxy sorghum cultivars produced inferior sorghum bread, it appears that amylose retrogradation plays a critical role for crumb stabilisation (Hugo et al., 1997). Mechanical starch damage is also critical, with an excess resulting in coarse crumb due to increased amylolytic degradation

(Schober et al., 2005), emphasising the importance of a strong starch gel.

3.2. Cakes and cookies

The section focuses on studies where no wheat was used and will deal with the functionality of the ingredients. It will also address gluten-free breads containing egg, because of their similarity to cakes.

Important functions of egg ingredients are surface-activity and emulsifying properties of egg white and yolk, and heat coagulation of egg white that helps in the setting of the bread or cake structure (Cauvain, 1998; Forsythe, 1970; Satin, 1988). Moore et al. (2004) using confocal laser-scanning microscopy described a continuous film-like protein structure similar to gluten in egg-containing, gluten-free bread made from rice flour, corn starch and potato starch. This bread also staled more slowly than egg-free gluten-free breads. As a result of these effects, egg ingredients might have assisted the formation and stabilisation of liquid films at the interface as well as with the stabilisation of the semi-liquid matrix before and after baking in the egg-containing sorghum breads described by Cauvain (1998) and Keregero and Mtebe (1994), and the cassava bread of Satin (1988). Egg protein, however, is known to have an allergenic potential, especially for children (http://www.aaaai.org/patients/resources/easy_-reader/food.pdf). Thus, its use in a staple food like bread might be problematical.

However, in many types of cake, eggs are normal ingredients expected by the consumer. A cake recipe for a sorghum or millet/cassava starch mixture (70/30) has been developed by Olatunji et al. (1992a). Although the formula was comparatively lean for a cake mix (e.g. only 5% for each sugar, fat and egg), the authors described the problems encountered as insignificant in comparison to those with wheat-free bread. Thus, even these small amounts of extra ingredients seem to be beneficial for structure formation and stabilisation. Similarly, Oyidi (1976) reported that in contrast to bread, cake, and cookies could be successfully made from flour originating from a mutant sorghum with twin-seeded spikelets. This is not surprising, since gluten formation is neither required nor desired in cakes and cookies. Nevertheless, Oyidi (1976) found that cake and biscuits made from wheat flour were larger, and the sorghum flour did not hold moisture, dried and crumbled easily and had an off-flavour. The question to be addressed is therefore not, whether cakes and cookies can be formulated from sorghum, but why sorghum yields products of inferior quality.

Glover et al. (1986) studied systematically why sorghum addition to wheat in the production of high ratio cakes reduced volume, and caused brittle crumb structure and inferior crust appearance. Using fractionation-reconstitution techniques, they identified lipids and starch of sorghum as responsible components. Unlike wheat lipids, sorghum lipids had no functionality, resulting in lower volumes and inferior crumb structure in comparison to cakes baked with wheat lipids. They suggested that the lack of glyco- and phospholipids in sorghum might have been responsible. Additionally, replacing wheat starch with sorghum starch resulted in distinctly lower volumes and inferior texture. After baking, a high percentage of non-gelatinised starch granules was found in the centre of the cake. The high gelatinisation temperature of sorghum starch was assumed to be responsible for the these effects. This hypothesis was confirmed by replacing sucrose with glucose, which resulted in more complete starch gelatinisation, and improved cake volume and crumb properties. Both, the high gelatinisation temperature and the lack in glyco- and, less so, phospholipids are in agreement with physico-chemical analyses of sorghum (Chung and Ohm, 2000; Lineback, 1984).

Badi and Hoseney (1976) studied the production of cookies from 100% sorghum or pearl millet. Such cookies could be produced, but were described by the authors as "tough, hard, gritty, and mealy in texture and taste". They also lacked spread and top surface cracks, both traits being regarded as desirable by the authors in this kind of product. They identify lipid composition as partly responsible for this inferior quality. Adding wheat-flour lipids to defatted sorghum flour improved top surface texture and spread of the cookies, although they were still clearly inferior in quality to cookies made from soft wheat. The sorghum and millet cookies could also be improved by unrefined soybean lecithin or refined lecithin plus monoglycerides. Further improvement could be achieved by hydrating the sorghum or millet flour for several hours with malt syrup or water and then air drying it, and by increasing the pH of the cookie dough, using sodium carbonate instead of bicarbonate. While the authors aimed at removing damaged starch by the malt syrup treatment, it might also be that simply soaking and drying, and the higher pH due to the use of carbonate helped to break up the matrix proteins of endosperm particles. With the described treatments, the resulting sorghum or millet cookies were rated as satisfactory. In sensory tests with cookies from mixtures of sorghum and soft wheat, only grittiness of 100% sorghum cookies was significantly worse than grittiness of soft wheat control cookies, whereas appearance, taste, texture, and off-flavour showed no significant differences. The findings of Badi and Hoseney (1976) support that the hypothesis that the lack of polar lipids in sorghum is partly responsible for inferior quality of sorghum cakes and cookies relative to wheat products, in agreement with Glover et al. (1986). Grittiness in sorghum cookie doughs can most likely be attributed to hard, sharp-edged endosperm particles or bran. After baking, it might also be a consequence of the high gelatinisation temperature of sorghum starch, leaving starch granules ungelatinised. This is in agreement with the considerations made with regard to sorghum bread.

In contrast to Badi and Hoseney (1976), Morad et al. (1984) found that sugar cookies from 100% sorghum

generally had the highest spread factor (width to thickness) relative to cookies from a commercial wheat cookie flour and cookie flour–sorghum mixtures. They explained this apparent contradiction in terms of differences in extraction rate and particle size of the sorghum flours and different formulations.

3.3. Tortillas, snack foods, parboiled sorghum, and noodles

A traditional use for sorghum is in tortillas. Although tortillas are generally made from maize, sorghum has been used in several Central American countries, and due to its better drought tolerance, its importance has increased in recent decades (Murty and Kumar, 1995; Rooney and Waniska, 2000). Sorghum can partially or totally substitute for yellow maize in tortilla production when properly processed, i.e. decorticated to remove outer bran layers and cooked and steeped shorter than maize) (Choto et al., 1985). The nutritional value of the tortillas is not seriously affected by such substitution (Serna-Saldivar et al., 1988b), although soya addition increases the amount of lysine, and thus the protein quality, in composite maize-decorticated sorghum (75/25) tortillas (Serna-Saldivar et al., 1988a). Further details on sorghum tortillas are given by Murty and Kumar (1995), Rooney and Serna-Saldivar (2000), and Rooney and Waniska (2000).

Concerning snack foods, tortilla chips can be produced from white food-grade sorghum without problem, just by reducing lime concentration and cooking time of sorghum relative to maize. Sorghum tortilla chips have a bland taste, which might be advantageous in snack products in which a strong maize flavour is not desired (Serna-Saldivar et al., 1988c). In this context it is noteworthy that recently, extruded sorghum snacks from US white sorghum hybrids have been very successful in Japan. This has been attributed to the bland flavour, light colour and good expansion properties of these sorghums (http://intsormil.org/icwbusssn.htm; http://www.statpub.com/open/9560.html; http://www.tard.state.tx.us/index.php?mode=-Listing&rl_id=489).

Jowar crunch, a snack food with a light crunchy texture, prepared by deep- fat frying of dried kernels (pellets) of alkaline-cooked whole sorghum was developed by Suhendro et al. (1998). The product was based on an Indonesian food from maize made by the same basic procedure. The optimised process for sorghum involved autoclaving for 60 min at 120 °C, rinsing, drying to 9% moisture (room temperature and then 50 °C) and deep-fat frying at 220 °C. The authors explained that during frying, the moisture in the pellets acted as plasticiser, allowing polymers to move and the kernels to expand. Water inside the pellets was superheated, the increased pressure finally caused the pellets to rupture and the product became expanded, similar to popcorn. Comparison of different sorghum cultivars showed that overall, cultivars with intermediate to soft endosperm were more expanded than cultivars with hard endosperm. Additionally, it is noteworthy that a waxy cultivar produced a fried product with an "undesirable, sticky, pasty mouthfeel", recalling the unacceptable quality for waxy sorghum bread found by Hugo et al. (1997).

Young et al. (1990) studied parboiling of sorghum for the production of a rice-like product from decorticated sorghum. Parboiling increased the yield of decorticated grain, reduced kernel breakage, and caused increased firmness and reduced stickiness of the final cooked kernels. Increased yield of decorticated grain was attributed to hardening of the parboiled kernels during drying, with the improvement in decortication yield being most pronounced for cultivars with soft endosperm. Parboiling by a process involving boiling, then soaking for 12 h and re-boiling before draining and drying was superior to just soaking for 12 h at room temperature and then boiling, draining and drying. In the latter process, the increase in decortication yield and reduction in kernel breakage was less pronounced. Microscopic examinations showed also that the soaking and boiling process did not permit sufficient hydration to allow complete cooking of the kernels, and that most kernels had ungelatinised centres. This is in agreement with the high resistance of hard sorghum endosperm to water penetration, due to hydrophobic matrix proteins, described by Munck (1995).

Sorghum noodles made from only decorticated sorghum flour, water and salt have been studied by Suhendro et al. (2000). The procedure comprised mixing, preheating, extrusion, and drying. Since the product was extruded using a pasta die, it might be regarded as pasta based on its shape. However, following the definition of Hoseney (1994) since the product was made from flour rather than semolina and contained salt it could be considered as noodles despite the fact it did not contain egg. Heterowaxy sorghum produced noodles of inferior quality relative to normal sorghum. Such noodles were sticky, soft and had a high dry matter loss during cooking. Increased amylopectin and reduced amylose content in the heterowaxy sorghum-limited retrogradation. Similar to the finding of Hugo et al. (1997) for sorghum bread, amylose retrogradation upon cooling after gelatinisation seems to be important for the stabilisation of the noodle structure. Suhendro et al. (2000) further reported that the timing of amylose dispersion (solubilisation), formation of noodles, and amylose retrogradation was critical. Flour particle size was also critical with finer flour producing better quality noodles. Good quality sorghum noodles could be produced when processing conditions were optimised and when the noodles were properly cooked.

4. Malting and brewing

Malting and brewing with sorghum to produce lager and stout, often referred to as clear beer as opposed to traditional African opaque beer, has been conducted on a large, commercial scale since the late 1980s, notably in Nigeria (Olori et al., 1996). Nigeria brews in excess of 900 million litres of beer annually (Institute of Brewing and

Distilling, 2005), most of this is brewed with at least some sorghum. Brewing with sorghum is now also taking place in east Africa (Mackintosh and Higgins, 2004), southern Africa (J.R.N. Taylor, personal observation) and the USA (www.bardsbeer.com). There has been extensive research and development work and several excellent reviews published covering enzymes in sorghum malting, sorghum malting, and brewing technology (Agu and Palmer, 1998; Hallgren, 1995; Owuama, 1997, 1999; Taylor and Dewar, 2000, 2001). This review will focus on major outstanding problem areas in sorghum brewing that are specific to characteristics of sorghum grain and sorghum malt. These include the use of tannin sorghum in malting and brewing, starch gelatinisation, the role of the endosperm cell walls and *beta*-amylase activity in malt. In contrast, millet malting and brewing to produce clear beer is still at the experimental stage and research has been far less extensive. Here important recent research will be reviewed.

4.1. Sorghum

4.1.1. Utilisation of tannin sorghums

A significant proportion of sorghum varieties, both types II and III, contain condensed tannins, which are located in the testa (seed coat) layers of the grain (Awika and Rooney, 2004). Tannins confer valuable agronomic properties on sorghum, including protection against insects, birds and weather damage (Waniska et al., 1989). However, tannins inactivate extracted malt amylases (Beta et al., 2000a–c; Daiber, 1975a), significantly reducing starch breakdown and sugar production during brewing (Daiber, 1975a). In southern Africa, sorghum maltsters generally treat tannin sorghum by steeping it in very dilute formaldehyde to inactivate the tannins (Daiber, 1975b). The formaldehyde apparently polymerises phenolic compounds such as tannins into a phenol–formaldehyde resin (Morrison and Boyd, 1983). As there are concerns about the toxicity of formaldehyde in food applications, other more food-compatible methods of inactivating tannins have been investigated. Probably the most practical with respect to sorghum malting was found to be steeping the grain in dilute (up to 0.3% (w/v)) NaOH (Beta et al., 2000a–c). These authors found that when grain of two different tannin sorghum cultivars was steeped in dilute NaOH, 78–88% of the total malt amylase activity was preserved compared to the levels of amylase activity obtained with steeping in 0.05% (v/v) formaldehyde. In contrast, steeping in water preserved only 14–41% of amylase activity compared to formaldehyde steeping. The authors suggested that the NaOH brought about oxidative polymerisation of the tannins. In Nigeria, sorghum maltsters now routinely steep the sorghum in dilute NaOH (J.R.N. Taylor, personal observation) as it is effective in reducing fungal contamination on the malt in addition to inactivating tannins. It may also enhance malt quality in terms of amylase activity (see Section 4.1.4).

4.1.2. Starch gelatinisation

Probably the two most important differences between sorghum and barley are the higher gelatinisation temperature of sorghum starch and the much lower level of level of *beta*-amylase (EC 3.2.1.2) activity in sorghum malt. The consequences of these differences are that the simultaneous gelatinisation and hydrolysis of starch that occurs when mashing barley malt, are problematical with sorghum malt. Hence, starch breakdown and fermentable sugar production are generally limited, but they are strongly affected by the mashing procedure employed (Igyor et al., 2001; Taylor, 1992). Current industrial clear beer brewing with sorghum almost exclusively involves using the sorghum only as a starchy adjunct (Little, 1994; Mackintosh and Higgins, 2004; J.R.N. Taylor, personal observation). Sorghum grain or sorghum malt is first cooked to gelatinise the starch and then the starch is hydrolysed using barley malt, commercial enzymes or a combination of the two.

Sorghum starch gelatinisation temperature ranges of 67–73 °C have been reported for sorghums grown in southern Africa (Beta and Corke, 2001) and 71–81 °C for sorghums grown in India (Akingbala et al., 1982). These are far higher than the range quoted for barley starch of 51–60 °C (Lineback, 1984). For the reasons indicated above, it would be of value to produce sorghums with lower starch gelatinisation temperature. Starch gelatinisation temperature is influenced by many factors, in particular the lengths of the various chains in the amylopectin molecule, with gelatinisation temperature increasing with longer chain length (Matsuki et al., 2003). In a study of 30 sorghum varieties, Dufour et al. (1992) found a few with low gelatinisation temperatures, approaching that of barley. More recently, Beta et al. (2000a–c) found that Barnard Red, a traditional South African sorghum variety which was selected for its good malting and opaque beer characteristics, had a low onset starch gelatinisation temperature of 59.4 °C and gave high paste viscosity. This was despite the fact that the starch had a normal amylose-amylopectin ratio. To date the clear beer brewing properties of these low-starch gelatinisation temperature varieties have apparently not been investigated.

With regard to the effect of amylose–amylopectin ratio, there has been considerable research into brewing with waxy sorghum. It is suggested that waxy sorghums gelatinise more rapidly, have a relatively weak endosperm protein matrix and are more susceptible to hydrolysis by amylases and proteases than normal endosperm sorghums and hence should be better for brewing (Del Pozo-Insfran et al., 2004). Figueroa et al. (1995) investigated mashing 20 sorghum adjuncts of varying endosperm structure with barley malt. They found that the waxy and heterowaxy types gave much shorter conversion times (time to starch disappearance as indicated by iodine yellow colour) than normal types. They attributed this to the lower starch gelatinisation temperatures, 69.6 °C for waxy type, 71.1 °C for the heterowaxy type and 71.1–73.3 °C for the normal

types. Interestingly, the worts from the waxy and heterowaxy sorghums did not contain glucose or fructose, unlike the worts of the normal types. Another comparison of different sorghums as adjunct showed that grits from white waxy sorghum produced wort with a very high filtration rate (Osorio-Morales et al., 2000). The fermentation behaviour of worts from waxy sorghum adjunct was found to be normal (Barredo-Moguel et al., 2001a) and the resulting beer was normal in terms of concentration of ethanol and fusel oils (Barredo-Moguel et al., 2001b).

Starch granule characteristics are not the only factor limiting starch gelatinisation and solubilisation when brewing with sorghum. Chandrashekar and Kirleis (1988) showed that the degree of starch gelatinisation was lower in hard endosperm sorghum than in soft endosperm types and that the addition of the reducing agent 2-mercaptoethanol markedly increased the degree of gelatinisation. These findings suggested that the endosperm protein matrix that envelops the starch granules limits starch gelatinisation. This in turn seems to adversely affect starch digestibility. Zhang and Hamaker (1998) found that the *alpha*-amylase digestibility of cooked sorghum flours was 15–25% lower than that of maize flours, whereas the digestibility of starches from the flours was the same. Of direct importance to brewing, these authors further showed that cooking the flours with the reducing agent sodium metabisulphite could significantly improve sorghum flour starch digestibility but had no effect on the digestibility of maize flour. The fact that reducing agents improved sorghum starch digestibility suggests that disulphide bond cross-linking within the kafirin-containing endosperm protein matrix is responsible for the reduced gelatinisation in sorghum. This is the same mechanism that has been implicated in the reduced protein digestibility of cooked sorghum (Duodu et al., 2003). This interpretation is supported by the work of Ezeogu et al. (2005) who found evidence of polymerisation through disulphide bonding of prolamins on cooking of sorghum and maize flours, with the formation of high molecular weight polymers ($M_r > 100$k). Of particular relevance to brewing, these authors found that pressure cooking the flours improved starch digestibility of vitreous (hard) and floury (soft) endosperm maize and sorghum flours and markedly so for sorghum vitreous endosperm flour. They suggested that pressure cooking could have physically disrupted the protein matrix. Interestingly, Ortega Villicaña and Serna-Saldivar (2004) found that when brewing with waxy sorghum adjunct, highest beer ethanol content and lowest residual sugar content were obtained if the adjunct was first heated at 80 °C then pressure cooked. It may be of relevance to the above findings that the matrix protein in sorghum is intimately bound to the endosperm cell walls (Glennie, 1984). The mechanism of this attachment is not known, but it is possible that the phenolic acid, ferulic acid plays a role (Glennie, 1984; Parker et al., 1999).

4.1.3. Cell walls of the starchy endosperm

The cell walls of the starchy endosperm of sorghum are also fundamentally different in composition from those of barley and wheat but not of maize. In sorghum (Verbruggen et al., 1993, 1995) and maize (Huisman et al., 2000) the predominant component seems to be water unextractable (insoluble) glucuronoarabinoxylans (GAX), in contrast to barley where the $(1\rightarrow3,1\rightarrow4)$-$\beta$-glucans predominate (Henry, 1987). The GAX of sorghum (Verbruggen, 1996) and maize (Huisman et al., 2000) are also much more complex and highly substituted than the arabinoxylans of barley (Fig. 3) (Verbruggen, 1996) and wheat (Gruppen et al., 1992), which do not appear to be substituted with glucuronic acid (Gruppen et al., 1992; Viëtor et al., 1992). One point of similarity between sorghum and barley and wheat endosperm cells is that the sorghum GAX appear to be esterified to the ferulic acid, a hydroxycinnamic acid (Glennie, 1984; Parker et al., 1999), as are the barley and wheat arabinoxylans (Mandalari, 2005). As mentioned in Section 4.1.2, ferulic acid may be the means of attachment of matrix protein to the cell walls. The sorghum GAX have a degree of polymerisation of approximately 1500–9300 (Verbruggen, 1996). The molar arabinose: xylose ratio in sorghum and maize GAX is 1.12 and 0.80, respectively and the substitution with glucuronic acid is 8.3 and 9.8% (w/w), respectively (Huisman et al., 2000). Strangely, in view of the higher level of arabinose in sorghum GAX, it is apparently somewhat less substituted (70%) than the maize GAX (87%), as calculated as the ratio of the number of branches attached to xylose residues to the total number of residues in the backbone (Huisman et al., 2000). This apparent anomaly was explained by terminally linked

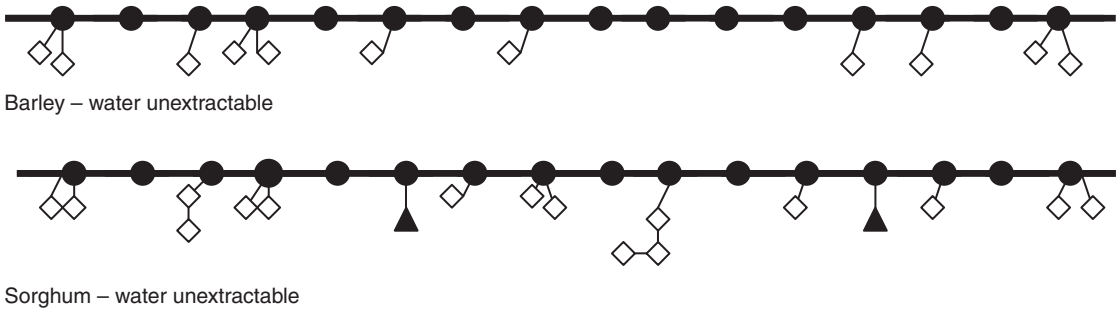

Fig. 3. Structure of sorghum and barley water-unextractable arabinoxylans. Redrawn from Verbruggen (1996) with the permission of the copyright holder Wageningen Agricultural University. Circle, xylose; diamond, arabinose; triangle, glucuronic acid.

xylose residues being present in side chains and the existence of oligomeric arabinose side chains.

Verbruggen (1996) found that the sorghum GAX were hydrolysed only to a limited extent by endoxylanase. This appears to be because of the high degree of arabinose substitution and the presence of considerable amounts of glucuronic acid. GAX, especially that extractable with 4 M KOH, is substituted with arabinose and glucuronic acid according to a strict pattern which hinders enzyme action (Verbruggen et al., 1998). The use of accessory enzymes to remove the arabinose side chains improved degradation of the GAX (Verbruggen, 1996). When brewing with sorghum malt supplemented with cell wall degrading enzymes, Verbruggen (1996) obtained inconclusive results as to the effect of GAX on wort filtration and concluded that the GAX in the malt was partially solubilised during mashing but only partly degraded. Comparative studies on mashing with sorghum malt and barley malt concluded that sorghum, unlike barley, does not contain β-xylosidase activity but has arabinosidase (α-arabinofuranosidase) activity and that the water-soluble pentosans in sorghum wort are arabinans (EtokAkpan, 2004).

Sorghum endosperm cell walls contain some (1→3,1→4)-β-glucans (Earp et al., 1983; Huisman et al., 2000; Woolard and Rathbone, 1976). Research by EtokAkpan (1992a, 1993) indicated that sorghum (1→3,1→4)-β-glucans were only poorly degraded during malting and it was suggested that sorghum had very low β-glucan endohydrolase activity. Apparently as a consequence of poor (1→3,1→4)-β-glucans degradation during malting, EtokAkpan (1992b) found that worts prepared from sorghum malts contained five to seven times more (1→3,1→4)-β-glucans than barley malt wort. However, in apparent contradiction Ogbonna and Egunwu (1994) and Ogu et al., (2004) found extensive (1→3,1→4)-β-glucan degradation during malting. Possibly of significance with regard to extract is the finding that sorghum (1→3,1→4)-β-glucans have a much lower ratio of (1→4)- to (1→3)-linkages than barley (1→3,1→4)-β-glucan, approximately 2:3 compared with 7:3 (Ramesh and Tharanathan, 1998). On the basis of chemical and enzymic studies it has been proposed that there are two distinct types of sorghum (1→3,1→4)-β-glucan chains, one shorter and more highly branched, with β-(1→6) branch points, and the other longer and fewer (1→6)- branches (Onwurah, 2001). It was suggested that these two types of chains are interspersed in a crystalline region which reduces their susceptibility to enzymic degradation during malting.

Probably related to the composition of the sorghum endosperm cell walls, is the important issue that they are not substantially degraded during germination (malting) (Glennie, 1984; Palmer, 1991), unlike in barley. It has been suggested that fuco-xyloglucan may contribute to the resistance of the cell walls to enzymic attack during germination (EtokAkpan, 1993). Ingress of hydrolytic enzymes into the cells and egress of endosperm hydrolysis products seems to be via openings in the cell walls, which appear to develop as a result of partial degradation of the cell walls during germination (Glennie, 1984; Palmer, 1991).

4.1.4. Beta-amylase

Ungerminated sorghum, unlike ungerminated barley, does not exhibit *beta*-amylase activity (Taylor and Robbins, 1993). It appears that tropical (C4) cereal grains such as pearl millet, sorghum and maize possess only the "ubiquitous" form of *beta*-amylase, i.e. the enzyme isoform which is synthesised during germination (Ziegler, 1999). The temperate Triticeae tribe cereals such as barley, wheat and rye also posses an "endosperm-specific" form which is present in these grains at seed maturity and requires the use of papain or reducing agent such as cysteine for complete extraction. Hence, sorghum malt always has lower *beta*-amylase activity than barley malt. In a survey of malts of 30 sorghum and 47 barley varieties Dufour et al. (1992) found that 60% of the sorghum malts had very low *beta*-amylase activity, less than 25% of the activity of any of the barley malts when *beta*-amylase activity was calculated as the difference between total amylase (diastatic) activity and *alpha*-amylase activity. Using the specific Megazyme Betamyl *beta*-amylase assay, which employs *p*-nitrophenyl malto-oligosaccharides as substrate (McCleary and Codd, 1989), Taylor and Robbins (1993) found a similar relative percentage, 80 U/g for sorghum malt compared to over 400 U/g for barley malt, even when using a sorghum variety giving malt of high total diastatic activity. Beta et al. (1995) also used the Betamyl assay and found even lower level levels of *beta*-amylase activity, 11–41 U/g in malts of 16 sorghum varieties.

The effect of malting conditions has been extensively investigated in an attempt to increase sorghum malt *beta*-amylase and amylase activity in general. Ezeogu and Okolo (1994, 1995) found that steeping regime, and in particular the use of air-rests and a final warm water (40 °C) steeping period enhanced sorghum malt quality, including *beta*-amylase activity. Later work specifically confirmed the importance of air-rests on the level of sorghum malt *beta*-amylase activity (Okungbowa et al., 2002). It is probable that use of air-rests simply provides more oxygen and hence more rapidly increases seedling metabolic activity. Dewar et al. (1997a, b) found that sorghum malt diastatic power (combined *alpha*- and *beta*-amylase activity) increased with time of steeping and was directly related to steep-out moisture. Steeping the sorghum grain in dilute alkali (up to 0.3% $Ca(OH)_2$, KOH or NaOH) has been shown to significantly enhance sorghum malt diastatic activity (Dewar, et al., 1997a, b; Ezeogu and Okolo, 1996, 1999). This was attributed to increased water uptake by the grain. Specifically regarding malt *beta*-amylase activity, Okolo and Ezeogu (1996) found that steeping in 0.1% NaOH enhanced activity and Okungbowa et al. (2002) found that steeping in 0.1% $Ca(OH)_2$ generally enhanced activity, while surprisingly steeping in the same

concentration of KOH had the opposite effect . No explanation was offered for this apparent contradiction. Germination conditions also affect sorghum malt *beta*-amylase activity. Taylor and Robbins (1993) showed that high germination moisture and relatively low germination temperature (24 °C) gave the highest malt *beta*-amylase activity. The requirement for a relatively low germination temperature may be related to the fact that the *beta*-amylase is more thermolabile than *alpha*-amylase (Taylor, 1992).

Mashing conditions for brewing with sorghum malt have also been widely investigated in attempts to conserve *beta*-amylase and amylase activity in general and hence maximise starch hydrolysis and fermentable sugar production. Taylor and Daiber (1988) showed that a calcium ion concentration of 200 ppm gave greatest reducing sugar production and wort yield, and increased extract. Malt *alpha*-amylase activity in mashing was directly related to calcium ion concentration and hence it was concluded that the effects were due to preventing thermal inactivation of the *alpha*-amylase. Probably of importance in this respect, is the recent finding the *alpha*-amylase of sorghum malt is considerably more thermostable than that of barley malt, with a midpoint of thermal inactivation of 70 °C, as against 57 °C (Kumar et al., 2005).

The effects of various mashing temperature–time regimes have also been investigated. Under experimental conditions high levels of extract with a reasonable proportion of fermentable sugar have been obtained by decantation (Igyor et al., 2001; Palmer, 1989) and decoction (Taylor, 1992) mashing of sorghum malt. Decantation involves making an enzymic extract of the malt, cooking the starchy solids to fully gelatinise the starch, cooling to mashing temperature (e.g. 65 °C) and then adding the enzymic extract back to hydrolyse starch. Decoction involves removing portions of the mash (e.g. one-third) at intervals during the mashing period, cooking the removed portion to gelatinise the starch and then adding the cooked starch back to the mash. However, probably due to their relative complexity, neither of these two processes appears to have been widely adopted in practice (J.R.N Taylor, personal observation). Instead, much research has concentrated on supplementation of the sorghum malt amylase activity with industrial amylase enzymes. For example with regard to the lack of *beta*-amylase activity, Del Pozo-Insfran et al. (2004) found that the addition of amyloglucosidase during sorghum malt mashing with sorghum malt and maize or waxy sorghum adjuncts significantly boosted the levels of wort fermentable sugars through the production of glucose.

4.2. Millets

The millets, like sorghum, have high-starch gelatinisation temperatures, pearl millet (*Pennisetum glaucum* (L.) R. Br.) 61–68 °C and finger millet (ragi) (*Eleucine coracana* (L.) Gaertn.) 65–69 °C (Serna-Saldivar and Rooney, 1995). Hence, they are subject to the same constraints in terms of conservation of enzymic activity during brewing. Like sorghum, arabinoxylans seem to be the major cell wall component of pearl millet (Hadimani et al., 2001) and finger millet (Subba Rao and Muraliskrisna, 2004). As with sorghum, the arabinoxylans of pearl millet are also substituted with uronic acids (Hadimani et al., 2001). However, uronic acid was not reported in analysis of finger millet non-starch polysaccharides (Subba Rao and Muraliskrisna, 2001). There is some evidence of cell wall degradation in finger millet during malting (Subba Rao and Muraliskrisna, 2001; Subba Rao et al., 2004).

The optimum malting conditions for pearl millet seem to be essentially the same as for sorghum. Muoria and Bechtel (1998) suggested a germination temperature >22 °C and Pelembe et al. (2002) found 25–30 °C to be optimal with a germination period of 3–5 days, although they suggested that higher temperatures 30–35 °C could be used if the germination was short (1–3 days). Pelembe et al. (2002) also reported similar levels of diastatic power, free amino nitrogen (FAN), *alpha*-amylase, *beta*-amylase (by difference between diastatic power and *alpha*-amylase activity) and malting loss in pearl millet malt as for sorghum malt. However, when pearl millet malt *beta*-amylase activity was measured by the specific Betamyl assay it was found to be substantially higher than in sorghum malt (Pelembe et al., 2004). In apparent contrast, Muoria and Bechtel (1998) found pearl millet malts to have higher diastatic power and *alpha*-amylase activity than sorghum malts. Unfortunately, these authors did not determine malt *beta*-amylase activity.

Brewing processes for millet have not been extensively investigated. Using a rising temperature mashing regime, from 45–70 °C, Nzelibe and Nwasike (1995) obtained substantially higher extracts with pearl millet and fonio (*Digitaria exilis* (Kippist) Stapf) malts than with sorghum malt, whereas Pelembe et al. (2004) mashing at 60 °C constant temperature obtained similar levels of extract for pearl millet malt as sorghum malt. Interestingly, with pearl millet malt, Eneje et al. (2001) found that decantation mashing gave higher extract than decoction or constant temperature, infusion mashing, possibly as a result of more complete starch gelatinisation. Soluble nitrogen and FAN levels were lower with decantation and decoction mashing, probably due to protein denaturation because of the higher temperatures used. However, a general observation was that wort soluble nitrogen and FAN were high. This is in agreement with the very high FAN level reported for pearl millet malting in comparison to sorghum malt (Pelembe et al., 2004) and is probably a consequence of the precocious seedling growth that takes place.

5. Bio-industrial uses

5.1. Bioethanol

Sorghum has potential for being used in the production of bio-industrial products, including bioethanol. Sorghum

is a starch-rich grain with similar composition to maize, and, as with all cereals, its composition varies significantly due to genetics and environment (Rooney and Serna-Saldivar, 2000). Starch ranges of 60–77% and 64–78% have been reported for sorghum and maize, respectively (Shelton and Lee, 2000). As such, sorghum grain would be appropriate for use in fermentation similar to the use of maize for the production of bioethanol. Its use may be of particular benefit in countries where rainfall is limiting and maize does not grow well. With regard to the USA, currently, approximately 95% of the bioethanol is produced from maize starch, primarily in the maize growing regions. Sorghum production in the USA in 2004 was 11.6 million metric tons (http://faostat.fao.org) equivalent to approximately 457 million bushels, and 10–20% of those were used for ethanol production (http://www.sorghumgrowers.com). In the same year in the USA, 3.4 billion gallons (12.9 billion litres) of ethanol were produced from 1.22 billion bushels of grain (http://www.ksgrains.com/ethanol/useth.html). From this, it may be calculated that 1.2–2.3 million metric tons sorghum was used for ethanol production, 3.7–7.5% of the grain for ethanol production was sorghum, and 0.13–0.25 billion gallon (0.49–0.95 billion litres) of ethanol originated from sorghum. While significant research into the production of ethanol from maize grain has been conducted, comparatively little research has been done on the conversion of sorghum grain into bioethanol. This review will focus only on the use of sorghum grain, not biomass, for ethanol production. Research on the use of sweet-stemmed sorghum for the production of bioethanol has been reported elsewhere (House et al., 2000; Schaffert, 1995).

Suresh et al. (1999a) developed a simultaneous saccchar-ification and fermentation system for producing ethanol from damaged sorghum and rice grains. These authors later utilised a similar method to compare ethanol production from damaged and high quality sorghum (Suresh et al., 1999b). It was noteworthy that the latter method involved no cooking step. Raw flour starch was saccharified by *Bacillus subtilis* and fermented by *Saccharomyces cerevisiae*. Their damaged grain sample comprised 50% damaged and 50% sound grains, and the damaged portion included kernels that were broken, cracked, attacked by insects, dirty or discoloured. The high-quality sorghum flour was obtained locally. They found that using a level of 25% (w/v) substrate yielded 3.5% (v/v) ethanol from the damaged grain sample. For comparison, the high-quality sorghum flour yielded 5.0% (v/v) ethanol. The damaged grain sample was reported to be ten times cheaper than high-quality grain and thus may be an economical way to produce ethanol even though yields were lower. The authors further emphasised that utilisation of raw starch would save energy.

Zhan et al. (2003) investigated the impact of genotype and growth environment on the fermentation quality of sorghum. Eight sorghum hybrids grown in two different locations were used to produce ethanol. The process included heating with thermostable *alpha*-amylase at 95 °C and then 80 °C (liquefaction), incubation with amyloglucosidase at 60 °C (saccharification), inoculation with *S. cerevisiae* and fermentation for 72 h at 30 °C. It was found that ethanol concentrations varied relatively narrowly (about 5%) across the 16 samples, and that significant genotype × environment interactions existed. The correlation between ethanol concentration and starch content was positive, as expected, but low ($r = 0.35$, $P > 0.05$), while a much more distinct negative correlation between ethanol concentration and protein content was found ($r = -0.84$, $P < 0.001$). Typically, protein and starch content are negatively correlated, so it is not surprising that opposite correlations for these two measures to ethanol production would be found. However, it is interesting that protein had a much stronger relationship to ethanol yield than did starch. More research is needed to determine exactly what components in the grain, and their interactions, are responsible for ethanol yields in sorghum. It is possible that during the initial heating steps, a disulphide-mediated protein polymerisation process occurred, resulting in web-like or sheet-like protein structures, as described by Hamaker and Bugusu (2003). Under these conditions, some of the starch might be trapped in these protein webs, and its full gelatinisation and degradation by amylases might be hampered. Evidence for this is provided by the work of Zhan et al. (2006) who investigated cooking sorghum using supercritical-fluid-extrusion (SCFX) to gelatinise the starch. In SCFX supercritical carbon dioxide is used in place of water as the blowing agent. Using SCFX increased ethanol yields by around 5% compared to non-extrusion cooked sorghum.

In addition to breeding sorghum specifically for fermentation quality, pre-processing the grain can be used to improve ethanol yields and process efficiency. Corredor et al. (2006) investigated decorticating sorghum prior to starch hydrolysis and ethanol fermentation. In general, decortication decreased the protein content of the samples up to 12% and increased starch content by 5–16%. Fibre content was decreased by 49–89%. These changes allowed for a higher starch loading for ethanol fermentation and resulted in increased ethanol production. Ethanol yields increased 3–11% for 10% decorticated sorghum and 8–18% for 20% decorticated sorghum. Using decorticated grain also increased the protein content of the distillers dried grains with solubles (DDGS) by 11–39% and lowered their fibre content accordingly. Using decorticated sorghum may be beneficial for ethanol plants as ethanol yield increases and animal feed quality of the DDGS is improved. The bran removed before fermentation could be used as a source of phytochemicals (Awika et al., 2005) or as a source of kafirin and wax (see Section 5.3).

There is one report on the potential of pearl millet for ethanol production (Wu et al., 2006). On a starch basis, ethanol yield was similar to that of sorghum and maize with an efficiency of 94.2%. On account of pearl millet being rich in protein and lipid, the protein and energy contents of the pearl millet DDGS were higher than those

from sorghum and maize, indicating that pearl millet DDGS could be a good animal feedstuff.

5.2. Starch wet milling

Ethanol can also be produced from sorghum by first wet milling the grain to isolate the starch, the so-called wet-grind process. Isolated sorghum starch could also be used in other industrial applications in a similar fashion to corn starch. In fact, sorghum starch was commercially produced in the US from 1948 until the 1970s (Munck, 1995).

In general the wet milling of sorghum is similar to that of maize. A thorough review of early research on wet milling of sorghum can be found in Munck (1995). However, a problem particular to sorghum is that where polyphenolic pigments are present in the pericarp and/or glumes, they stain the starch (Beta et al., 2000a–c). In recent years several new developments in sorghum wet milling have been reported. Perez-Sora and Lares-Amaiz (2004) investigated alkaline reagents for bleaching the starch and found a mixture of sodium hypochlorite and potassium hydroxide to be the most effective. To help improve the economics of sorghum wet-milling Yang and Seib (1995) developed an abbreviated wet-milling process for sorghum that required only 1.2 parts fresh water per part of grain and that produced no waste water. The products of this abbreviated process were isolated starch and a high moisture fraction that was diverted to animal feed. Buffo et al. (1997b) investigated the impact of sulphur dioxide and lactic acid steeping on the wet-milling properties of sorghum and reported that the amount of lactic acid used during steeping had the most impacted wet-milling quality characteristics such as starch yield and recovery. These authors also investigated the relationships between sorghum grain quality characteristics and wet-milling performance in 24 commercial sorghum hybrids (Buffo et al., 1998). Perhaps not surprisingly, they found that grain factors related to the endosperm protein matrix and its breakdown and subsequent release of starch granules important factors in wet-milling of sorghum. Related to this, Mezo-Villanueva and Serna-Saldivar (2004) found that treatment of steeped sorghum and maize with proteinase increased starch yield, with the effect being greater with sorghum than maize.

Wang et al. (2000) optimised the steeping process for wet-milling sorghum and reported the optimum steeping process to utilise 0.2% sulphur dioxide, 0.5% lactic acid at a temperature of 50 °C for 36 h. Using this steeping process, wet-milling of sorghum produced starch with an L lightness value of 92.7, starch yield of 60.2% (db), and protein in starch of only 0.49% (db). Beta et al. (2000a–c) found that both polyphenol content and sorghum grain properties influence sorghum starch properties. Using sorghum grits as the starting material for wet-milling rather than whole sorghum produced lower yields, but the isolated starch was higher in quality. Sorghum starch matching the quality of a commercial corn starch was successfully produced by wet-milling sorghum grits (Higiro et al., 2003). Xie and Seib (2002) developed a limited wet-milling procedure for sorghum that involved grinding sorghum with in the presence of 0.3% sodium bisulphite. This procedure was produced starch with an L value of 93.7 and a starch recovery of 78%. Large grain sorghum hybrids wet-milled by this "no steep" procedure were reported to produce high-quality starches with L values from 93.1 to 93.7 (compared to 95.2 for a commercial corn starch). Some of the large grain hybrids tested showed promise for easy recovery of the germ by flotation in a similar fashion as is done for maize (Xie et al., 2006). Park et al. (2006) reported the use of ultrasound to rapidly purify starch from sorghum. This procedure resulted in very high-purity starch with only 0.06% residual protein in the starch. New developments in wet-milling procedures for sorghum as well as breeding sorghum hybrids with improved wet-milling characteristics should be of benefit to the industrial use of sorghum starch, either directly for the production of bioethanol or other industrial uses such as the production of activated carbon (Diao et al., 2002) or isolation of phytosterols from wet-milled fractions (Singh et al., 2003).

5.3. Biopolymer films and coatings

Sorghum grain polymers are being investigated for their potential to make biodegradable, edible, bioplastic films and coatings. Rojas et al. (2002) produced films from sorghum flour and starch incorporating nisin. These "active" films inhibited the growth of the Gram-positive bacterium *Lactobacillus debrueckii*.

Kafirin, the sorghum prolamin storage protein, is a good choice for making bioplastics as it is the most hydrophobic of the prolamins (Belton et al., 2006; Duodu et al., 2003) and its digestibility is reduced with wet heating (Duodu et al., 2003). Belton et al. (2006) review the structure of kafirin films and its influence on functionality. Here, practical aspects of kafirin coatings and films will be reviewed; their functional properties and potential applications. Buffo et al. (1997a) found that cast plastic films could be made from kafirin extracted from sorghum gluten, a by-product of wet milling. When plasticised with glycerol and polyethylene glycol (PEG) 400, kafirin films had similar tensile and water vapour barrier properties to films made from commercial maize zein plasticised in the same way. Da Silva and Taylor (2005) showed that kafirin films could also be made from kafirin extracted from different sorghum dry milling fractions including bran, a by-product of dry milling (or potentially in bioethanol production). Films prepared from kafirin extracted from bran were darker than those extracted from flour and films from kafirin from red pericarp sorghum were darker than those from white pericarp sorghum. The colour of the films was attributed to phenolics, which are concentrated in the bran and co-extracted with the kafirin. With a combination of glycerol, PEG 400 and lactic acid as plasticiser, the kafirin

films were found to have higher tensile strength, lower strain and higher water vapour permeability than films prepared from commercial zein plasticised in the same way. An important difference in methodology between this work and that of Buffo et al. (1997a) is that the kafirin was extracted in the presence of the reducing agent sodium metabisulphite which would result in the extraction of more kafirin, as well as different subclasses of kafirin, that was insoluble in the non-reducing solvent due to being disulphide bonded into large polymers in the grain. This could account for the different findings regarding kafirin film functional properties between these studies. Emmambux et al. (2004) showed that the properties of kafirin films could be modified by cross-linking with hydrolysable or condensed tannins, the latter being extracted from tannin sorghum. Tensile stress was increased by 50–100% and strain decreased three to four-fold with increasingly level of tannin modification, up to 20% tannin relative to kafirin. Modification with tannins also reduced oxygen permeability by more than 50% but did not affect water vapour permeability (WVP). The modification of film properties using natural components from plants seems to be appropriate for the "green" image of bioplastics. Kafirin film properties can also be modified by first applying heat to the protein. Byaruhanga et al. (2005) showed that heating kafirin to 90–96 °C using microwave energy greatly increased the tensile strength and substantially reduced tensile strain and WVP of cast kafirin films. Sodium dodecyl sulphate–polyacrylamide electrophoresis showed intermolecular cross-linking of the kafirin monomers as a result of heating, which was suggested as being responsible for these effects. In related research it was found that subjecting kafirin to elevated temperature during drying increased the proportion of intermolecular β-sheet structure (Gao et al., 2005). This effect was also suggested as being associated with observed changes in tensile and WVP properties of cast kafirin films made from the kafirin. It was concluded that to produce kafirin films of optimal quality, industrial-scale extraction of kafirin must minimise protein aggregation and maximise native α-helical structures.

Traditionally, cast prolamin films are prepared by first dissolving the protein in aqueous ethanol at elevated temperature, pouring the solution onto a flat surface and allowing the solvent to evaporate. Taylor et al. (2005) found that kafirin and zein films of consistent quality could be produced using glacial acetic acid at ambient temperature as the solvent, thus avoiding potential problems with the use of ethanol such as the requirement for a license and religious objections, as well as reducing the flammability hazard.

Kafirin coating of fruits seems to be highly beneficial in some applications but not others. Buchner (www.sik.se/enviropak) showed that coating pears (variety Packham's Triumph) with kafirin, delayed ripening, reduced stem-end shrivelling and increased their shelf-life (Fig. 4). Following export by sea from South Africa to the United Kingdom kafirin-coated pears were still fit for consumption after 13 days storage at 20 °C, whereas the uncoated pears had decayed. These effects were apparently due to the kafirin coating reducing the pears' respiration rate at the climacteric peak. Gobhurdhun (www.sik.se/enviropak) working with litchis also found that kafirin coating reduced respiration rate. However, the coating caused an unacceptable darkening of the litchi peel surface and the formation of a white powdery deposit on the peel.

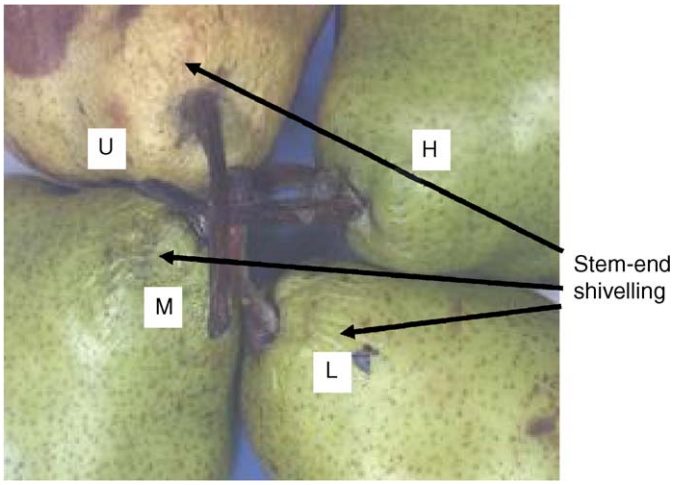

Fig. 4. Effect of kafirin coating of Packham's Triumph pears stored for 3 weeks at 20 °C (www.sik.se/enviropak). Reproduced with the permission of the author S. Buchner. U, uncoated; L, low thickness coating; M , medium thickness coating; H, high thickness coating.

Weller and co-workers (1998a,b) have investigated the utility of sorghum pericarp wax for coatings and in films. Sorghum wax has generally similar properties as carnauba palm wax, which is widely used in food applications. The melting points are also similar, sorghum 77–85 °C and carnauba 78–86 °C, although they differ in acid values and saponification numbers, sorghum 10–16 and 16–49 and carnauba 2–10 and 77–95 (Hwang et al., 2002b). Wang et al. (2005) showed that wax and other lipids could be extracted from sorghum DDG, the by-product of bioethanol production, using *n*-hexane.

Mixtures of sorghum wax or carnauba wax together with medium chain length triglyceride oil were compared as edible coatings for gelatine-based candies (Weller et al., 1998b). Both wax-based coatings were equally effective at reducing solubility of the candies in water and they also slowed down melting. However, the candies coated with sorghum wax had lower sensory scores for appearance, off flavour and aftertaste. Notwithstanding this, it was concluded that sorghum wax may be used an edible protective coating for confections. Mixtures of sorghum wax or carnauba wax with oil were also investigated as coatings for cast zein films to make bilayer films (Weller et al., 1998a). Sorghum and carnauba waxes were equally effective in greatly improving the water vapour barrier properties of the films, without any appreciable adverse effect on film tensile properties. Sorghum wax has also

been investigated as a component in cast soya protein isolate films (Ki Myong et al., 2002, 2003). The wax was incorporated into the film by adding it to the film-forming solution. Water vapour permeability, elongation at break and film solubility were reduced. When added in combination with the plasticisers glycerol and sorbitol, all three affected the WVP, tensile strength, elongation at break and solubility of the films as established using response surface methodology. The sorghum wax decreased the WVP and elongation at break of the film, while sorbitol increased permeability and film solubility.

6. Concluding remarks

Sorghum and the millets have huge potential for wider use. With sorghum this potential is starting to be realised, although some serious technical problems remain. The millets remain virtually unresearched and their potential untapped.

With regard to sorghum breadmaking, future work might focus on attempts to create a viscoelastic protein network. Another central issue is the need to prolong the keeping quality of sorghum bread and gluten-free breads in general. Although some of the studies mentioned above did address the problem of quick staling, it appears that this issue needs further research. Longer keeping quality is critical for a broad acceptance of gluten-free sorghum bread by consumers, if it is to be produced industrially and not on a daily basis by home baking. Concerning sorghum brewing, sorghum malt brewing without exogenous enzymes seems to require genetic modification of the grain to reduce starch gelatinisation temperature and increase malt *beta*-amylase activity.

Bio-industrial uses for sorghum are technically feasible. However, cost reductions in bio-ethanol production, including the use of co-products as bioplastics and nutraceuticals, and pro-active government policies to promote a more ''green economy'' are probably prerequisites for commercialisation to take place.

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