

Lipid stabilisation and partial pre-cooking of pearl millet by thermal treatments

By

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Declaration

I declare that the dissertation herewith submitted for the MSc (Agric) Food Science and Technology degree at the University of Pretoria has not previously been submitted by me for a degree at any other university or institution of higher education.

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Abstract

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Pearl millet is a cereal crop cultivated by subsistence farmers in semi-arid parts of Africa and Asia. In Namibia, pearl millet porridge is a staple food for over half of the population. Healthful Harvest, a cooperative of subsistence farmers in a rural area in Namibia is developing a flour product with extended shelf life and a short cooking time comprising pearl millet and cowpea. This requires the application of simple technology.

The pearl millet grain is small (3-15 mg) but has a proportionally larger germ than all other cereal grains, except perhaps maize. Therefore, it tends to contain a high content of triglycerides, which are rich in unsaturated fatty acids. Pearl millet flour is susceptible to rancidity within a few days due to lipolysis and subsequent oxidation of the de-esterified unsaturated fatty acids.

To try to prevent rancidity and to pre-cook, pearl millet grain was subjected to toasting, boiling and toasting then boiling before reduction to flour. The effects of these different thermal treatments on fat acidity, peroxide value (PV) and conjugated diene and triene values of pearl millet flour before and after three months storage at ambient conditions were determined. The degree of cook of starch was determined on fresh flours. The porridges made from the flour of the treated grains were evaluated by a trained panel and by consumers. Analyses of energy demands and practicality of the thermal treatments and extrusion cooking as processing technologies in manufacturing pearl millet flour in rural parts of Namibia were made.

Fat acidity for the untreated flour increased significantly from 0.11 to 3.72 g KOH kg⁻¹, whereas no significant increase observed in the flours of wet thermally-treated grains. This indicates that wet thermal treatments inhibited triglyceride hydrolysis. The PVs of the flours of the wet thermally-treated grain increased seven-fold, while the PV of the untreated flour decreased. A similar trend was observed for the conjugated diene values. The conjugated triene values increased significantly for all the samples. These results indicate autoxidation in the thermally-treated samples and that there was accumulation of hydroperoxides.

The degree of cook of the wet thermally-treated grain (~40%) was twice that of the untreated and toasted grains, indicating that the wet thermal treatment partially gelatinised the grain. Porridges prepared using untreated flours were associated with rancid flavours, while those of other treatments were not, indicating that the thermal treatments can prevent rancidity. Consumers preferred the porridge prepared using flour of the boiled grain, presumably because it was fully cooked, whereas others were not. Thus, the boiling treatment can be applied to extend the shelf life of and pre-cook pearl millet flour.

The energy demands for boiling and extrusion cooking were estimated to be 0.6 and 0.2 kWh kg⁻¹, respectively. The energy demand for the boiling process can be minimised by sun-drying instead of using electricity. The cost of an extruder would be prohibitively costly for Healthful Harvest. Thus, boiling the grain is a suitable appropriate technology that can be applied in the Healthful Harvest situation by ordinary people, with no specialist skills.

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CHAPTER 1: INTRODUCTION

Pearl millet (*Pennisetum glaucum* (L.) R. Br., also classified as *P. typhoides*, *P. americanum* or *P. spicatum*) and locally known as mahangu (Namibia), bajra (India) and dukhon (Senegal), is a cereal grass cultivated almost exclusively on a subsistence basis by farmers in semi-arid parts of Africa and Asia (ICRISAT and FAO, 1996; Jain and Bal, 1997a, Taylor, 2004). In these areas, pearl millet is a major source of energy and proteins for about 500 million people.

Pearl millet's advantage over other cereals is that it can and is grown in marginal agricultural areas where annual rainfall is variable, unpredictable and very low (200-500 mm) and where daily temperatures reach in excess of 30°C (ICRISAT and FAO, 1996). Moreover, its nutrient content and properties are equivalent or even superior to those of other cereals (Obilana and Manyasa, 2002).

Quantitatively, pearl millet is the most important of all millets (ICRISAT and FAO, 1996). Major areas where pearl millet is cultivated are India and northern Africa. It is also cultivated in eastern and southern Africa. World annual production is estimated to be about 14 million tons (ICRISAT and FAO, 1996). India and Nigeria are the largest pearl millet producing countries, with average annual production figures estimated around 6.2 and 4.5 million tons, respectively.

Yields are, however, generally very low, on average ~750 kg per hectare (ICRISAT and FAO, 1996). This is mainly because pearl millet is grown in areas of low rainfall, high temperature and on light, well-drained soils. Moreover, traditional farming practices are predominantly used, with very low inputs (no biocides or inorganic fertilizers) and the use of traditional landraces is widespread (ICRISAT and FAO, 1996). However, in areas where new varieties, some irrigation and higher input agriculture are used, yields can be well in excess of 2 tons/ha.

Nonetheless, the importance of pearl millet should not be based solely on the absolute production figures. In Namibia, for instance, pearl millet is a staple food in the northern, most populous part of the country. But the average annual production is only ~65 000 tons (Taylor, 2004). This should, however, be seen in perspective as Namibia's population is only about 2 million.

The main primary processing technology of pearl millet is milling. This technology reduces pearl millet grain into flour. The resulting flour is then used to prepare various food products such as porridges or unleavened breads.

Pearl millet cultivation is still almost exclusively limited to subsistence farms in rural areas. This could be due to the lack of productivity and trade (rural and urban) of value-added products from this cereal. In Namibia, improved varieties have led to an increase in the yield of pearl millet crop. Consequently, there is a surplus over and above immediate household requirements. The surplus is thus available for trade and processing. Thus there is a need to add value to pearl millet by improving and increasing processing. Moreover, rapid urbanization in countries such as Namibia appears to offer considerable opportunity for the development of value-added, convenience forms of traditional food products that meet the needs (processed foods that are far quicker and more convenient to prepare) of the urban consumers. Healthful Harvest, a cooperative of subsistence farmers in north-central Namibia made use of this opportunity to use pearl millet in the manufacture of value-added food products. This cooperative is in the process of developing a tasty, nutritious, convenient shelf stable and affordable flour product. The product will be made from locally grown pearl millet and cowpeas and should be quicker to cook. Hence, the flour should be pre-cooked. The overall aim of this research project was to assist the Healthful Harvest cooperative in terms of improving the shelf stability of pearl millet flour through pre-cooking by thermal treatments.

1.1 STATEMENT OF PROBLEM

The pearl millet grain is small but has a proportionally larger germ than all other cereal grains, except perhaps maize (Taylor, 2004). Hence, pearl millet tends to contain a higher content of triglycerides. These are rich in unsaturated fatty acids (Rooney, 1978; Lai and Varriano-Marston, 1980a; Kapoor and Kapoor, 1990).

When pearl millet is reduced into flour, the resulting flour is noted as having poor keeping quality especially under conditions of moderately high moisture and oxygen exposure (Abdelrahman, Hosney and Varriano-Marston, 1983; Chaudhary and Kapoor, 1984). This is attributed to the deterioration of its triglycerides through lipolysis and subsequent oxidation of de-esterified unsaturated fatty acids (Lai and Varriano-Marston, 1980b). These chemical changes manifest themselves as off-odours and/or off-taste of the flour or in products made from the flour. Thus it becomes unpleasant to eat.

Traditionally, pearl millet is manually pounded, generally using pestle and mortar, into flour in an amount that is just enough for a few days of household use. Since Namibia became independent in 1990 mechanical mills are in the increase in rural areas. They are increasingly used since they eliminate a considerable amount of hard labour. However, households can only store pearl millet flour for short periods because it quickly goes rancid and becomes unpleasant to eat. There is also a demand for processing value-added, traditional, convenient food products made from locally grown raw materials such as pearl millet especially in urban areas. These factors therefore require a longer storage life for pearl millet flour. There is, however, scant information on how to improve the shelf life of pearl millet flour.

This research project therefore investigated the effects of different thermal treatments to prevent the development of rancidity in order to produce shelf stable flour and value added products.

1.2 LITERATURE REVIEW

1.2.1 GRAIN STRUCTURE

Pearl millet grains are shaped like a liquid drop (Jain and Bal, 1997a) (Figure 1.1). They thresh free of the hull (Taylor, 2004). The grains can be up to 2 mm in length and their weight ranges between 3 mg and 15 mg. This is small in comparison with other tropical cereal grains such as maize and sorghum. Thus, pearl millet grains pack closely together, leaving little air space compared to other cereal grains such as maize. Consequently, pearl millet grain has a density of $\sim 1.6 \text{ g/cm}^3$ (Serna-Saldivar and Rooney, 1995; Jain and Bal, 1997a), which is significantly higher than that of wheat (1.39 g/cm^3), maize (1.39 g/cm^3), rice (1.24 g/cm^3) and sorghum (1.24 g/cm^3) grains (Serna-Saldivar and Rooney, 1995). The colour of pearl millet grains varies from pearly white to yellow, grey, brown and purple (Taylor, 2004). Even individual grains may not have a uniform colour.

The pearl millet grain comprises about 8% pericarp, 17% germ, (which is proportionally large) and 75% endosperm (Serna-Saldivar and Rooney, 1995). A thin waxy cutin layer covers the surface of the pericarp. This layer helps decrease the effects of weathering. Beneath the pericarp, is a thin layer of seed coat, and then a single aleurone layer (one-cell thick).

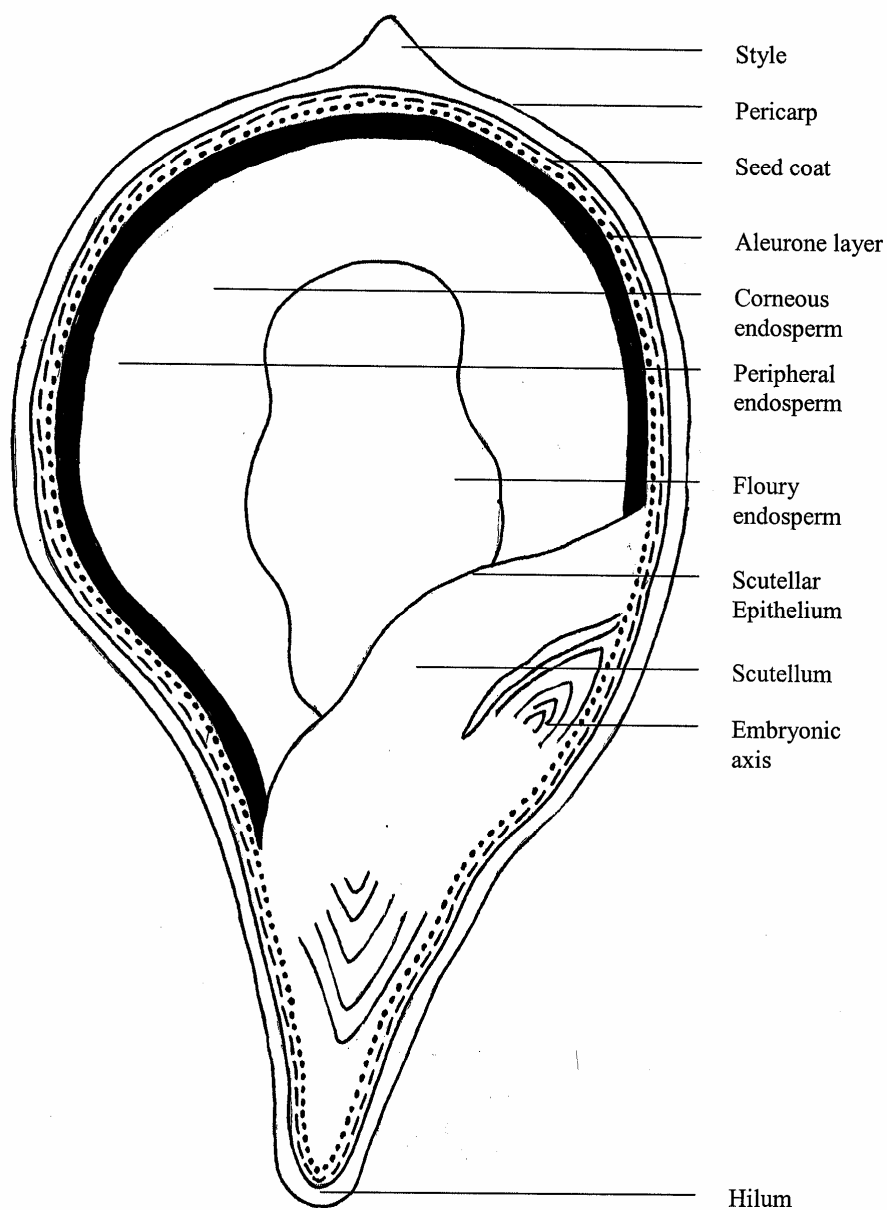


Figure 1.1: Schematic diagram of longitudinal section through a pearl millet grain (from Taylor, 2004)

1.2.2 CHEMICAL COMPOSITION OF PEARL MILLET GRAIN

The chemical composition of pearl millet grains is the same with those of other cereal grains, with minor exceptions (Obilana and Manyasa, 2002). Generally, pearl millet has

more oil and higher protein than most other cereal grains grown under similar conditions. Its starch, fibre, ash and sugar levels are similar to those for sorghum.

1.2.2.1 Energy

Whole pearl millet grain has a high energy content, which ranges from 1646 kJ/100 g to 1691 kJ/100 g (db) (Taylor, 2004). Because pearl millet has high oil content, this energy value is relatively higher than that of all other cereal grains, except perhaps maize.

1.2.2.2 Carbohydrates

Carbohydrate components of pearl millet grain comprise starch, dietary fibre and soluble sugars (Figure 1.2). Starch, which consists of glucose in the form of amylose and amylopectin, is the predominant component in the pearl millet endosperm, as it is in all cereal grains (Hoseney, 1994; Abdalla, El Tinay, Mohamed and Abdalla, 1998; Taylor, 2004).

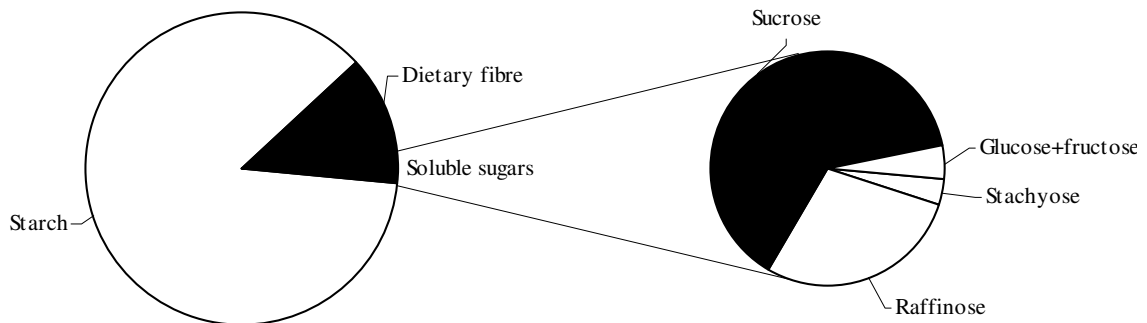


Figure 1.2: Proportions of pearl millet grain carbohydrates (84% db) (adapted from Taylor, 2004)

Pearl millet grains have a starch content typically around 71.6% (db) (Taylor, 2004). This is slightly lower in comparison with other cereal grains because of the proportionally larger germ and thus relatively smaller endosperm. The proportion of amylose in pearl millet starch ranges from 17% to 21.5%, which falls within the range of other cereal

grains. Pearl millet grain dietary fibre, approximately 8% (db), is lower than that of other cereal grains (Serna-Saldivar and Rooney, 1995; Taylor, 2004). Pearl millet, like other cereal grains, has a low content of soluble sugars, mostly sucrose and raffinose (Serna-Saldivar and Rooney, 1995).

1.2.2.3 Protein

The protein content of pearl millet grain ranges from 8.6% to 19.4% but is typically about 14.5% (db) (Serna-Saldivar and Rooney, 1995). This content is high for cereal grains. This is attributed to the proportionally larger germ. Consequently, prolamins, aqueous alcohol-soluble proteins exclusively located in the endosperm, are lower in pearl millet grains than in other cereal grains (Chandna and Matta, 1990; Taylor, 2004). Albumins (aqueous soluble) and globulins (saline soluble) are found in amounts somewhat higher than in most other cereal grains. Pearl millet protein amino acid composition is characterised by a relatively high content of lysine compared to most cereal grains. This increases the potential for pearl millet proteins to be involved in non-enzymatic browning, especially Maillard reaction when subjected to thermal treatments.

1.2.2.3.1 Enzymes

Pearl millet like other cereal grains contains lipase, plus many other enzymes (Hoseney, 1994; Galliard, 1999). Lipase, which is concentrated in the pericarp, aleurone layer and the germ (Lai and Varriano-Marston, 1998a), plays a major role in catalysing the hydrolysis of pearl millet grain triglycerides (section 1.2.6). Pearl millet lipase shows relatively higher activity than that of most other cereal grains (Galliard, 1999). Unlike other cereal grains, pearl millet supposedly does not contain lipoxygenase enzymes (Hoseney, 1994), which catalyse the oxidation of unsaturated fatty acids of triglycerides. However, pearl millet contains polyphenol oxidase and peroxidase, which according to Bangar, Bhide, Kachare and Chavan (1999) are involved in browning reactions. This action may give whole pearl millet flour its characteristic mousy odour that may be objectionable to consumers of its products (Reddy, Faubion and Hoseney, 1986; Hanna, Singh, Faubion and Hoseney, 1990).

1.2.2.4 Lipids

The term lipid denotes a heterogeneous group of substances, which have a common property of insolubility in water but solubility in non-polar solvents such as hexane or petroleum ether (Hoseney, 1994). Included in the group are oils and phospholipids, the latter being associated with cell membranes.

Lipids can be classified as free or bound. This distinction is based upon solubility. If the lipid is soluble in a non-polar solvent such as petroleum ether, it is considered free (Hoseney, 1994). If it requires a polar solvent for extraction, it is considered bound. Bound lipids may be covalently bonded to non-lipid materials such as proteins or starch components in the grain.

Furthermore, the free or bound fraction usually contains polar and/or non-polar lipids. The non-polar lipid components, both free and bound in pearl millet, were identified as triglycerides, diglycerides and monoglycerides (Hoseney, 1994). Triglycerides (triacyl glycerols) are esters of the trihydric alcohol glycerol (propane-1,2,3-triol) and three fatty acid (Figure 1.3) residues, which may or may not be identical. Polar lipids of bound lipids are lysophosphatidyl choline, digalactosyl diglycerides, phosphatidyl ethanolamine and free fatty acids. It is reported that free lipids of pearl millet contain no polar components (Badi, Hoseney and Casady, 1976; Lai and Varriano-Marston, 1980b).

The overall lipid content of pearl millet grain ranges between 1.5 to 6.8% (db) (Taylor, 2004). It is typically about 5.1% (db). This is higher than that of all other cereal grains, except perhaps maize (Rooney, 1978; Ahuja, Sekhon and Sehgal, 1979). This is because pearl millet and maize grains have proportionally very large germs where most of the lipid content is located (Abdelrahman, Hoseney and Varriano-Marston, 1984).

The free and bound lipid contents of pearl millet range from 5.6 to 6.1% and 0.6 to 0.9% respectively. Pruthi and Bhatia (1970) studied two varieties of pearl millet. They found that the free and bound lipid contents were 5.0 and 0.5%, respectively. Triglycerides constituted from 84 to 87% of the total non-polar lipid fraction. The major component of

the polar fraction was phosphatidylcholine. Pearl millet also contained other phospholipids and sterol-containing glycolipids.

According to Osagie and Kates (1984), the oil in of pearl millet grain consists of 85% neutral (non-polar) lipids, 12% phospholipids and 3% glycolipids. Neutral lipids comprise about 85% triglycerides and small amounts of mono- and diglycerides, sterols and free fatty acids. Sterols comprise of campesterol and stigmasterol. Lysophosphatidylcholine, phosphatidylcholine and lysophosphatidylethanolamine are the major phospholipids. These researchers also found that the major glycolipids were esterified sterol glycoside, sterol glucoside and mono- and digalactosyldiacylglycerol.

Besides minor constituents such as vitamins A and E (Serna-Saldivar and Rooney, 1995), pearl millet lipid is essentially triglycerides (Badi *et al*, 1976; Lai and Varriano-Marston, 1980a; Osagie and Kates, 1984). Monocarboxylic fatty acids i.e. fatty acids that have only one carboxyl group, are the structural components common to most of the lipids of cereals (Coultate, 2002). Since many of the properties of cereal lipids can be accounted for directly in terms of their glycerides fatty acid composition, they will be considered in some detail.

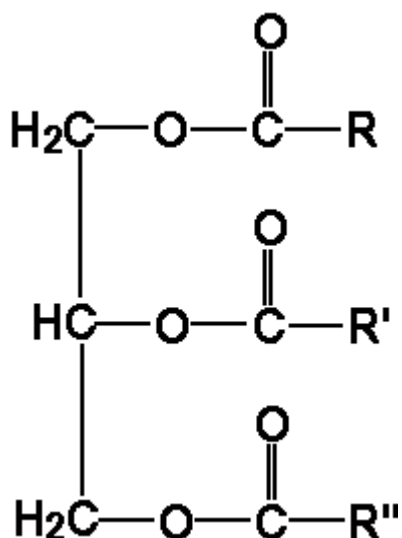


Figure 1.3: Generic chemical structure of a triglyceride, R = fatty acid chain

Almost all fatty acids that make up the glycerides in foodstuffs contain an even number of carbon atoms in an unbranched chain, e.g. linoleic acid (Coultate, 2002) (Figure 1.4). Besides the saturated fatty acids, of which palmitic acid (C16:0) is an example, unsaturated fatty acids having one, two, or more double bonds are common. When the fatty acid has two or more double bonds the bonds are CH₂- interrupted rather than conjugated (Figure 1.4). However, on oxidation of the unsaturated bonds, the bonds shift in position and become conjugated.

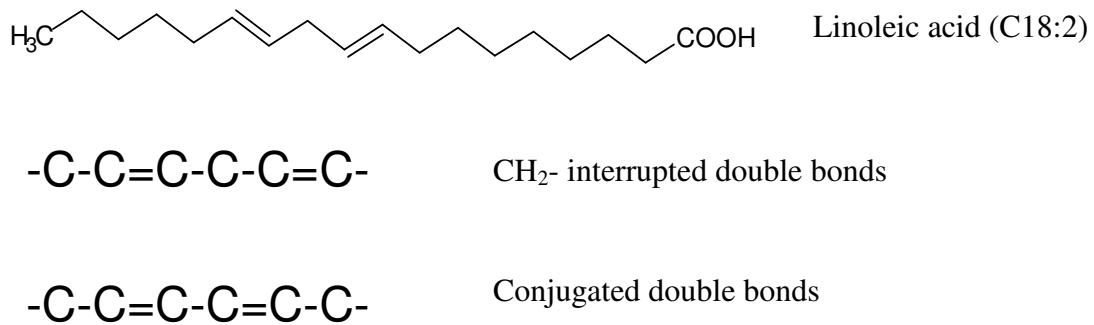


Figure 1.4: Fatty acid structures

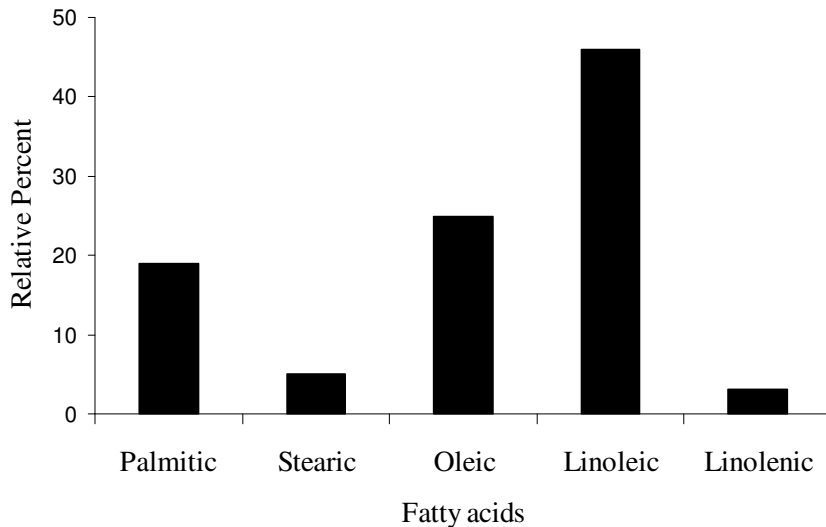


Figure 1.5: Major fatty acid composition of pearl millet triglycerides (adapted from Rooney, 1978)

Pearl millet triglycerides contain about 74% unsaturated fatty acids (Figure 1.5), mainly oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids (Rooney, 1978; Lai and Varriano-Marston, 1980a; Kapoor and Kapoor, 1990). The remaining fraction is made up of saturated fatty acid residues (palmitic (C16:0) and stearic (C18:0)).

For cereal grains the major fraction of lipids is found in the germ (Abdelrahman *et al*, 1984). This is also the case for pearl millet. This is especially so in pearl millet because as mentioned, the germ is proportionally larger than that of almost all other cereal grains. About 88 % of the lipid fraction is found in the germ (Abdelrahman *et al*, 1984). The pericarp and endosperm contain 6% each. As stated the high content of triglycerides and relatively high proportion of polyunsaturated fatty acids that constitute the triglycerides negatively affect the shelf life of untreated pearl millet flour (Abdelrahman *et al*, 1983, Chaudhary and Kapoor, 1984).

1.2.2.5 Minerals

The ash content of whole pearl millet grain ranges between 1.6% and 3.6% (Serna-Saldivar and Rooney, 1995). In terms of actual minerals, pearl millet grain, like other cereal grains, is an adequate source of dietary minerals such as magnesium, iron, zinc and copper. Quantitatively, phosphorus and potassium are the major minerals in pearl millet grain. Anti-nutrients such as phytate may, however, limit the bioavailability of phosphorus, iron and calcium. Iron and copper are also known to be pro-oxidants (Galliard, 1999) even at concentrations as low as parts per million. They may be of significance to the deterioration of triglycerides.

1.2.2.6 Vitamins

Like other cereal grains, pearl millet grain is an important source of thiamin, niacin and riboflavin (Taylor, 2004). Riboflavin has, however, been implicated in lipid deterioration in the presence of light (Hamilton, 1999). Thus, it may also be a potential enhancer of the deterioration of pearl millet triglycerides. Because of its high oil content, pearl millet is also a good source of lipid-soluble vitamin E. Its content in pearl millet is about 2 mg/100 g (Taylor, 2004). Besides its nutritional role in foods, vitamin E is also known for its

antioxidant activity in the form of tocopherols (Huang, Frankel and German, 1995; Bramley, Elmadfa, Kafatos, Kelly, Manios, Roxborough, Schuch, Sheehy and Wagner, 2000). Its presence could be of importance to pearl millet as an antioxidant that may curb triglyceride deterioration. Moreover, pearl millet is also a good source of the lipid-soluble vitamin A. Vitamin A content for pearl millet is typically about 24 Retinol Equivalents (Taylor, 2004). These lipid-soluble vitamins are mainly located in the germ.

1.2.2.7 Anti-nutrients

One of the anti-nutrients of pearl millet grain is phytate. Phytate content of pearl millet is in the approximate range of 172 and 327 mg per 100 g (Taylor, 2004). This range falls within the range typical of cereal grains. Phytate binds multivalent metal ions such as calcium and iron thereby interfering with their absorption in the gut. In contrast, the fact that phytate binds pro-oxidant cations (Eskin and Przybylski, 2001) such as iron and copper ions may be desirable for the stability of pearl millet flour triglycerides.

Unique to pearl millet, is the presence of the phenolic compounds, C-glycosyl flavones (Akingbala, 1991). These are concentrated in the outer layers of the grains and contribute to the grey colour of the grain (Taylor, 2004). In areas of Sudan where pearl millet is also a staple these compounds have been implicated in goitre (Elnour, Leiden, Bourdoux, Elton and Khalid, 1997). Furthermore, C-glycosyl flavones are believed to be the cause of the previously mentioned disagreeable mousy odour of damp pearl millet grain flour. Bangar, Bhite, Kachare and Chavan (1999) attributed this to peroxidase action on the C-glycosyl flavones. Unlike sorghum, tannins are apparently absent in pearl millet grain (Taylor, 2004).

1.2.3 GRAIN STORAGE

In Namibia, pearl millet is traditionally stored in granaries (iigandhi) made of woven mopane (*Colophospermum mopane*) wood branches (FAO, 1994). In general, grain storage bins include cylindrical galvanized steel containers and modified metal or plastic water tanks (FAO, 1994). Pearl millet can suffer severe storage losses during post-harvest stages. This is particularly caused by insects such as rice moth (ICRISAT and FAO,

1996). Unlike its flour, intact pearl millet grain, like other cereal grains, is quite stable to chemical changes (Kaced, Hosney and Varriano-Marston, 1984). Thus, pearl millet grain is shelf stable unless when infested by destructive pests (ICRISAT and FAO, 1996).

1.2.4 MILLING

In Namibia, milling is regarded as a chore for women in the household. It is mainly done traditionally using a pestle and mortar. After independence in 1990, there have been a growing number of entrepreneurs who have introduced hammer mills in rural areas. The milling process in Namibia involves decortication, steeping (fermentation) and reduction of grain to flour. The pearl millet grain is decorticated first, whereby the bran (pericarp and germ) is generally removed (Taylor, 2004). This aims to improve the palatability and storage quality of the flour.

The decorticated pearl millet grain is then steeped in ambient temperature water overnight. This steeping process is actually also a lactic acid fermentation step. Usually a lactic acid bacteria “culture” from the previous steep is inoculated into the steep water (back slopping). The steeping process, among other effects, softens the grain, thereby facilitating its reduction into flour. The decorticated and steeped grain is partially dried before milling (Taylor, 2004). After milling, the flour is fully dried to a moisture content of ~10%.

Drying the decorticated and steeped grain is achieved through sun drying and/or alternatively by mixing it with decorticated, unsteeped grain. The flour is then dried by sun drying. The partially dried, decorticated, steeped grain is then milled into flour using a powerful hammer mill fitted with a ~1 mm screen or using a pestle and mortar.

1.2.5 PEARL MILLET FLOUR QUALITY

As mentioned, when pearl millet flour is processed at elevated moisture levels (30% w/v), the product may develop and impart a mousy odour, which could be disagreeable especially to those unfamiliar with the food (Reddy *et al*, 1986; Hanna *et al*, 1990). Bangar *et al* (1999) found that peroxidase action on C-glycosylflavones is responsible for

this characteristic odour. According to Seitz, Wright, Waniska and Rooney (1993), 2-acetyl-1-pyrroline caused the mousy odour in wetted pearl millet flour. It is interesting that 2-acetyl-1-pyrroline in millet caused a disagreeable mousy odour, whereas in the aroma profile of wheat bread crust it was found to be the key odourant evoking the popcorn-like and toasty flavour notes (Grosch and Schieberle, 1997). However, at normal storage moisture level (~10%), the main quality defect of pearl millet flour that has been stored is the development of unpleasant odours and off-taste (Kaced *et al*, 1984). These flavours make its products unpleasant to eat. As discussed, pearl millet grain contains a relatively high proportion of oil. Hydrolysis of pearl millet flour triglycerides and subsequent oxidation of the released de-esterified unsaturated fatty acids occur during storage at ambient conditions (Lai and Varriano-Marston, 1980b; Chaudhary and Kapoor, 1984; Kaced *et al*, 1984, Kapoor and Kapoor, 1990). It is these chemical changes that are manifested as undesirable tastes and odours in pearl millet flour that has been stored.

Essentially, how soon triglycerides deteriorate, determines the shelf life of whole pearl millet flour (Kapoor and Kapoor, 1990). Milling whole cereal grains into flour introduces instability in the lipids (Galliard, 1999). In the undamaged grain, triglycerides are compartmentalised in the spherosomes in the germ. This prevents the onset of enzymic activity with their substrates. Processing technology such as milling leads to redistribution of lipids and mixes the enzymes with their substrates and increases the surface area exposed to atmospheric oxygen. Pro-oxidant metal contamination from equipment may also occur.

1.2.6 TRIGLYCERIDE HYDROLYSIS

Hydrolysis of triglycerides entails the cleavage, in presence of water, of ester bonds that attach fatty acid residue to glycerol (Galliard, 1999). Fatty acids are thus set free from glycerol. Pearl millet lipase enzymes, which incidentally show a higher activity than in most other cereal grains (Table 1.1), catalyse this hydrolysis (Galliard, 1999).

Kaced *et al* (1984) studied the effect of milling pearl millet grain into flour on lipid hydrolysis. The fat acidity levels increased more rapidly in pearl millet flour, while intact grains showed no significant change during the same storage period and conditions.

Table 1.1: Lipase activity in various cereal grains (adapted from Galliard (1999))

Material	Lipase activity^b
Millet, whole grain (presumed to be pearl millet)	6-10
Sorghum, whole grain	6
Wheat, whole grain	2-2.5

^bExpressed in relative units of oleic acid liberated from a mixture containing ground sample (2 g) and olive oil (100 mg) at 30°C for 72 hours ($a_w = 0.8$).

It is, thus, no surprise that these authors observed an increase in fat acidity level (from 10 to 60 mg KOH per 100 g of pearl millet flour during 10 days storage at ambient conditions). Of considerable importance is the fact that de-esterified unsaturated fatty acids are more prone to oxidation than when esterified to glycerol (Galliard, 1999).

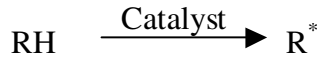
1.2.7 TRIGLYCERIDES OXIDATION

The level of unsaturation in a de-esterified fatty acid influences the rate of its oxidation (Eskin and Przybylski, 2001). Also, the rate of oxidation increases significantly with the level of fatty acid unsaturation. For example, relative oxidation rates of oleic, linoleic and linolenic fatty acids are 1:12:25, respectively (Hamilton, 1999).

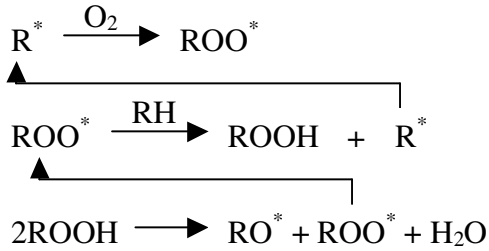
The oxidation of unsaturated fatty acids can occur through autoxidation and/or enzymatic action (Eskin and Przybylski, 2001). When light energy initiates autoxidation, it is often described as photoxidation. Photoxidation only occurs in the presence of light and photosensitisers such as chlorophyll, riboflavin and heavy metal ions (Eskin and Przybylski, 2001). Autoxidation is a three-stages process, namely initiation, propagation and termination (Figure 1.6).

The initiation stage involves the formation of unsaturated fatty acid radicals (R^*) in the presence of light, heat, other radicals or catalysts including pro-oxidant cations such as iron and copper ions (Eskin and Przybylski, 2001). A fatty acid radical has an unpaired electron. Therefore they are short-lived and are highly reactive as they seek a partner for their unpaired electron. During the propagation stage, fatty acid radicals react with oxygen and become peroxy radicals (ROO^*), which abstract a hydrogen atom (hydrogen radical) from another unsaturated fatty acid to form unstable and odourless fatty acid hydroperoxides ($ROOH$) and more unsaturated fatty acid radicals (R^*). These radicals are autocatalytic and propagate the oxidation of unsaturated fatty acids. The termination stage occurs when any component deactivates the radicals and stable products are formed.

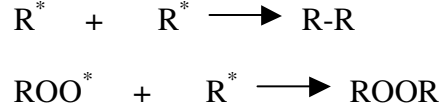
Initiation:



Propagation:



Termination:



RH = unsaturated lipid radical
 R* = lipid radical
 RO* = alkoxy radical
 ROO* = lipid peroxy radical

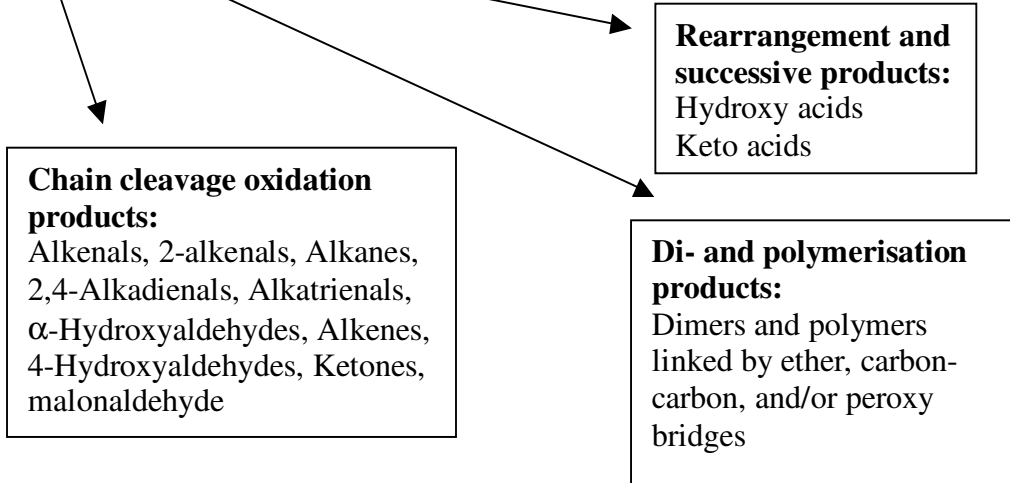
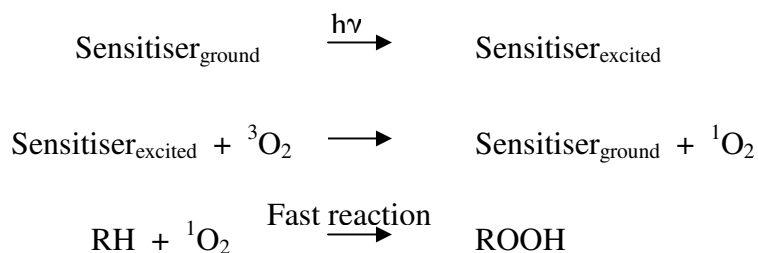


Figure 1.6: Mechanism of unsaturated fatty acid oxidation (Adapted from Hamilton (1999) and Eskin and Przybylski (2001))

Of importance is initiation of oxidation of unsaturated fatty acids by the singlet oxygen (1O_2) (Eskin and Przybylski, 2001). The stable triplet oxygen (3O_2) is not very reactive and is unlikely to react directly with unsaturated fatty acids (Eskin and Przybylski, 2001). Activation of triplet oxygen to the highly reactive singlet oxygen can be induced by electronic excitation through photosensitisation ($h\nu$), by metal cations and natural pigments such riboflavin and chlorophyll (Hamilton, 1999; Eskin and Przybylski, 2001; Coultate, 2002).

The conversion of stable oxygen to singlet oxygen by photosensitisation (Hamilton, 1999) is shown below:



Singlet oxygen is known to react with linoleic acid about 1500 times faster than ground state oxygen (Hamilton, 1999). Oxidation of unsaturated fatty acids by singlet oxygen can be inhibited by compounds that react faster with this initiator such as quenchers, which deactivate it to the ground (triplet) stable form (Hamilton, 1999). The most efficient natural quenchers are, among others, tocopherols, β -carotene, amino acids, proteins and phenols (Eskin and Przybylski, 2001).

The hydroperoxides formed during propagation are unstable intermediates in the oxidation process (Eskin and Przybylski, 2001). As stated, during the propagation step the hydroperoxides break down to produce propagatory alkoxy (RO^*) and peroxy (ROO^*) radicals that perpetuate the propagation process. They disintegrate to form a wide range of products that are also unstable. These products (Figure 1.6), in turn, undergo oxidation and/or decompose to stable products most of which are responsible for disagreeable flavours associated with rancid oils (Table 1.2) (Eskin and Przybylski, 2001).

Radicals and hydroperoxides may accumulate and show little or no decomposition to odorous products (Hamilton, 1999; Eskin and Przybylski, 2001). Beyond this period, the rate of radical oxidation and hydroperoxide decomposition accelerates rapidly and the food product may begin to taste and/or smell rancid due to the formed secondary oxidation products.

Table 1.2: Characteristics of some of the individual unsaturated fatty acid oxidation volatile aldehydes (adapted from Malcolmson, Vaisey-Genser, Przybylski, Ryland, Eskin and Armstrong (1996))

Volatile Aldehyde	Reported odour descriptor
Saturated	
Pentanal	Painty, herbal
Hexanal	Fatty, green, fruity, cut grass, herbal, rancid, painty, crushed weeds
Heptanal	Weeds, green, sour, sweaty, herbal, painty, rancid
Octanal	Lime, grassy, citrus, sharp, heavy, candle-like, crushed weeds
Nonenal	Green, soapy, rubbery, beany
Decanal	Fruity, candle-like
Monounsaturated	
3-Hexenal	Green, apple-like
2-Nonenal	Green, fatty, tallowy
2-Decenal	Metallic
Polyunsaturated	
2,4-Heptadienal	Fatty, nutty
2,4-Decadienal	Waxy, fatty, green

Lai and Varriano-Marston (1980b) studied the oxidative changes in terms of peroxide value in pearl millet flour during storage for 180 h at 19°C and 58% relative humidity (rh); 27°C and 64% rh and 42°C and 75% rh. The peroxide values increased steadily early during storage, reached a maximum and then decreased under all three storage conditions. However, the rates at which peroxide values changed differed for each storage treatment. The time when they began to show a decrease corresponded to the onset of odour defects in the flour as detected by panelists (Lai and Varriano-Marston, 1980b). Another aspect worthy of mention is that chemical detection of secondary products of triglycerides oxidation may not always correlate well with rancid odours. For example, Kaced *et al* (1984) detected hexanal, an important unsaturated fatty acid oxidation product, in pearl millet flour after 21 days of storage. However, rancid odours

were noted far earlier before the detection of hexanal. It could also be that the rancid odour noted was not from triglyceride oxidation but was perhaps from the C-glycosyl flavones responsible for “mousy” odour described in section 1.2.5.

Triglyceride oxidation can also be brought about by the action of lipoxygenases (Galliard, 1999). These enzymes catalyse the oxidation of unsaturated fatty acids especially when the fatty acids are not esterified. Apart from the fact that lipoxygenases are specific to substrates and chemical bonds they act upon, the basic stoichiometry of their oxidation of unsaturated fatty acids is not different from that of autoxidation (Galliard, 1999). The presence or absence of these enzymes in pearl millet is not well investigated, though Hosney (1994) alludes to their absence. Presumably lipid oxidation can also be brought about by other oxidative enzymes such as peroxidases known to be present in pearl millet (Reddy *et al*, 1986).

1.2.8 EFFECT OF STORAGE ENVIRONMENT ON WHOLE PEARL MILLET FLOUR STABILITY

Storage conditions especially temperature and relative humidity under which flour is kept affect its moisture content (Kumar and Anandswamy, 1979; Lai and Varriano-Marston, 1980b). Lai and Varriano-Marston (1980b) stored pearl millet flour in cotton bags for 180 h at 19°C and 58% rh and 42°C and 75% rh. The moisture content of pearl millet flour stored at 42°C and 75% rh increased by 30% more than that stored at 19°C and 58% rh. Consequently, triglyceride hydrolysis and peroxidation increased more rapidly at 42°C and 75% rh relative to 19°C and 58% rh. This, in turn, caused more rapid (40 hours earlier) development of off-flavours in whole pearl millet flour stored at 42°C and 75% rh than that stored at 19°C and 58% rh (Lai and Varriano-Marston, 1980b).

1.2.9 PRESERVATION OF WHOLE PEARL MILLET FLOUR

As explained in the previous section, the quality of whole pearl millet flour decreases drastically during storage and is manifested through the development of disagreeable odours and/or tastes that occur because of triglyceride deterioration (Lai and Varriano-

Marston, 1980b; Chaudhary and Kapoor, 1984; Kaced *et al*, 1984; Kapoor and Kapoor, 1990). This severely limits the shelf life of whole pearl millet flour.

Various attempts have been made to prevent deterioration of the triglycerides in pearl millet. These include decortication (Abdelrahman *et al*, 1983); use of various containers for storage (Kaced *et al*, 1984); salting (Kapoor and Kapoor, 1990), defatting (Kapoor and Kapoor, 1990), use of antioxidants (Kapoor and Kapoor, 1990), thermal treatment of flour (Pruthi, 1981; Kapoor and Kapoor, 1990; Patel and Parameswaran, 1992; Chavan and Kachare, 1994; Arora, Sehgal and Kawatra, 2002), application of dry heat (Pruthi, 1981; Patel and Parameswaran, 1992; Chavan and Kachare, 1994; Arora *et al*, 2002) or wet heat (Chavan and Kachare, 1994; Palade, Kadlag, Kachare and Chavan, 1996) and acid-soaking (Chavan and Kachare, 1994) of the grain.

1.2.9.1 Decortication

As stated, the traditional pearl millet milling process in Namibia involves a decortication step. During this step, not all the germ is removed. This is because the germ of pearl millet grain is tightly attached to the endosperm (Varriano-Marston and Hoseneey, 1983; Jain and Bal, 1997b). As a result it is hardly ever removed entirely. Decortication can reduce the amount of triglycerides in the resulting flour (Abdelrahman *et al*, 1983). It is however, unlikely to prevent the deterioration of the residual triglycerides.

1.2.9.2 Defatting

Kapoor and Kapoor (1990) defatted pearl millet flour using n-hexane. The fat acidity and peroxide values did not change during one-month storage at ambient conditions. This indicated a complete prevention of the deterioration of triglycerides, if indeed significant amount remained, in the defatted pearl millet flour. One of the disadvantages of defatting is that it may also remove essential nutrients such as the lipid-soluble vitamin A and vitamin E. The loss of these essential nutrients makes this method undesirable not only from the nutritional point of view but because these vitamins also have antioxidant activities (Eskin and Przybylski, 2001). Furthermore, defatting requires a relatively expensive chemical solvent. It also requires energy and appropriate equipments to

evaporate and recover the solvent. The cost of safety precautions required for the use of the highly flammable hexane is also another major issue. This processing method will surely not be economically feasible for application in rural communities. The use of flour treated this way, as food may also be questionable by consumers.

1.2.9.3 Use of different Storage Packaging Materials

Kaced *et al* (1984) compared cotton and polyethylene bags for pearl millet flour storage. The fat acidity increased more rapidly in pearl millet flour sample that was stored in cotton bags than the one, which was stored in the polyethylene bags. The fat acidity for flours stored in cotton and polyethylene bags increased from 0.4 to 2.2 and 1.5 g KOH kg⁻¹ meal, respectively within 150 h of storage. This effect was explained as being due to the cotton bags allowing moisture entry as was indicated by a marked increase in flour moisture level, which favours lipase hydrolytic activity hence an increased fat acidity. Nevertheless, the increases in fat acidity indicate that triglyceride deterioration is not adequately curbed by either cotton bag or polyethylene bag. Moreover, storing products that are prone to triglyceride deterioration in polyethylene bags may not be a wise idea, especially if the storage duration spans several months. This is because polyethylene may contain a plasticiser that gives the bag its flexibility (Potter and Hotchkiss, 1995). The plasticiser could react with the triglyceride deterioration products leading to undesirable effects on both the packaging material and perhaps the food product stored in them (Potter and Hotchkiss, 1995). Polyethylene bags are most likely to be impermeable to triglyceride deterioration volatiles (Potter and Hotchkiss, 1995). This may lead to trapping and accumulation of these volatiles of disagreeable odours. Cotton or paper bags that would permit the escape of volatiles could be preferred for storing whole pearl millet flour. Cotton and paper bags may also be of economical importance to both the consumer and the environment.

1.2.9.4 Acid-Soaking

Chavan and Kachare (1994) used 0.05 M hydrochloric acid solution to soak pearl millet grain for 12 h at ambient temperature. This method was aimed at lowering the pH to inactivate the lipase enzymes. The grain was washed with tap water and dried to 10%

moisture before milling. The flour was stored in cloth bags at ambient conditions. It was analysed for changes in fat acidity during 30 days storage. They found that fat acidity of untreated flour increased by about 6-fold. The fat acidity of acid-soaked grain flour increased by about 1.5-fold. This indicates that this treatment inhibited the hydrolysis of triglycerides quite substantially. Hydrochloric acid, however, introduced questionable effects such as bleaching of the flour and imparted a sour taste to the flour (Chavan and Kachare, 1994). These effects could also result in objectionable sensory quality in food products made from the flour.

1.2.9.5 Salting

In some parts of India a lump of rock salt (presumably sodium chloride) is kept inside the earthen pot containing pearl millet flour (Kapoor and Kapoor, 1990). The rock salt presumably lowers the water activity of the flour due to its hygroscopic properties. This treatment was, however, found to be unsuccessful in retarding pearl millet flour triglyceride deterioration because the fat acidity level and peroxide values were almost the same for both untreated and rock salted-flours.

1.2.9.6 Antioxidants

Antioxidants are compounds that retard autoxidation of triglycerides (Eskin and Przybylski, 2001). Antioxidants can be classified into two broad categories, namely primary and secondary ones. Primary antioxidants act by inhibiting the radical propagation stages in the triglyceride oxidation process (Eskin and Przybylski, 2001). Examples of primary antioxidants include butylated hydroxy anisole (BHA), tocopherols and a range of phenolics. Secondary antioxidants may act as oxygen scavengers, chelating agents and/or hydrogen donors to the primary antioxidants (Eskin and Przybylski, 2001). An example of secondary antioxidant could be ascorbic acid. Ascorbic acid acts by scavenging for oxygen or chelating pro-oxidant metal ions (Eskin and Przybylski, 2001).

Kapoor and Kapoor (1990) studied the effects of adding BHA, butylated hydroxy toluene and ascorbic acid to whole pearl millet flour on its shelf life. They found that addition of

these antioxidants resulted only in a slight decrease in the peroxide level in comparison to the control sample during storage. This indicates their ineffectiveness in preventing triglycerides deterioration. Another important issue is that the use of synthetic chemicals such as BHA has also been met with skepticism from consumers many of whom today demand food products without synthetic additives (Eskin and Przybylski, 2001).

1.2.9.7 Thermal Treatments

Heat energy application is a treatment that has been widely investigated with the aim of inactivating lipase in pearl millet. Thermal treatments that have been attempted include, hot air oven heating (Pruthi, 1981; Kapoor and Kapoor, 1990; Patel and Parameswaran, 1992; Chavan and Kachare, 1994; Arora *et al*, 2002) or boiling-water blanching (Palade *et al*, 1996; Chavan and Kachare, 1994) of pearl millet grain before milling as well as application of dry heat treatment to pearl millet flour at specific temperatures for specific durations.

1.2.9.7.1 Grain heat treatments

Chavan and Kachare (1994) heated pearl millet grain in a hot air oven at 50°C for 1 h; at 100°C for 10 min and also subjected the grain to boiling water (blanching) at 98°C for 30 s. The fat acidity during storage at ambient conditions for a month increased over 5-fold both in the flour of the control and flour of hot-air heated grain, whereas it remained almost unchanged in the flour of the blanched grain. Similar effects were also observed by Palade *et al* (1996). These authors also observed that unlike dry heat treatments, boiling-water blanching of dry whole pearl millet grains for 10 s effectively retarded the development of fat acidity in flour during a storage period of about a month at ambient conditions.

In the heat application to pearl millet grain studies, generally little emphasis was placed in determining the effect of these treatments on oxidative rancidity. However, Chavan and Kachare (1994) observed that no accumulation of peroxides occurred in oil extracted from either untreated or heat-treated samples during the same storage duration and conditions. In the absence of tests to measure secondary lipid oxidation products, these

findings are inconclusive. This is because the peroxides are intermediate products and thus may have broken down into secondary products.

Arora *et al* (2002) used a dry oven at $\sim 100^{\circ}\text{C}$ to heat dry pearl millet grain for 2 h and evaluated the extent of hydrolytic rancidity of the resulting flour during a one-month storage at ambient conditions. Fat acidity and free fatty acids increased during storage, though heat-treated grain flour increased by less than two-fold while the untreated grain flour increased at least four-fold.

Palade *et al* (1996) and Arora *et al* (2002) evaluated consumer acceptability of chapatti (roti) prepared from the flour of heat-treated whole pearl millet grain. Respectively, they conducted the sensory evaluations at intervals of five (Palade *et al*, 1996) and seven (Arora *et al*, 2002) days. The chapattis of flour of heat-treated grain remained sensorially acceptable during the entire one-month storage without any adverse effects on their acceptability by consumers, whereas those of the untreated grain flour were not acceptable after 10 days. These results show that the applied heat treatment before milling significantly improves the flour keeping quality for at least one month.

1.2.9.7.2 Flour heat treatment

Besides dry heat application to pearl millet grain before milling, some researchers have investigated the effect of dry heat application to the flour after milling. Whole pearl millet flour has been held in a dry oven at 100°C for 1 h (Kapoor and Kapoor, 1990) or 2 h (Patel and Parameswaran, 1992). For these treatments, there were significant, though not necessarily meaningful differences in fat acidity and peroxide values between heat-treated flour and unheated flour during same storage conditions. Kapoor and Kapoor (1990) reported a fat acidity value of about 3 g KOH kg^{-1} flour for the fresh untreated flour. After storage of 30 days at ambient conditions, the fat acidity value of the heat-treated and untreated flour increased to about 6 and $6.3 \text{ g KOH kg}^{-1}$ flour, respectively. The trend for peroxide value was similar. This indicates that subjecting the flour to dry heat treatment is not successful in inhibiting hydrolysis of triglycerides most probably by

lipase. This is presumably because the enthalpy of dry heat is lower relative to that of wet heat.

Generally, subjecting the grain to heat treatment to stabilise its flour during storage appears to be more effective in reducing lipase activity in pearl millet. Galliard (1999) has, however, cautioned that the use of heat to inactivate lipase may predispose triglycerides to oxidation by activating potential pro-oxidants and destroying antioxidants that may be present in the flour.

1.2.10 OTHER EFFECTS OF HEAT TREATMENT ON PEARL MILLET GRAIN

Heat treatments may also have other effects besides stabilising the lipids. Boiling for example could gelatinise the starch of pearl millet (Mousia, Edherly, Pandiella and Webb, 2004). Heat treatments especially toasting could also induce non-enzymatic browning reactions such as caramelisation and Maillard reaction (Bredie, Mottram, Hassel and Guy, 1998). These reactions could in turn introduce sensory flavours such as toasted, burnt, pop-corn, nutty and caramel-like (Bredie *et al*, 1998).

1.2.11 CONCLUSIONS

Pearl millet flour is not stable during storage. This is because it develops disagreeable sensory flavours. Pearl millet flour triglycerides deterioration results in aldehydes that contribute to these disagreeable sensory flavours. Urbanisation in developing countries such as Namibia appears to offer opportunities for value-added traditional food products that are quicker to cook. Thermal treatments have been applied to pearl millet to stabilise the flour. But only limited improvement in the flour keeping quality observed. Furthermore, there appears to be no thermal treatments applied to simultaneously stabilise and pre-cook the flour.

1.3 OBJECTIVES

To determine the effect of toasting, boiling and toasting then boiling of whole pearl millet grain on the lipid quality of its flour before and after storage for 3 months at prevailing ambient conditions.

To determine the effect of subjecting pearl millet grain to different thermal treatments on the degree of cook of its starch.

To determine the effect of the different thermal treatments and storage of flours of treated grain on the sensory quality of their whole pearl millet porridges.

To determine which of the flours of the thermally-treated grain makes a porridge preferred by consumers.

1.4 HYPOTHESES

It is expected that triglycerides of flour of thermally-treated whole pearl millet grain will not suffer from lipolysis and from subsequent enzymatic oxidation because the thermal treatments applied will denature both lipase and lipoxygenase. Denaturation of these enzymes will render them inactive. This will prevent both the lipolytic hydrolysis of triglycerides and subsequent lipoxygenase-catalysed oxidation of any de-esterified unsaturated fatty acids.

Boiling whole pearl millet grain will pre-cook the grain because heating the grain in water will gelatinise the starch, thereby reducing the time required to make porridge.

The sensory properties of porridges prepared using the flour of toasted grain will have pleasant sensory flavours. This is because toasting causes caramelisation and Maillard reactions that produce pleasant caramel and toasted flavours. Consequently, consumers will also show more preference for porridges prepared using flour of toasted whole pearl millet.

CHAPTER 2: RESEARCH

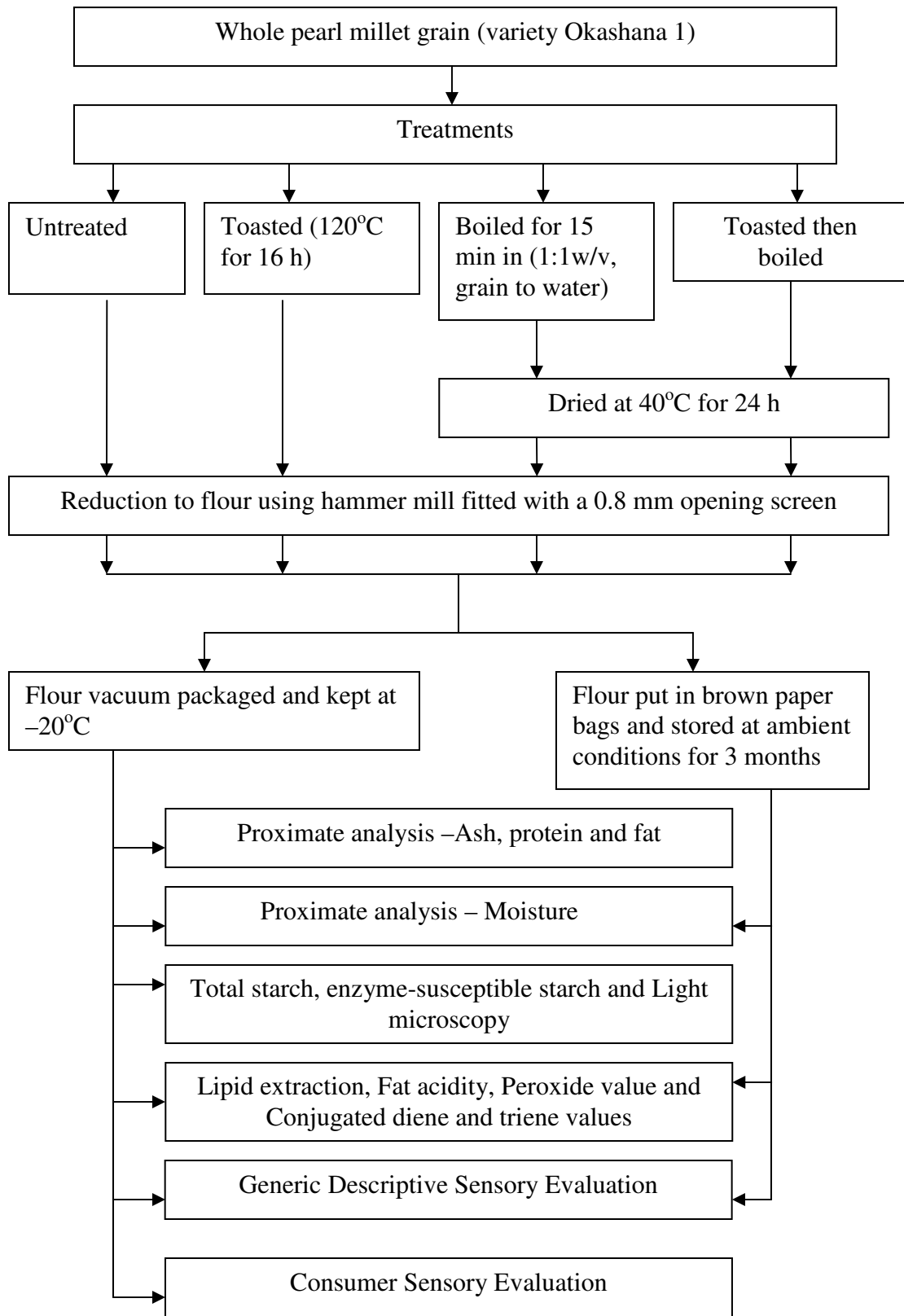


Figure 2.1: Experimental design for determining the effect of thermal treatments on whole pearl millet flour stability

2.1. Thermal treatments to preserve and pre-cook whole pearl millet flour

Abstract

Pearl millet flour is highly susceptible to the development of rancidity during storage. Urbanization has created a demand for pearl millet flour with longer shelf life and short cooking time. To try to prevent rancidity and pre-cook, pearl millet grain was subjected to the thermal treatments of toasting, boiling and toasting then boiling before milling. Fat acidity for flour from the untreated grain increased from 0.11 to 3.73 g KOH kg⁻¹ flour during 3 months storage, whereas wet thermally-treated samples showed no significant increase. Peroxide values of wet thermally-treated samples increased seven-fold, whereas that of flour from untreated grain decreased. This indicates that unsaturated fatty acid oxidation was non-enzymatic and that less peroxides were broken down for wet thermally-treated samples. Wet thermally-treated grains degree of cook was 40%, two times higher than that of all other samples. Descriptive sensory evaluation revealed that porridges of flour from untreated grain were associated with rancid off-flavours, whereas those of flours from thermally-treated grains were not. Consumers preferred the porridge prepared from flour of boiled grain. Thermal treatments can be applied to extend whole pearl millet flour shelf-life and the treatment of boiling can be used to produce pearl millet flour that cooks quicker.

Keywords: pearl millet; rancidity; thermal treatments; fat acidity; pre-cook; porridge

2.1 INTRODUCTION

Pearl millet (*Pennisetum glaucum* (L.) R. Br.) is a cereal crop cultivated by subsistence farmers in semi-arid parts of Africa and Asia, where it constitutes a major source of energy and protein for about 500 million people (ICRISAT and FAO, 1996). For example, in Namibia more than half (~600 000) of the population consumes pearl millet as a staple food, mainly as porridge. Rapid urbanization in developing countries such as Namibia appears to offer considerable opportunity for the development of value-added, convenience forms of traditional food products. A cooperative of subsistence farmers is in the process of developing a composite flour comprising locally grown pearl millet and cowpeas and would like it to be pre-cooked, thereby quicker to cook to reduce the time and fuel required to cook the porridge.

Pearl millet grain is small (3-15 mg) but has a proportionally larger germ than all other cereal grains, except perhaps maize (Taylor, 2004). Therefore, pearl millet tends to contain a higher content of triglycerides, which are rich in unsaturated fatty acids (Lai and Varriano-Marston, 1980a). Pearl millet flour is thus susceptible to the development of rancidity within a few days due to hydrolytic de-esterification of triglycerides and subsequent oxidation of the resulting de-esterified unsaturated fatty acids (Lai and Varriano-Marston, 1980b). These chemical changes are usually manifested as off-flavours during storage, especially under conditions of moderately high moisture and oxygen exposure. Various treatments have been applied to pearl millet to prevent this lipid deterioration including decorticating the grain (Abdelrahman, Hoseney and Varriano-Marston, 1983), use of antioxidants (Kapoor and Kapoor, 1990), application of dry heat to grain (Chavan and Kachare, 1994) or flour (Kapoor and Kapoor, 1990), acid soaking and hot-water blanching (Chavan and Kachare, 1994). However, only limited improvement in flour keeping quality was observed. Furthermore, there appears to have been no research that applied thermal treatments to pearl millet with a view of not only producing shelf-stable but also pre-cooked flour. The objective of this research was to develop a simple technique of both preserving and pre-cooking pearl millet flour for porridge-making.

2.2 MATERIALS AND METHODS

2.2.1 Pearl millet grain

About 50 kg of whole pearl millet grain (variety Okashana 1), harvested in 2004, was obtained from Omusati Farmers Cooperative in north-central Namibia. The grain was cleaned by sieving out small sand particles that could pass through a 0.5 mm opening sieve.

2.2.2 Grain treatment

The grain was divided into four samples of about 2 kg each for the four treatments. One sample was the control which was left untreated. The second sample was spread out (layers ~2 cm deep) on metal trays and placed in an oven set to 120°C and toasted for 16 h. The third sample was held in a pan of boiling water (1:1 grain to water, weight to volume basis) for 15 min. After boiling, the water was drained using a colander. Thereafter, the wet grain was laid out on solid steel trays in thin layers of less than 2 cm. The trays were then placed in a forced air circulation oven set at 40°C for drying for 24 h. The fourth sample was subjected to firstly toasting and then to boiling and drying, as described above. These four treatments are shown in Figure 2.1. Each treatment was replicated 3 times. The samples were milled to flour using an Alpine Augsburg universal hammer mill (Augsburg, Germany) fitted with a 0.8 mm opening screen.

From each independent replicate of the four treatments, appropriate amounts of flour were divided into two sets, fresh and stored flours. “Fresh flour” was vacuum packaged in polythene bags and kept at -20°C until analysis. Stored flour was put in brown paper bags. These bags were closed with an adhesive tape and stored at ambient conditions (average maximum and minimum temperatures approximately 25°C and 18°C) for 3 months until analysis.

2.2.3 Characterisation of pearl millet grain

Approved methods of the American Association of Cereal Chemists (2000) were used to determine moisture by the one-stage air oven drying, 103°C for 3 h (Method 44-15A), ash by combustion (Method 08-12) and fat by soxhlet extraction (Method 30-25). Protein content ($N \times 6.25$) was determined by combustion nitrogen analysis (LECO FP528 Protein/Nitrogen Analyser, St Joseph, USA).

2.2.4 Lipid extraction and quality analyses

Lipids were extracted using petroleum ether (boiling point, 40-60°C) as described by Viscidi, Dougherty, Briggs and Camire (2004). Fat acidity, peroxide values and UV measurements were conducted directly after the extraction. Approved methods of the American Association of the Cereal Chemists (2000) were used to determine fat acidity (Method 02-01A) and peroxide value (PV) (Method 58-16). Conjugated diene (absorbance at 232 nm) and triene (absorbance at 268 nm) values were determined according to the International Organization for Standardization, 3656 method (ISO, 1989).

2.2.5 Total and enzyme-susceptible starch

Total starch and starch hydrolysable by α -amylase without pre-gelatinisation was determined as described by Pelembe (1998). Starch hydrolysable by α -amylase without pre-gelatinisation expressed as a proportion of total starch gives an estimate of “degree of cook”.

2.2.6 Light microscopy

Flour samples were examined visually using light microscopy. Small amounts of sample were suspended in distilled water and observed using a magnification of 100 under direct transmitted and also under polarized light, and with and without iodine staining.

2.2.7 Descriptive sensory evaluation

Descriptive sensory evaluation of pearl millet porridges was conducted using the generic descriptive evaluation method of Lawless and Heymann (1998). Porridges were prepared

using the following whole pearl millet flour samples: fresh untreated; stored untreated; stored toasted; stored boiled and stored toasted then boiled. A suspension was prepared by mixing 1 part by weight of flour to 6 parts by volume of water. The suspension was immediately heated until it began to boil with constant stirring and was kept boiling for 3 min. The porridges were evaluated by a trained (6 h of training, each hour on a different day) panel of 9 judges (panelists) each in an evaluation booth. The panel consisted of three males and six female undergraduate and postgraduate students. Their ages were between 20 and 40 years. During the development of sensory descriptors, panelists were provided with the porridge samples in the sensory booths. They identified and described using their own words, the sensory differences between the porridges. The emphasis was on sensory differences, especially with regard to sensory attributes such as aroma, taste and flavour that can be influenced by lipid oxidation and non-enzymatic browning. With the facilitation of the panel leader, each panelist provided his/her descriptors. The panel leader wrote them down on a board for all to see. The panelists then developed and used 11 sensory descriptors (Section 2.3.3) in computerised forms. For each descriptor, the scoring of the perceived intensity was made on a 9-point number scale. This scale had verbal expressions (e.g. 1-attribute not intense and 9-attribute extremely intense) at the extreme ends. All five porridge samples were evaluated per session (1 h duration) in a completely randomised design. A glass of water was provided to each panelist for cleansing the palate before and in between tasting each porridge. The order of presentation of samples to panelists was also randomised within and between sessions. The evaluations were repeated 3 times. The first two evaluations were done on two consecutive days. The third was done one day after the second evaluation.

2.2.8 Consumer sensory evaluation

For consumer evaluation, 152 persons (86 women and 47 men (19 persons did not indicate their gender) of ages ranging between 18 and 45) for whom pearl millet was a staple food were recruited. The consumers were students and staff members at the University of Namibia-northern campus, Oshakati, Namibia. They were selected if they indicated that they consumed pearl millet porridge at least three times per week. Since it was intended that the pre-cooked flour would be a composite comprising cowpea flour in addition to pearl millet flour, black-eyed cowpea flour was also included. The cowpea was moisture conditioned in a ratio of 1 part by volume water to 2 parts by weight cowpea. Immediately thereafter, it was dehulled by hand. Dehulled cowpea was boiled for 25 min in a ratio of 1 part by weight cowpea to 4 parts by volume water. It was then sun-dried before hammer milling to a flour passing through 0.8 mm opening sieve. Cowpea flour was mixed with each of fresh flours of untreated pearl millet; toasted pearl millet; boiled pearl millet and toasted then boiled pearl millet. The composite flour comprised a ratio of 2 parts pearl millet flour to 1 part cowpea flour. Twenty grams sugar and 4 g salt were added to 200 g composite flour. Porridges were prepared by making a suspension of pearl millet/cowpea composite flour (224 g) in 1200 ml of water. The suspension was heated until it began to boil with constant stirring. It was kept boiling for 3 min. It was then removed from the heat source for serving. The samples were coded with random three-digit numbers. The order of presentation of samples to consumers was randomized. Consumers expressed their overall liking of each porridge using a 9-point hedonic scale ranging from 1 - Dislike very much to 9 - Like very much.

2.2.9 Statistical analysis

The effects of treatments on chemical properties and on individual sensory descriptors were determined using analysis of variance (ANOVA) and Fischer's least significant difference test (LSD, $p \leq 0.05$). The effects of panelists and evaluation sessions on the ratings of each descriptor were also determined. A perceptual map of the descriptive sensory descriptors (data for each descriptor averaged across the 9 trained panelists per evaluation session and then averaged across the triplicate sessions) was plotted using principal component analysis (PCA) of Statistica 7.0 (Statsoft Inc., Tulsa, OK).

Univariate analysis of the descriptive sensory evaluation showed significant differences among the samples for 9 of the 11 identified descriptors ($p \leq 0.05$). The two descriptors (uncooked/floury and fatty/greasy/oily flavours) that did not distinguish significantly ($p > 0.05$) among the samples were excluded from PCA analysis. The effect of gender and treatments on consumer liking of porridges were also analysed using ANOVA and Fischer's least significant difference test (LSD) ($p \leq 0.05$). In addition, the percentages of consumers who gave each porridge a rating of 3 and below, from 4 to 6 or 7 and above were plotted in a bar chart. To understand consumers' responses further, the liking ratings were analysed by k-means cluster analysis using Statistica 7.0. This method assigns rows (in this case consumers based on choosing observations (scores) that maximised initial-between cluster distances) with similar likings/dislikings for the four porridges to the same cluster. By means of PCA of the matrix of data, consisting of porridge samples (loadings) and consumers (ratings), the major variation within the liking data was identified in the porridges map and a consumer map.

2.3 RESULTS AND DISCUSSION

2.3.1 Effect of the treatments on the gross composition of pearl millet

Table 2.1 shows that the moisture contents of the fresh flours from the grains that were subjected to different thermal treatments were significantly lower ($p \leq 0.05$) than that of the fresh untreated sample. Of note is the 10-fold decrease in the moisture content of the sample that was subjected to toasting. This indicates that toasting caused a significant water loss from the grain. The moisture contents of the flours from the grains that were subjected to the different thermal treatments increased ($p \leq 0.05$) significantly during storage. Noteworthy is the nine-fold increase in the moisture content of sample that was toasted. This indicates that these flours picked up moisture from the storage atmosphere, presumably to reach equilibrium with the prevailing relative humidity. Nonetheless, the moisture contents of all the flours, both fresh and stored, were below the maximum moisture content limit (13%) for pearl millet flour recommended by FAO/WHO (1995). This is a maximum allowable standard quality acceptable for pearl millet flour intended for human consumption. The ash, fat, protein and total starch contents of the flours were not significantly ($p > 0.05$) affected by the different thermal treatments and were in the range reported in the literature (Taylor, 2004). The degree of cook showed a statistical significant increase ($p \leq 0.05$) of about two-fold for the wet thermally-treated pearl millet grains (boiled and toasted then boiled) compared to the untreated and toasted grains. This indicates a partial gelatinisation of the starch in the boiled and the toasted then boiled grains. Presumably, gelatinisation was only partial because there was limited amount of water that diffused into the grain to reach the endosperm.

Table 2.1: Effect of thermal treatments and storage on moisture and the effect of thermal treatments on ash, fat, protein, total starch and the degree of cook of starch of whole pearl millet flour¹

	Treatments			
	Untreated	Toasted	Boiled	Toasted then boiled
Moisture² (g kg⁻¹, as is)				
Fresh flour	90.3 ^c ±2.8	8.6 ^a ±4.6	67.8 ^c ±3.6	60.9 ^b ±2.1
Stored flour	87.1 ^e ±1.7	79.3 ^d ±2.7	82.1 ^d ±3.1	86.8 ^e ±5.3
Ash³ (fresh flour, g kg⁻¹, as is)	15.5 ^a ±1.2 (17.0)	16.1 ^a ±0.3 (16.2)	14.8 ^a ±2.2 (15.9)	14.4 ^a ±0.3 (15.4)
Fat³ (fresh flour, g kg⁻¹, as is)	50.9 ^a ±1.4 (56.0)	53.2 ^a ±0.0 (53.7)	48.8 ^a ±1.6 (52.3)	51.8 ^a ±2.1 (55.2)
Protein³ (fresh flour, g kg⁻¹, as is)	114.3 ^a ±5.8 (125.7)	119.7 ^a ±3.0 (120.6)	120.5 ^a ±4.3 (129.3)	119.5 ^a ±3.2 (127.3)
Total starch⁴ (fresh flour, g kg⁻¹)	708 ^a ±78	711 ^a ±48	711 ^a ±46	782 ^a ±13
Degree of cook⁴ (fresh flour, %)	19.3 ^a ±2.7	20.6 ^a ±3.2	37.3 ^b ±2.8	40.0 ^b ±2.7

¹All results are mean of three replicate experiments; mean±standard deviation (n = 3).

²Values with different letter superscripts in the block are significantly ($p \leq 0.05$) different from each other.

³Values with different letter superscripts in a row are significantly ($p \leq 0.05$) different from each other and values in parentheses are means (n = 3) expressed on dry basis, db.

⁴Values with different letter superscripts in a row are significantly ($p \leq 0.05$) different from each other.

Observation of the flour using direct transmitted light microscopy revealed that there were no obvious changes in physical appearance indicative of gelatinisation of starch granules between the untreated flours and the flours of wet thermally-treated grains. Under polarized light the starch granules in all the flours exhibited no obvious differences in terms of their birefringence (maltese) crosses, the appearance of which is related to starch granule semi-crystalline order (Hoseney, 1994). This indicates that there was qualitatively no significant loss of crystalline order in all the flours. Furthermore, when viewed with iodine staining, the starch granules in all the samples stained blue but not the solution. This indicates that little, if any, amylose had leached out of the starch granules. These observations support the degree of cook data that any gelatinisation that may have occurred was only partial.

2.3.2 Fat acidity, PV, conjugated diene and conjugated triene values

Table 2.2 shows that the fat acidity value of untreated grain was significantly higher ($p \leq 0.05$) by about a factor of 10 than those of the thermally-treated grains. This indicates increases of de-esterified fatty acids in the untreated grain, presumably caused by lipase hydrolysis of triglycerides during milling. The lower fatty acidity values of fresh thermally-treated grains than that of untreated grain indicates that there was lower level of de-esterified fatty acids in the thermally-treated grains than the untreated grain. This is presumably because thermal treatments had inhibited lipase before these grains were milled. The fat acidity values of untreated and toasted grains increased significantly ($p \leq 0.05$) during storage from 0.11 to 3.73 g kg⁻¹ and 0.01 to 0.69 g kg⁻¹, respectively. This indicates an increase of de-esterified fatty acids. This is presumably because of lipolysis and not because of thermal non-enzymatic hydrolysis. This is because untreated grain was not subjected to any thermal treatment and also no fat acidity increase occurred in the grains that were subjected to wet-thermal treatments, as described below. The fat acidity values of the boiled and the toasted then boiled pearl millet grains remained statistically the same ($p > 0.05$) during storage. This indicates that the triglycerides were not de-esterified in the wet thermally-treated grains during storage, presumably because wet-

thermal treatments inhibited lipase due to the higher specific enthalpy of wet heat than that of dry-thermal treatment of toasting. As discussed, the constant fat acidity values of wet thermally-treated samples during storage indicates that the increases in the fat acidity of the stored untreated and toasted flours could not have been a result of thermal non-enzymatic hydrolysis but most likely a result of lipolysis. These findings are similar to those of Chavan and Kachare (1994). These authors heated pearl millet grain in a hot air oven at 50°C for 1 h, at 100°C for 10 min and subjected the grain to boiling water (blanching) at 98°C for 30 s. The fat acidity increased over 5-fold both in the flour of the control and flour of hot-air heated grain, whereas it remained almost unchanged in the flour of the blanched grain during storage at ambient conditions for a month.

Table 2.2 also shows that of the fresh grain samples, only the toasted grain showed a statistically significantly ($p \leq 0.05$) lower PV than the untreated grain. This indicates that lower amounts of hydroperoxides were formed in the fresh toasted grain than in the fresh untreated grain, possibly because toasting can produce Maillard reaction products with antioxidant properties (Yoshimura, Iijima, Watanabe and Nakazawa, 1997), which probably scavenge radicals that initiate the formation of hydroperoxides, thereby preventing the formation of hydroperoxides. However, since peroxides are unstable intermediate lipid oxidation products (Eskin and Przybylski, 2001) this low amount observed may also indicate that some of the hydroperoxides formed had already broken down into secondary oxidation products. The PVs of the untreated and wet-thermally treated grains were not significantly different ($p > 0.05$). This indicates that there were same amounts of hydroperoxides formed in these grains. However, the PV of the untreated grain decreased significantly ($p \leq 0.05$) during storage, indicating a decrease of the hydroperoxides, presumably because the hydroperoxides broke down into secondary oxidation products (Eskin and Przybylski, 2001). The PV of the flour of toasted grain remained constant during storage. This may indicate that there was no further formation of hydroperoxides, possibly because the formation of hydroperoxides was prevented by Maillard reaction products with radical scavenging antioxidant properties (Yoshimura *et al*, 1997). The PVs of the flours of the boiled and the toasted then boiled grain showed a

statistically significant increase ($p \leq 0.05$) of about seven-fold during storage. This indicates that there was further formation and accumulation of hydroperoxides during storage. These higher PVs may also indicate a delay in the initiation step of oxidation perhaps because there were less de-esterified fatty acids, as indicated by the small fat acidity values, for oxidation to begin. In addition, it could also be that less hydroperoxides disintegrated into secondary oxidation products for these flour samples. Assuming that the wet thermal treatments were effective, in inactivating lipoxygenase that may have been present in the grains, then the formation of hydroperoxides in these samples indicates that the oxidation of unsaturated fatty acids occurred non-enzymatically.

A possible explanation for the non-enzymatic oxidation (autoxidation) in wet thermally-treated samples could be that the wet thermal treatments partially leached out the phenolic compounds that have antioxidant properties. These compounds would include flavonoids and p-hydroxybenzoic, caffeic, syringic, coumaric and ferulic acids that are naturally present in pearl millet grain (Serna-Saldivar and Rooney, 1995), which can scavenge for radicals needed for the initiation step of autoxidation (Eskin and Przybylski, 2001). It should, however, be noted that addition of synthetic antioxidants such as butylated hydroxyanisole (BHA), as stated in section 1.2.9.6 have not been shown to be effective in preventing oxidation of pearl millet flour lipids (Kapoor and Kapoor, 1990). The accumulation of hydroperoxides in the flours of wet-thermally treated grain could be due to the antioxidant properties of reductones and melanoidins, which are formed through thermal non-enzymatic Maillard and caramelisation reactions. The reductones and melanoidins can chelate pro-oxidant metal ions such as copper and iron (Yoshimura *et al*, 1997), which are known to catalyse the decomposition of hydroperoxides into secondary oxidation products (Eskin and Przybylski, 2001).

The conjugated diene values of wet thermally-treated grains were significantly higher ($p \leq 0.05$) than that of the untreated grain (Table 2.2). The conjugated diene values for all the samples showed significant increases ($p \leq 0.05$) during storage. Of note are about 3-fold increases in the conjugated diene values in the flours of the boiled and the toasted then boiled grains. Like PV, conjugated diene values indicate the formation of hydroperoxides

(Rossell, 1999). Thus the high conjugated diene values for the wet thermally-treated samples indicate that hydroperoxides were formed and probably less decomposed into secondary oxidation products relative to those of untreated samples. As with the high PVs of the flours of wet thermally-treated grains, this also indicates that non-enzymatic oxidation of unsaturated fatty acids occurred in the flours of the wet thermally-treated grains. Regarding conjugated trienes, only the fresh toasted then boiled grain showed a significantly higher ($p \leq 0.05$) conjugated triene value than the fresh untreated grain. During storage, the conjugated triene values for the flours of wet thermally-treated grain were significantly higher ($p \leq 0.05$) than that of the untreated flour. Conjugated triene values measures primary conjugated linolenic acid hydroperoxide and secondary oxidation products such as di-ketones (Rossell, 1999). These compounds are long-chain, tasteless and odourless. The higher conjugated triene value for the wet thermally-treated samples indicates that more conjugated linolenic acid hydroperoxide and di-ketones occurred in these samples than in any other samples. This indicates that there was a higher accumulation of these primary and secondary oxidation products. This accumulation in turn indicates that there was less disintegration of long chain primary and oxidation products into final oxidation products, especially in the flours of wet thermally-treated grain. These final products are often volatile carbonyls such as hexanal, octanal and nonanal that impart sensory flavours (Malcolmson, Vaisey-Genser, Przybylski, Ryland, Eskin and Armstrong, 1996), which may be disagreeable to consumers when eating food products containing lipids, especially those rich in unsaturated de-esterified fatty acids.

Table 2.2: Effect of thermal treatments and storage on fat acidity, peroxide value and conjugated diene and triene values of whole pearl millet flour¹

	Treatments			
	Untreated	Toasted	Boiled	Toasted then boiled
Fat acidity (g KOH kg⁻¹ flour, db)				
Fresh flour	0.11 ^b ±0.02	0.01 ^a ±0.01	0.00 ^a ±0.00	0.01 ^a ±0.01
Stored flour	3.73 ^d ±0.06	0.69 ^c ±0.15	0.04 ^{ab} ±0.04	0.05 ^{ab} ±0.04
Peroxide value (milliequivalents peroxides kg⁻¹ oil)				
Fresh flour	4.82 ^b ±0.22	1.39 ^a ±0.32	3.16 ^{ab} ±0.48	3.05 ^{ab} ±0.61
Stored flour	2.46 ^a ±1.60	2.20 ^a ±1.51	21.60 ^c ±3.54	21.94 ^c ±3.47
Conjugated diene values (g kg⁻¹ oil)				
Fresh flour	14.0 ^a ±1.5	16.5 ^{ab} ±1.2	18.5 ^{bc} ±1.9	18.9 ^{bc} ±0.9
Stored flour	21.8 ^{cd} ±1.2	25.0 ^d ±1.8	53.5 ^e ±7.4	52.6 ^e ±4.5
Conjugated triene values (g kg⁻¹ oil)				
Fresh flour	6.5 ^a ±0.6	7.2 ^{ab} ±0.3	6.9 ^{ab} ±0.7	9.1 ^d ±0.9
Stored flour	7.7 ^{bc} ±1.0	8.5 ^{cd} ±1.0	9.1 ^d ±1.8	10.8 ^e ±1.1

¹All results are mean of three replicate experiments; mean±standard deviation (n = 3). For the same parameter, values with different letter superscripts in a block are significantly (p ≤ 0.05) different from each other.

2.3.3 Descriptive sensory evaluation

The preliminary descriptors identified are given in Table 2.3. By elimination and/or addition, a final list of descriptors was agreed upon through consensus by the panelists. Panelists then created definitions to agree on the meaning of each descriptor they generated (Table 2.4).

Table 2.3: Preliminary descriptors identified by the sensory panel to describe the sensory properties of pearl millet porridges

Aroma	Taste/Flavour	After taste
Millet aroma	Peanut flavour	Aftertaste
Raw pork aroma	Sour taste	Spoiled aftertaste
Wet flour aroma	Nice and tasty flavour	Bitter aftertaste
Dirty dishwashing cloth aroma	Malt flavour	Sour aftertaste
General bad smell	Burnt flavour	Lingering aftertaste
Sweet aroma	Salty taste	Terrible aftertaste
Sourish aroma	Bitter taste	Watery aftertaste
Fruity aroma	Pleasant flavour	
Rancid aroma	Bland flavour	
Wheat-like aroma	Watery flavour	
Sorghum aroma	Sorghum flavour	
Bland aroma	Oily/Rancid flavour	
Uncooked biscuit aroma	Nut flavour	
Cooked/Uncooked porridge aroma	Nutritious flavour	
Burnt aroma	Floury/uncooked flavour	
Earthy aroma	Oily/greasy flavour	
Oily aroma	Spoiled flavour	
	Wild flavour	

Table 2.4: Descriptors and definitions developed and used by the trained sensory panel to describe the sensory properties of pearl millet porridges

Sensory descriptor	Definition
Cooked porridge aroma	Aroma associated with cooked porridge
Burnt aroma	Aroma associated with blackened/acrid carbohydrates e.g. burnt toast
Rancid aroma	Aroma associated with overused off-sunflower cooking oil
Soapy/Dirty dishwashing cloth aroma	Aroma associated with a dirty dishwashing cloth
Sweet/Fruity aroma	Aroma associated with caramelized sugar
Bitter taste	Taste on tongue stimulated by solutions of caffeine, quinine and certain other alkaloids
Fatty/Greasy/Oily flavour	A flavour perception of presence of cooking oil in a porridge
Peanut/Toasted flavour	Flavour of boiled or roasted peanuts
Uncooked/Floury flavour	Flavour associated with uncooked but wetted flour
Rancid flavour	Flavour associated with overused off-sunflower cooking oil
Bitter aftertaste	Lingering bitter taste after swallowing the porridge

These descriptors represent aroma, taste, flavour and aftertaste sensory attributes. Some of the sensory characteristics identified such as rancid aroma, soapy aroma and rancid flavour are normally associated with unpleasant or disagreeable off-flavours in lipid foods (Malcolmson *et al*, 1996). For the sensory quality of oat groats, Molteberg, Solheim, Dimberg and Frolich (1996) also found that rancid odour and flavour and a bitter taste and aftertaste sensory attributes, correlated negatively with the apparently pleasant sensory characteristics such as sweet and toasted flavours in cereal products. Cooked porridge aroma, sweet/fruitful aroma and peanut/toasted flavours are normally associated with pleasant Maillard reaction flavours (Angerosa, Servili, Selvaggini, Taticchi, Esposto and Montedoro, 2004). When characterising the sensory profile of cooked oatmeal, Lapvetelainen and Rannikko (2000) used the terms toasted, sweet, cereal and chemical for the odour and flavour, which are similar to those developed and used in this study.

When the porridges were evaluated there was an effect of panelist on the rating of each descriptor. This was mainly because some panelists tended to just use one side of the 9-point hedonic scale. Therefore not all panelists scored the porridges the same, on average, compared with each other. Nevertheless, the trend of scores for each porridge was generally similar between the panelists. The effect of panelist on descriptive sensory rating of the bitter taste shown in Table 2.5 to illustrate this trend.

Table 2.5: Effect of panelist and different thermal treatments and storage of flours of whole pearl millet grain on the bitter taste ratings of their porridges by trained panelists

Panelist ¹	Treatment					Effect of panelist ³
	Fresh Untreated ²	Stored Untreated ²	Stored Toasted ²	Stored Boiled ²	Stored Toasted then Boiled ²	
Panelist 1	1.3 ^{ab} ±0.6	7.7 ^k ±0.6	2.0 ^{abcd} ±1.0	1.0 ^a ±0.0	1.7 ^{abc} ±0.6	2.7 ^a ±2.6
Panelist 2	7.7 ^k ±0.6	7.3 ^{jk} ±1.2	5.3 ^{efghijk} ±2.5	3.7 ^{abcdefg} ±0.6	4.0 ^{bcdefgh} ±2.0	5.6 ^{bc} ±2.2
Panelist 3	2.3 ^{abcd} ±1.5	7.0 ^{ijk} ±1.0	4.3 ^{cdefghi} ±1.2	2.7 ^{abcde} ±1.2	2.3 ^{abcd} ±0.6	3.7 ^a ±2.1
Panelist 4	1.0 ^a ±0.0	6.3 ^{ghijk} ±4.6	4.7 ^{defghij} ±4.0	1.0 ^a ±0.0	4.0 ^{bcdefgh} ±4.4	3.4 ^a ±3.6
Panelist 5	4.0 ^{bcdefgh} ±0.0	6.0 ^{efghijk} ±1.0	3.3 ^{abcdef} ±0.6	1.0 ^a ±0.0	3.0 ^{abcde} ±2.0	3.5 ^a ±1.9
Panelist 6	7.7 ^k ±1.2	8.0 ^k ±1.7	8.0 ^k ±1.0	3.0 ^{abcde} ±1.0	2.7 ^{abcd} ±1.5	5.9 ^c ±2.8
Panelist 7	7.0 ^{ijk} ±1.7	6.7 ^{hijk} ±1.2	3.0 ^{abcde} ±2.0	1.3 ^{ab} ±0.6	1.3 ^{ab} ±0.6	3.9 ^{ab} ±2.8
Panelist 8	5.3 ^{efghijk} ±2.1	6.7 ^{hijk} ±0.6	3.7 ^{abcdefg} ±1.2	1.0 ^a ±0.0	2.7 ^{abcde} ±2.1	3.9 ^{ab} ±2.4
Panelist 9	3.7 ^{abcdefg} ±0.6	4.0 ^{bcdefgh} ±2.6	3.3 ^{abcdef} ±2.1	1.0 ^a ±0.0	1.0 ^a ±0.0	2.6 ^a ±1.9

¹Data are means ± standard deviation across the three evaluation sessions per panelist for each porridge. Values in the block with different letter superscripts are significantly different ($p \leq 0.05$) from each other.

²Data are means ± standard deviation across the three evaluation sessions. Values in the column with different letter superscripts are significantly different ($p \leq 0.05$) from each other.

³Data are means ± standard deviation across the three evaluation sessions and then meaned across all the porridges. Values in the column with different letter superscripts are significantly different ($p \leq 0.05$) from each other.

2.3.3.1 Effect of evaluation sessions and thermal treatments and storage on the ratings for sensory descriptors

The effect of evaluation sessions and thermal treatments and storage on the ratings for sensory descriptors are given in Table 2.6 to Table 2.16. There were no significant differences ($p > 0.05$) between evaluation sessions with any of the sensory descriptors (Tables 2.6 to 2.16). This indicates that the panelists were not overworked and no fatigue set in. The cooked porridge aroma was generally rated significantly higher ($p \leq 0.05$) in the porridges that were prepared using flours of pearl millet grain that were subjected to different thermal treatments than those prepared using fresh and stored untreated flours (Table 2.6). Cooked porridge aroma is apparently often associated with volatile compounds such as 2-methyl-propanal, which is produced during the early stages of non-enzymatic reactions in cereals (Angerosa *et al*, 2004). Because more Maillard browning and caramelisation reactions took place during the application of thermal treatments and additionally during cooking the porridge for the flours of thermally-treated grain, this indicates that these were more cooked than those prepared using flours from untreated grain. For the untreated flours, non-enzymatic Maillard and caramelisation reactions took place only once during porridge-making. Burnt aroma was rated significantly higher ($p \leq 0.05$) in the porridge of flour of toasted pearl millet grain than in the other porridges (Table 2.7). This indicates that the toasting treatment was excessive and burnt some of the grain. Rancid aroma was rated significantly higher ($p \leq 0.05$) in the porridge of fresh untreated flour than in the rest of the porridges (Table 2.8). Similarly, soapy/dirty dishwashing cloth aroma was rated significantly higher ($p \leq 0.05$) in the porridges of fresh and stored untreated flours than in the porridges of flours of thermally treated pearl millet grain (Table 2.9). The rancid and soapy aromas are mainly associated with volatile secondary products of lipid oxidation (Malcolmson *et al*, 1996). In particular, rancid aroma could be attributed to the presence of volatile hexanal and/or heptanal (Malcolmson *et al*, 1996). Some of the secondary oxidation products associated with the soapy aroma are octanal, nonanal and/or decanal (Angerosa *et al*, 2004). In lipid foods, all these aldehydes are secondary oxidation products of unsaturated fatty acids (Angerosa *et al*, 2004). It is significant that the sensory perception of soapy and rancid aromas was

almost absent in porridges of flours of thermally-treated grain. As with the conjugated diene and triene values (Table 2.2), this also indicates that there was little or no formation of small volatile aldehydes in the flours of thermally-treated grain. Rancid flavour, like soapy aroma, was rated significantly higher ($p \leq 0.05$) in the porridges prepared using fresh and stored untreated flours than in the porridges of flours of pearl millet grain that were subjected to the different thermal treatments (Table 2.10). Rancid flavour is presumably due to a complex perception of secondary oxidation products of unsaturated fatty acids. Sweet/fruity aroma was rated significantly higher ($p \leq 0.05$) in the porridges prepared using flours of pearl millet grain that was subjected to a toasting treatment (Table 2.11). The sweet/fruity aroma can be presumed to be a result of non-enzymatic Maillard and caramelisation reactions (Parker, Hassell, Mottram and Guy, 2000). Some of the compounds associated with this sensory note are 2-furfuryl alcohol, 2-methylfurfural, 2,6-dimethylpyrazine and acetylpyrazine (Fors and Schlich, 1989). In general, the perception of these volatile compounds is regarded as pleasant (Gutierrez-Rosales, Rios and Gomez-Rey, 2003). Bitter taste was rated significantly lower ($p \leq 0.05$) in the porridge prepared using flour of wet thermally-treated grain than in the rest of the porridges (Table 2.12). Generally, it is phenolic compounds that cause a bitter taste in most foods (Gutierrez-Rosales *et al*, 2003). Bangar, Bhite, Kachare and Chavan (1999), claimed that peroxidase in pearl millet enzymatically oxidized phenolics (presumably C-glycosyl flavones) to apigenin-like phenolic aglycones, which apparently gave a bitter taste and a mousy odour. Since the bitter taste was perceived to be low in porridges of flours of wet thermally-treated grain, wet thermal treatment presumably prevented the formation of bitter-causing compounds by inactivating the peroxidases. Bitter aftertaste, like bitter taste, was rated significantly lower ($p \leq 0.05$) in the two porridges prepared using flours of pearl millet grain that were subjected to a wet-thermal treatment than in the other porridges (Table 2.13). This aftertaste could be linked to the compounds that caused the bitter taste. The fatty/greasy/oily flavour was rated statistically the same among all the porridges (Table 2.14). Because there was no cooking oil added during cooking, this is simply a reflection of the inherent oil content ($\sim 51 \text{ g kg}^{-1}$ db, of whole grain flour) of pearl millet in all the porridges. Peanut/toasted flavour was rated significantly lower ($p \leq 0.05$) in the porridges prepared using fresh and stored untreated

flours than in the porridges of flours from grain that had been subjected to the various thermal treatments (Table 2.15). The peanut/toasted flavour, like the sweet/fruity aroma, could also be associated with Maillard and caramelisation products such as 2-furfuryl alcohol, 2-methylfurfural, 2,6-dimethylpyrazine and acetylpyrazine (Parker *et al*, 2000). Like the fatty/greasy/oily flavour, the uncooked/floury flavour was rated statistically the same among all the porridges (Table 2.16). The value was low in all cases. This suggests that all the porridges were cooked.

Table 2.6: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the cooked porridge aroma ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	2.4 ^a ±1.1	3.8 ^{abc} ±2.1	5.9 ^{cd} ±2.2	5.4 ^{cd} ±2.2	5.9 ^{cd} ±2.5	4.7 ^a ±2.4
Session 2	4.3 ^{abc} ±2.8	2.8 ^{ab} ±1.5	4.7 ^{bcd} ±2.4	6.3 ^d ±2.2	4.7 ^{bcd} ±2.9	4.6 ^a ±2.6
Session 3	4.1 ^{abc} ±2.5	3.9 ^{abc} ±2.1	4.4 ^{abcd} ±2.7	5.2 ^{cd} ±2.5	4.9 ^{bcd} ±2.8	4.5 ^a ±2.4
Effect of treatment ³	3.6 ^a ±2.3	3.5 ^a ±1.9	5.0 ^b ±2.4	5.7 ^b ±2.3	5.1 ^b ±2.7	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.7: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the burnt aroma ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	1.2 ^a ±0.7	1.4 ^{ab} ±0.9	3.7 ^{cde} ±3.3	2.8 ^{abcd} ±2.8	3.4 ^{bcde} ±3.0	2.5 ^a ±2.5
Session 2	1.6 ^{abc} ±0.9	2.7 ^{abcd} ±2.8	5.3 ^e ±3.1	1.4 ^{ab} ±0.7	2.1 ^{abc} ±2.1	2.6 ^a ±2.5
Session 3	1.8 ^{abc} ±1.4	2.2 ^{abc} ±2.7	4.7 ^{de} ±3.0	1.8 ^{abc} ±1.4	3.0 ^{abcd} ±2.5	2.7 ^a ±2.5
Effect of treatment ³	1.5 ^a ±1.0	2.1 ^{ab} ±2.3	4.6 ^c ±3.1	2.0 ^{ab} ±1.9	2.9 ^b ±2.6	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.8: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the rancid aroma ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	4.2 ^c ±2.6	3.7 ^{bc} ±2.2	2.8 ^{abc} ±2.2	2.9 ^{abc} ±2.1	1.9 ^{ab} ±1.5	3.1 ^a ±2.2
Session 2	3.7 ^{bc} ±2.7	3.3 ^{abc} ±2.2	1.6 ^a ±0.7	2.4 ^{abc} ±2.4	3.2 ^{abc} ±2.4	2.8 ^a ±2.2
Session 3	4.1 ^c ±2.1	2.8 ^{abc} ±2.0	2.1 ^{ab} ±2.1	3.0 ^{abc} ±1.4	2.3 ^{abc} ±1.7	2.9 ^a ±1.9
Effect of treatment ³	4.0 ^b ±2.4	3.3 ^{ab} ±2.1	2.1 ^a ±1.8	2.8 ^a ±1.9	2.5 ^a ±1.9	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.9: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the soapy/dirty dishwashing cloth aroma ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	6.9 ^f ±2.5	5.1 ^{ef} ±2.8	1.9 ^{ab} ±1.8	3.3 ^{abcde} ±2.8	1.3 ^a ±0.5	3.7 ^a ±3.0
Session 2	4.6 ^{cde} ±3.6	5.1 ^{ef} ±2.8	1.4 ^a ±1.0	2.6 ^{abc} ±2.3	2.0 ^{ab} ±1.1	3.1 ^a ±2.7
Session 3	4.8 ^{def} ±3.0	3.8 ^{bcde} ±3.0	1.8 ^{ab} ±2.3	2.8 ^{abcd} ±2.0	1.7 ^{ab} ±1.4	3.0 ^a ±2.6
Effect of treatment ³	5.0 ^b ±3.1	4.7 ^b ±2.8	1.7 ^a ±1.8	2.9 ^a ±2.3	1.7 ^a ±1.1	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.10: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the rancid flavour ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	4.4 ^d ±2.9	3.8 ^{abcd} ±2.7	3.0 ^{abcd} ±2.3	2.4 ^{abcd} ±2.2	2.6 ^{abcd} ±2.2	3.2 ^a ±2.5
Session 2	4.1 ^{bcd} ±2.8	4.3 ^{cd} ±3.0	2.2 ^{abc} ±1.6	2.1 ^{ab} ±1.4	2.8 ^{abcd} ±2.3	3.1 ^a ±2.4
Session 3	4.2 ^{bcd} ±2.4	4.3 ^{cd} ±2.9	3.0 ^{abcd} ±2.7	2.2 ^{abc} ±1.7	1.8 ^a ±1.7	3.1 ^a ±2.5
Effect of treatment ³	4.3 ^b ±2.6	4.1 ^b ±2.7	2.7 ^a ±2.2	2.3 ^a ±1.7	2.4 ^a ±2.1	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.11: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the sweet/fruity aroma ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	1.6 ^{abc} ±1.3	2.6 ^{abcde} ±2.7	3.2 ^{bcdef} ±2.7	1.4 ^{ab} ±1.0	3.3 ^{cdef} ±2.5	2.4±2.2 ^a
Session 2	2.1 ^{abcd} ±1.8	1.6 ^{abc} ±1.0	4.3 ^{ef} ±3.0	2.4 ^{abcd} ±1.7	4.7 ^f ±2.7	3.0±2.4 ^a
Session 3	1.2 ^a ±0.4	1.4 ^{ab} ±0.9	3.4 ^{def} ±2.4	2.1 ^{abcd} ±1.3	3.0 ^{abcdef} ±1.9	2.2±1.7 ^a
Effect of treatment ³	1.6 ^a ±1.3	1.9 ^a ±1.7	3.7 ^b ±2.6	2.0 ^a ±1.4	3.7 ^b ±2.4	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.12: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the bitter taste ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh	Stored	Stored Toasted		Stored Toasted	
	Untreated	Untreated	Stored Toasted	Stored Boiled	then Boiled	
Session 1	4.6 ^{def} ±3.3	6.9 ^g ±1.9	3.9 ^{bcd} ±2.2	1.6 ^a ±1.0	3.4 ^{abcd} ±2.8	4.1 ^a ±2.9
Session 2	4.3 ^{cd} ±2.3	6.4 ^{efg} ±2.3	4.4 ^{de} ±2.2	1.9 ^{ab} ±1.3	2.3 ^{abc} ±1.4	3.9 ^a ±2.5
Session 3	4.4 ^{de} ±2.7	6.6 ^{fg} ±2.1	4.2 ^{cd} ±2.8	1.8 ^a ±1.2	1.8 ^a ±0.8	3.8 ^a ±2.7
Effect of treatment ³	4.4 ^b ±2.7	6.6 ^c ±2.0	4.2 ^b ±2.4	1.7 ^a ±1.1	2.5 ^a ±1.9	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.13: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the bitter aftertaste ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	4.8 ^{cde} ±3.2	6.4 ^e ±2.1	4.1 ^c ±2.9	2.0 ^{ab} ±1.1	2.8 ^{abc} ±2.0	4.0 ^a ±2.8
Session 2	4.1 ^c ±2.6	6.2 ^{de} ±2.2	4.0 ^{bc} ±2.3	1.7 ^a ±1.3	2.0 ^{ab} ±1.1	3.6 ^a ±2.5
Session 3	4.2 ^{cd} ±2.7	6.8 ^e ±1.9	3.2 ^{abc} ±3.1	1.6 ^a ±1.0	2.0 ^{ab} ±1.0	3.6 ^a ±2.8
Effect of treatment ³	4.4 ^b ±2.7	6.5 ^c ±2.0	3.8 ^b ±2.7	1.7 ^a ±1.1	2.3 ^a ±1.4	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.14: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the fatty/greasy/oily flavour ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	3.8 ^{ab} ±2.9	4.9 ^b ±2.9	2.9 ^{ab} ±2.7	3.3 ^{ab} ±2.1	3.8 ^{ab} ±2.7	3.7 ^a ±2.7
Session 2	2.8 ^{ab} ±1.7	2.1 ^a ±1.8	3.8 ^{ab} ±2.9	3.3 ^{ab} ±2.5	4.1 ^{ab} ±2.8	3.2 ^a ±2.4
Session 3	4.2 ^{ab} ±2.8	4.0 ^{ab} ±2.7	3.9 ^{ab} ±2.6	3.6 ^{ab} ±2.7	4.3 ^{ab} ±2.8	4.0 ^a ±2.6
Effect of treatment ³	3.6 ^a ±2.5	3.7 ^a ±2.7	3.5 ^a ±2.7	3.4 ^a ±2.4	4.1 ^a ±2.7	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.15: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the peanut/toasted flavour ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	1.2 ^a ±0.4	1.2 ^a ±0.4	3.4 ^{cde} ±2.6	2.7 ^{abcde} ±1.8	3.6 ^{de} ±2.9	2.4 ^a ±2.1
Session 2	1.4 ^{ab} ±1.0	1.1 ^a ±0.3	2.0 ^{abcd} ±1.1	3.3 ^{cde} ±2.7	3.9 ^e ±2.7	2.4 ^a ±2.1
Session 3	1.7 ^{abc} ±1.1	1.2 ^a ±0.7	3.2 ^{bcde} ±2.1	3.2 ^{bcde} ±2.6	4.2 ^e ±2.7	2.7 ^a ±2.1
Effect of treatment ³	1.4 ^a ±0.9	1.2 ^a ±0.5	2.9±2.1 ^b	3.1 ^b ±2.3	3.9 ^b ±2.7	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

Table 2.16: Effect of evaluation sessions and different thermal treatments and storage of flours of whole pearl millet grain on the uncooked/floury flavour ratings of their porridges by trained panelists

Sessions ¹	Treatment					Effect of evaluation session ²
	Fresh Untreated	Stored Untreated	Stored Toasted	Stored Boiled	Stored Toasted then Boiled	
Session 1	3.3 ^a ±2.6	3.4 ^a ±3.0	4.0 ^a ±2.5	3.4 ^a ±3.0	3.3 ^a ±2.5	3.5 ^a ±2.6
Session 2	3.6 ^a ±2.2	2.7 ^a ±2.7	3.1 ^a ±2.7	3.2 ^a ±3.2	2.1 ^a ±1.5	2.9 ^a ±2.4
Session 3	3.0 ^a ±3.0	3.1 ^a ±2.7	3.8 ^a ±2.7	3.3 ^a ±2.8	3.4 ^a ±2.4	3.3 ^a ±2.6
Effect of treatment ³	3.3 ^a ±2.6	3.1 ^a ±2.7	3.6 ^a ±2.6	3.3 ^a ±2.9	3.0 ^a ±2.2	

¹Data are means ± standard deviation across the nine trained panelists per evaluation session for each porridge. Values in the block with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

²Data are means ± standard deviation across the nine trained panelists and then meaned across all the porridges per each evaluation session. Values in the column with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

³Data are means ± standard deviation across the nine trained panelists and then meaned across the three evaluation sessions. Values in the row with different letter superscripts are significantly ($p \leq 0.05$) different from each other.

2.3.3.2 Principal component analysis (PCA) of descriptive sensory data

Principal component 1 and 2 (PC 1 and PC 2) described about 96% of the variance (Figure 2.2). According to Destefanis, Barge, Brugiapaglia and Tassone, 2000) variables close together in the loading plot are positively correlated, while variables lying opposite to each other are negatively correlated. Correlations for the porridges showed that the porridges prepared from untreated flours and those prepared from flours of thermally treated grain were lying opposite to each other (Figure 2.2A). This indicates that they were negatively correlated. The sensory descriptors, sweet/fruity, burnt and cooked porridge aromas, peanut/toasted flavour were opposite to rancid and soapy/dirty dishwashing cloth aromas, rancid flavour and bitter taste and aftertaste (Figure 2.2B). This indicates that these descriptors were negatively correlated. Porridges prepared from fresh and stored untreated flour were associated with rancid and soapy/dirty dishwashing cloth aromas. They were also associated with a rancid flavour. As discussed, these sensory characteristics indicate the presence of secondary products of unsaturated fatty acid oxidation. In terms of taste, these samples were associated with bitter taste. Additionally, they were also associated with leaving a bitter aftertaste in the mouth. The porridges prepared from flours of thermally-treated grain were not associated with rancid and soapy/dirty dishwashing cloth aromas, rancid flavour and bitter taste and aftertaste. This indicates the absence of secondary oxidation of unsaturated fatty acids. The porridge prepared from flour of toasted grain was associated with burnt and sweet/fruity aromas. The porridge prepared from flour of boiled grain was associated with cooked porridge aroma. These associations support the chemical data that thermal treatments inhibited lipolysis, thereby improving the storage life of whole pearl millet flour. These associations also indicate that thermal treatments produced sensory notes in pearl millet grain that are generally regarded as pleasant (Angerosa *et al*, 2004).

Figure 2.2: Effects of the thermal treatments and storage on sensory attributes of pearl millet flour. Plot of the first two principal component loading vectors of the porridges of the flours (A) and of the ratings of sensory descriptors of the porridges of the flours (B). M (O) = porridge of fresh untreated flour, M (3) = porridge of stored untreated flour, TM (3) = porridge of stored toasted flour, BM (3) = porridge of stored boiled flour, TBM (3) = porridge of stored toasted then boiled flour.

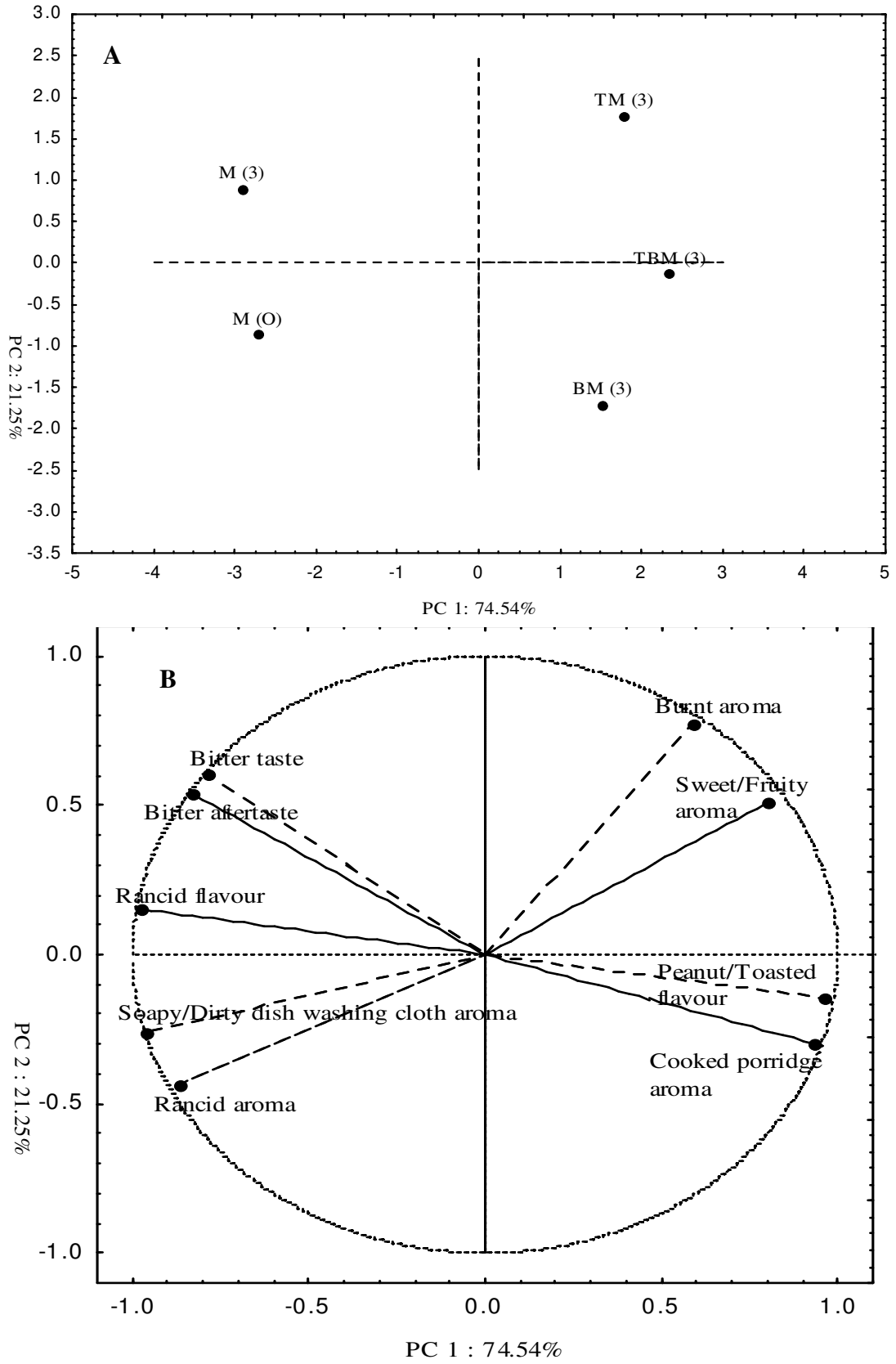


Figure 2.2

2.3.4 Consumer sensory evaluation

The porridge prepared using flour of boiled grain and that prepared using flour of toasted grain were given statistically significant higher ratings ($p \leq 0.05$) than the porridge prepared from untreated flour (Table 2.17). This indicates an overall slight preference for the porridges prepared using flour of boiled grain and flour of toasted grain compared to the porridge of the untreated flour. The gender of consumers did not have significant effect ($p > 0.05$) on consumer liking ratings. It is important to note that the mean data in Table 2.17 do not highlight diverse consumer likings. Therefore, to try to understand consumer evaluation results further, frequencies, PCA and k-cluster analysis of consumers' ratings on 9-point hedonic scale for the porridges were performed.

Table 2.17: The effects of gender of consumers and treatments of pearl millet grain on consumer liking ratings of pearl millet and cowpea composite porridges¹

Gender	Treatments ²				Effect of gender ³
	Untreated	Toasted	Boiled	Toasted then Boiled	
Female (n = 86)	4.5 ^{abc} ±2.6	5.1 ^{bcde} ±2.8	5.4 ^{de} ±2.6	4.8 ^{bcd} ±2.5	4.9 ^a ±2.7
Male (n = 47)	4.2 ^{ab} ±2.6	5.0 ^{bcde} ±2.6	5.3 ^{cde} ±2.6	4.5 ^{abcd} ±2.8	4.8 ^a ±2.7
Gender not indicated (n = 19)	3.3 ^a ±2.4	5.4 ^{bcde} ±2.9	6.3 ^e ±2.1	4.0 ^{abc} ±2.7	4.7 ^a ±2.8
Effect of treatments ⁴	4.3 ^a ±2.6	5.1 ^{bc} ±2.7	5.5 ^c ±2.6	4.6 ^{ab} ±2.6	

¹All results are mean±standard deviation.

²Values with different letter superscripts in the block are significantly ($p \leq 0.05$) different from each other.

³Values with different letter superscripts in the column are significantly ($p \leq 0.05$) different from each other.

⁴Values with different letter superscripts in the row are significantly ($p \leq 0.05$) different from each other.

With regard to frequencies, consumers (n = 152) were grouped into three general frequency groups, those who rated either 3 and below (dislike extremely), those who rated from 4 to 6 (dislike slightly to like slightly) or those who rated 7 and above (like extremely) for each porridge (Figure 2.3). About 40% of consumers gave the porridge prepared using flour of the boiled grain a rating of 7 and above. Similarly, the porridge prepared using flour of the toasted grain was given a rating of 7 and above by about 40% of consumers, whereas only about 20% of consumers gave the porridge of untreated flour a rating of 7 and above. In other words, there was about twice the number of consumers who liked extremely the porridges prepared using flour of the boiled grain and toasted grain than those who liked extremely the porridge of the untreated flour.

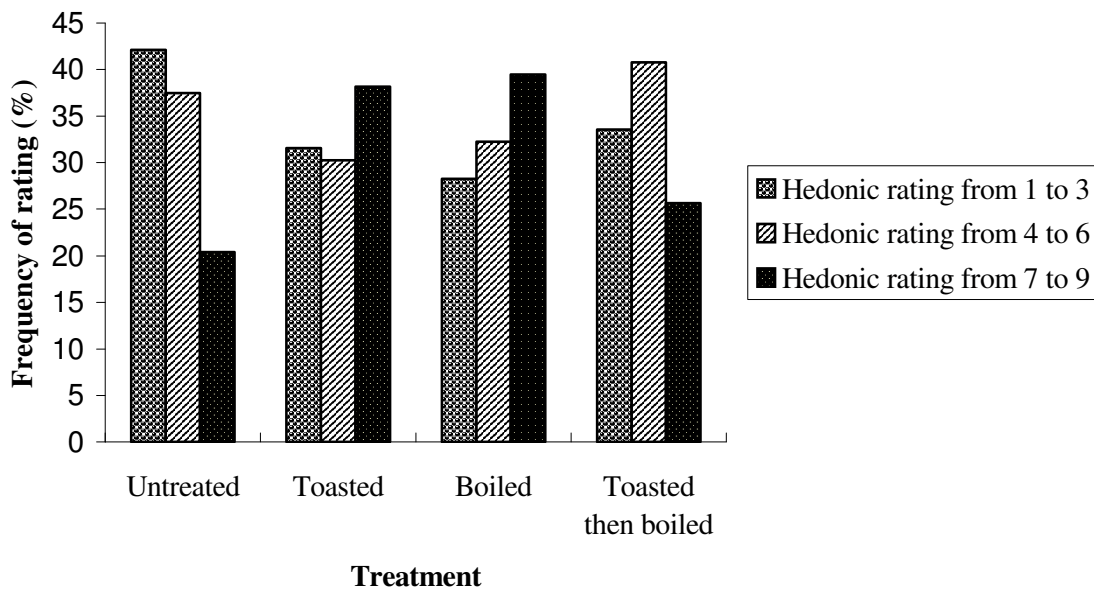


Figure 2.3: The frequency of consumers (in percentage, n = 152) who rated either 3 and below, from 4 to 6 or 7 and above for each porridge

To gain further insight, PCA of the consumer evaluation results was performed. The first 2 principal components explained 58% of the variance in consumers' ratings of the four porridges (Figure 2.4). The porridges lay distinctively on the left side of the x-axis (Figure 2.4A). This indicates that these principal components separated consumers that liked at least one of the four porridges from those that did not like any of the porridges.

PC 2 (22%) separated the porridge of flour from boiled grain (BM) from the other porridges. As mentioned, to understand consumers' responses further, the consumer liking ratings were analysed by k-means cluster analysis. This method assigns rows (in this case consumers based on choosing observations (scores) that maximised initial-between cluster distances) with similar ratings for the four porridges to the same cluster. Cluster analysis allows the analyst to decide on the number of clusters and also to give meaning to the clusters. In this case, three clusters were decided upon to give a cluster that comprised of about 50 consumers or more. The mean consumer rating for each porridge in a cluster was used as a basis of giving a meaning to the cluster. For instance, the mean consumer rating for the porridge prepared using flour of the boiled grain was the only one above 7 and those of all other porridges in the same cluster were below 5, then it followed that the consumers in this cluster represented consumers who liked extremely the porridge of the flour of boiled grain.

The three distinct clusters to which consumers were assigned through cluster analysis of their hedonic data, are shown in Figure 2.4B. For the first cluster, hedonic ratings did not differ much between the porridges and cluster means were in the range of 6 to 7 on a 9-point hedonic scale. All porridge samples scored equally well. Hence, the group of consumers in this cluster was categorised as general porridge likers (GPL), i.e. those who liked any of the four porridges and represented about 35% of consumers ($n = 152$). The second cluster comprised 33% of the consumers. Consumers in this cluster were categorized as porridge dislikers (PD), i.e. those who liked none of the porridges. For this group, hedonic ratings did not differ much between porridges and cluster means ranged between 3 and 4. No specific porridge dominated and all porridges scored almost equally badly. The third cluster comprised 32% of consumers. They were categorised as BM likers (BL), i.e. those who distinctively liked extremely (rated 7 and above) the porridge prepared using flour boiled grain. They gave the highest cluster mean of about 7 for this porridge and rated (cluster mean 2.8) the porridge prepared using untreated flour as the least liked. Since general porridge likers can eat comfortably any of the porridges, then cluster analysis indicates that about 67% of consumers liked the porridge prepared using flours of the boiled grain. The liking of the porridge prepared using flour of the boiled

grain was probably partly a result of partial gelatinisation of the starch of the boiled grain prior to cooking. In general, cooking pearl millet porridge in Namibia takes at least 15 min. Taking into account that the porridges were cooked for just 3 min, boiling the grain not only made a porridge liked by consumers but it also took much shorter than normal time to cook it.

Figure 2.4: Effects of thermal treatments of pearl millet on consumers' ratings of porridges of the flours. Plot of the first two principal component loading vectors of the porridges (A) and consumers (B). Consumers' positions are indicated by the cluster group in which they were categorized. M = untreated fresh sample, TM = toasted fresh sample, BM = boiled fresh sample, TBM = toasted then boiled, fresh sample. GPL = General porridge likers, BL = BM (fresh boiled flour) porridge likers, PD = Porridge dislikers.

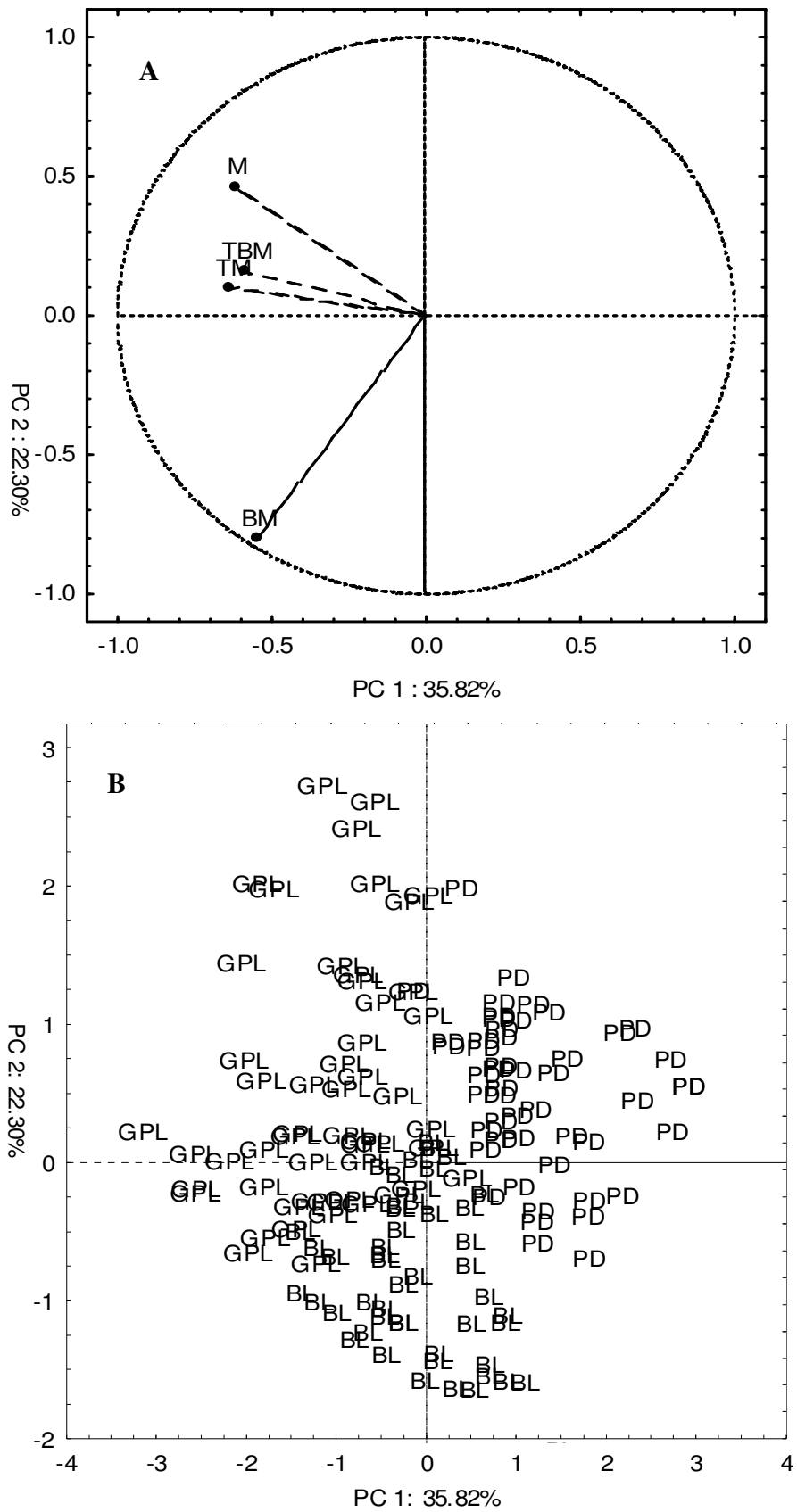


Figure 2.4

2.4 CONCLUSIONS

Thermal treatments can be used to inhibit lipolysis and consequently to prevent the development of rancid off-flavours. They thereby stabilise whole pearl millet flour. Wet thermal treatment also substantially reduces porridge cooking time. The boiling treatment is recommended as a simple processing technique that can be used in the manufacture of preserved whole pearl millet flour, which makes preferred porridges that can be cooked in just three minutes.

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CHAPTER 3: GENERAL DISCUSSION

This chapter will first describe the principles and highlight the strengths and weaknesses of the major methods used in this study, namely lipid extraction, fat acidity, peroxide value, conjugated diene and triene values the “degree of cook of starch” and the sensory evaluations. This discussion will also focus on the effects of toasting, boiling and toasting then boiling of pearl millet grain on stabilization and pre-cooking its flour. It will then examine the practicality of using these thermal treatments as processing techniques in rural parts of Namibia in the manufacturing of whole pearl millet flour. An estimation and comparison of their relative energy demand will also be made. Lastly, an estimation of energy demand and the practicality of extrusion cooking process will be compared with those of the thermal treatments.

3.1 Principles, strengths and weaknesses of lipid extraction, lipid quality assays, degree of cook and sensory evaluations

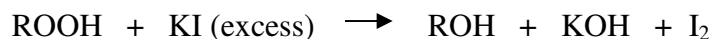
For the lipid quality assays to be carried out, oil had to be extracted from the flour. Lipid extraction is based upon the solubility of the lipids in an organic solvent (Hoseney, 1994). Furthermore, based on solubility, lipids (oil) can be defined as free or bound. If the lipid is soluble in non-polar solvent such as petroleum ether, it is considered free. If a polar solvent is used for extraction, the lipid is considered bound. In this study petroleum ether was the extracting solvent and thus free lipids were extracted. The extraction of free lipids and subsequent determination of lipid quality was considered sufficient for this study because the major components of free lipids are triglycerides, which are prone to deterioration leading to rancidity (Hamilton, 1999). Cold extraction (ambient temperature i.e. not employing heat to facilitate the penetration of the extracting solvent) was used for analysis. Furthermore, the petroleum ether was evaporated from the oil using a distillation unit at the relatively low temperature of 50°C. The reason for cold extraction and cool solvent evaporation was to avoid oxidation of the lipids. If high temperatures are used as for example during soxhlet extraction, they may lead to the decomposition of already formed hydroperoxides and heating for a long period can form additional hydroperoxides

(Prior and Löliger, 1999). This means that factors such as heat that may increase the rate of oxidation must be kept at a minimum. The disadvantage of cold extraction is the longer extraction time (~ 3 h) required to allow sufficient penetration of the solvent into the flour and subsequently dissolving the oil as when compared to the Soxhlet extraction procedure (~ 1 h).

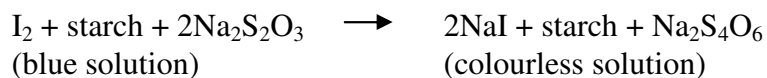
Another problem with extracting oil from cereal grains is that large amounts of cereal and extracting solvent have to be used, as compared to that required for oil seeds. Whole pearl millet flour oil content is about 50 g kg⁻¹ flour (Table 2.1). Therefore, to obtain about 5 g oil from the flour about 100 g and 300 mL of flour and extracting solvent, respectively were used. Therefore, for cereals the tests to be used for lipid quality analyses should not require tens of grams of the oil.

Fat acidity was used to estimate the level of triglyceride hydrolytic degradation. AACC (2000) method 02-01A was used for this determination. The fat acidity method measures total fatty acids in the grain (AACC, 2000). It is based on the acid-base reaction between an alkali and the free acids and determined by titration of the free acids (assumed to be de-esterified fatty acids) present in the extracted oil with standardised potassium hydroxide (KOH). The concentration of the free acids in the original sample can therefore be estimated from the amount of KOH needed to neutralise the acid. Generally, there is little or no de-esterified fatty acids present in cereal grains (Galliard, 1999). However, due to the action of lipase, fatty acids can be de-esterified from triglycerides. Thus, fat acidity gives an indication of the extent of hydrolytic activity that has occurred in the oil of the grain or the flour. Fat acidity was reported as grams of potassium hydroxide required to neutralise free acids from 1 kg flour on dry matter basis (AACC, 2000). The advantage with this assay is that it requires small quantities (~0.5 g) of oil, which in turn requires small amounts of both the grain and extracting solvent. One problem encountered with this assay was emulsions that were formed during titration, partially masking the end point as indicated by phenolphthalein. This could be due to the high fat-acidity values of the samples (AACC, 2000). To overcome this, a pH meter was used to determine the end point.

Peroxide value (PV) measures the hydroperoxides formed during the initial stages of oxidation of unsaturated fatty acids (Rossell, 1999). Method 58-16 of the American Association of Cereal Chemists (2000) was used. PV is based on the ability of peroxides (ROOH) to liberate iodine from potassium iodide (Rossell, 1999):



Once this redox reaction has gone to completion, the amount of peroxides that has reacted can be calculated from the amount of standardized sodium thiosulphate needed to complete the titration. Since the iodine released forms a complex with soluble starch, it is used as an end-point indicator:



The higher the level of peroxides, more iodine is liberated, and the higher the PV. PV is expressed in terms of milliequivalents (meq) peroxide per kg of oil sample. Peroxides reach a peak value and then decrease as they are oxidized to secondary oxidation products (Hamilton, 1999). They therefore give an indication of the progress of lipid oxidation. This means that a low PV is not necessarily an indication of good sensory scores. This is because a low PV may indicate that the hydroperoxides have broken down into secondary oxidation products. The principal disadvantage of this assay is the amount of oil sample required, ~5 g, which required relatively large quantities of grain and extracting solvent to obtain. PV is also associated with two errors (Rossell, 1986). When hydroperoxides liberate iodine, liberated iodine can react with the unsaturated fatty acids. This can lead to low PV than what might be expected. Furthermore, oxygen present in the solution to be titrated can also oxidise iodide to iodine, thereby leading to high PV (Rossell, 1986). Thus, it is mandatory for the titration to be performed immediately after the iodide solution and the oil sample have been mixed for exactly 1 min (AACC, 2000). There is also the possibility of thiosulphate to decompose into tetrathionate when exposed to light (Harris, 1999). Thus, sodium thiosulphate solution must be stored in a tightly capped amber bottle in a dark cool place (AACC, 2000). The PVs are therefore hard to compare with those in literature because of the empirical nature (i.e. variety of experimental factors

such as timing, light and temperature) of this method. It is noteworthy that in this study there was no direct determination of secondary lipid oxidation products, which can be measured for instance by p-anisidine value and thiobarbituric acid assays (Rossell, 1999). However, descriptive sensory evaluation discussed later on was used to give among others an indication of rancidity flavours, which are a manifestation of secondary lipid oxidation products in the product (porridge) made from the flour samples.

Conjugated diene and trienes also measure the primary products of unsaturated fatty acids oxidation. The determination of the conjugated diene and triene values was done according to the ISO 3656 method (ISO, 1989). It is based on the fact that conjugated dienes and trienes absorb ultraviolet radiation strongly at 232 nm and 268 nm, respectively. Almost immediately after peroxides are formed, the non-conjugated multiple bonds (e.g. C=C-C-C=C) that are present in natural unsaturated fatty acids are converted to conjugated multiple bonds (e.g. C=C-C=C) (Rossell, 1999). The extent of multiple bond displacement is directly related to the degree of oxidation of the oil. The conjugated diene and conjugated triene (di-ketones and conjugated trienes) fatty acids are intermediate products. Thus, they break down further to other oxidation products (Rossell, 1999). It should, however, be noted that the absorption of various compounds overlap in this UV range (Rossell, 1999). Oxidation products formed from antioxidants during the oxidation of triglycerides may interfere with conjugated diene determination (Prior and Löliger, 1999). For example, α -tocoquinone formed from α -tocopherol oxidation contributes to the absorption at 232 nm. Moreover, not all hydroperoxides possess a conjugated diene or triene group (Prior and Löliger, 1999). Oleic acid hydroperoxide is an example of this fact. The major advantage of the measurement of conjugated dienes and trienes is that it is a simple and rapid assay to perform. It also requires small quantities of the oil sample, < 0.25 g.

The degree of cook of starch was used to measure enzyme susceptible (gelatinised) starch in treated pearl millet grain samples. In the assay used to determine the degree of cook total starch and enzyme susceptible starch had to be measured, because it is from which the degree of cook can be calculated. Total starch was determined by pressure-cooking

the samples to completely gelatinise the starch. For the determination of enzyme-susceptible starch in the samples, the pressure-cooking step was omitted. Temperature and pH were adjusted and then α -amylase and amyloglucosidase were added. α -Amylase hydrolyses the starch polymers into maltodextrins, whereas amyloglucosidase hydrolyses the maltodextrins into glucose (Hoseney, 1994). Glucose concentration in the samples was determined in terms of ferricyanide reduction colorimetrically at 420 nm from which the total starch content and enzyme susceptible starch were calculated. The degree of cook was then calculated as the ratio between enzyme susceptible starch and total starch.

Starch is present in the endosperm as granules (Hoseney, 1994). The starch polymers, amylose and amylopectin are tightly packed in raw starch granules. When starch is heated in the presence of water, it gelatinises (Hoseney, 1994). This means that the starch granules absorb water and undergo an irreversible swelling and destruction of the internal crystalline structure (Hoseney, 1994). In the process of gelatinisation, amylose leaches out of the granules. Upon the addition of amylase and amyloglucosidase, water facilitates these enzymes to enter and hydrolyse the polymers of starch in the swollen starch granule. Starch polymers therefore become more susceptible to degradation by amylase and amyloglucosidase enzymes into glucose.

Sensory evaluation relies on humans to assess the acceptability and define the sensory attributes of a product (Lawless and Heymann, 1998). No instrument can replicate or replace the human response. In this study, both descriptive and consumer sensory evaluations were used. Descriptive sensory evaluation detects, describes and quantifies sensory attributes differences between products (Lawless and Heymann, 1998). It gives information on how raw material and process variables affect sensory characteristics. The generic descriptive sensory evaluation procedure described by Lawless and Heymann (1998) was applied in this study. In conjunction with the PV and conjugated dienes and trienes, descriptive sensory evaluation was used to give an indication of the effect of the grain thermal treatments on the sensory quality in terms of rancid and other flavours of the porridges. It involves panel selection and training, generation of terms (descriptors), preparation of score sheet and a series of evaluation sessions. Essentially, panelists are

used as sensory analytical instruments. The panelists through the training process acquire a common qualitative and quantitative frame of reference for use of a standard language and a common scale (Murray, Delahunty and Baxter, 2001). Descriptive sensory evaluation is generally regarded as the most comprehensive, flexible and useful sensory method providing detailed information on all sensory properties of a food product (Murray *et al*, 2001). Some drawbacks were encountered with descriptive sensory evaluation. Panelists did not score the porridges the same, on average, compared to each other. This indicated that at least one panelist tended to consistently use one side of the scale, e.g. the lower side of the 9-point scale although samples should be representative of the full scale. Consequently, panelists did not always evaluate the porridges the same. The dissimilar evaluation also indicated that two or more of the panelists had a different perception of the differences between the samples. To avoid this effect in the future, it is necessary, if possible, to select and train twice the number of panelists as required for the project (ISO, 1993). This allows for inconsistent panelists to be rejected and allows the panel leader to remain with the required minimum number of panelists. Furthermore, it reduces the panelists factors such as personality, concentration, motivation, dietary habits and reluctance to eat unfamiliar food products, which apparently have a large impact on the success or failure of sensory panelists (Murray, *et al*, 2001) probably because it is difficult to monitor these factors effectively.

Consumer sensory evaluation is one of the important market research tools to evaluate food product likes and dislikes (Lawless and Heymann, 1998). Consumers are given food products to taste and then either indicate which one they like or rate on a scale how much they like each of the food products. Often consumer evaluation data can be analysed in relation to demographic data such as age of consumers. In this study, however, demographic data such as the age of consumers were not obtained. Thus, the consumer data could not be related to the age categories of consumers. This was mainly because almost all consumers that participated were in the age range of 18 to 24, representing the major subset of the potential consumers of the product. They were mainly first year young undergraduate students and recent high school learners upgrading their grades to qualify for tertiary education.

Another noteworthy issue is that consumer evaluation was conducted at a central location and not in the laboratory. This did not allow for lengthy interaction of the consumers with the food product, especially because there was no facility to allow the porridge to be kept warm after serving. Therefore, it was important to minimise the number of questions per sample to allow some interaction and also to ensure that all the porridges were tasted within about 5 min so that the samples would be more or less at the same temperature. Thus, only overall liking of each sample was asked although there was also space for consumers to write down any comment per sample if they had any. This has its disadvantages in that one does not get an idea of which attributes in terms of colour, flavour, aroma, taste or texture that consumers like or do not like. For example, most comments were suggestions that more sugar and salt should be added to all the samples. However, sugar and salt were simply added in minimal amounts to give some taste to the porridges. For the envisaged composite flour product, consumers will be at liberty to add sugar, salt, cooking oil and even milk in any amounts they want. Thus, the comments that were written down were not necessarily useful in terms of understanding the drivers of like/dislike in terms of the effect of thermal treatments on pearl millet flour and addition of cowpea flour. One important observation was that there was no comment related to cowpea flour at all. This may suggest that cowpea flour had no influence on the overall liking of any porridge sample. Therefore, with the preference of the porridge prepared using composite flour of cowpea and boiled pearl millet grain, the nutritional level of consumers will be enhanced.

It should also be pointed out that this study did not determine the effect of storage of flours of thermally-treated pearl millet grain on consumer liking of the porridges. Since consumer sensory evaluation is relatively expensive to conduct, the effect of storage can be done in the future using flours of the treatment that gave the most liked porridges identified in this study.

3.2 Effect of thermal treatments on lipid quality, degree of cook and sensory evaluations

Thermal treatments such as toasting, boiling and toasting then boiling were expected to prevent the chemical changes that cause the disagreeable sensory qualities associated with stored untreated whole pearl millet flour. This is because thermal treatments can denature enzymes such as lipase, which hydrolyse triglycerides into de-esterified fatty acids (Galliard, 1999). Unsaturated fatty acids when de-esterified are prone to oxidation and subsequently contribute to rancidity. Wet thermal treatments were also expected to pre-cook the grain because heating starch in water can gelatinise the starch (Hoseney, 1994). Did the thermal treatments meet the stated expectations? With regard to fat acidity, as was hypothesised, it can be said that wet thermal treatments did denature the lipase. This is because the fat acidity of the flours of wet thermally-treated grain did not change, whereas that of the untreated flour increased significantly from 0.11 to 3.73 g KOH kg⁻¹ flour during storage (Table 2.2). Since this increase was more than that occurred in the flours of thermally-treated grain, these results indicate that lipolysis occurred and not the thermal hydrolysis of triglycerides. Regarding the thermal treatments, the toasting treatment was the least effective in denaturing lipase. This can be explained by the fact that dry heat has less specific heat capacity and penetrative power than wet heat (Singh and Heldman, 2001). For example the specific heat for dry air and saturated water both at 90°C are 1.0 and 4.2 kJ kg⁻¹ K⁻¹ respectively (Singh and Heldman, 2001).

The low fat acidity values of flours of thermally-treated grain relative to those of untreated flour indicate that there were low amounts of de-esterified fatty acids in these flours. This in turn suggests that there were little precursors (de-esterified unsaturated fatty acids) available for oxidation. These findings are in agreement with those in literature. Palade *et al* (1996) also observed that boiling-water blanching of whole pearl millet grain for 10 s resulted in no change of fat acidity in flour during one-month storage at ambient conditions. Arora *et al* (2002) used a dry oven at ~100°C for 2 h to heat pearl millet grain and evaluated the extent of hydrolytic rancidity of the resulting flour during a one-month storage period at ambient conditions. They found that fat acidity of flour of

heat-treated grain increased by less than two-fold while that of the untreated flour increased by at least four-fold during storage.

Regarding the PVs, the untreated flour showed a significant PV decrease during storage. This indicates that hydroperoxides were formed and broken down into secondary oxidation products. Assuming the presence of lipoxygenase, the formation of peroxides for the untreated flour could have been enzymatic. It is important to note that although the hydroperoxides are unstable and could thus ultimately break down, there appears to be factors that facilitate their break down. According McClements and Decker (2000) pro-oxidant cations can catalyse the break down of hydroperoxides. Furthermore, in many plant tissues and in beans an enzyme called hydroperoxide lyase further cleaves the hydroperoxides formed into aldehydes such as hexanal and nonanal (Gretchkin, 1998). However, there is no scientific literature published on the presence of this enzyme in pearl millet or in cereals in general. Since the presence of lipid oxidation products such as aldehydes are the same for hydroperoxide lyase-catalysed oxidation with those for autoxidation, the presence of this enzyme in cereals cannot be confirmed at this time. The presence of peroxidases in pearl millet has been reported (Bangar *et al*, 1999). Therefore, enzyme-catalysed formation of hydroperoxides and their subsequent break down in the untreated flour remains a possibility. Whatever the factors may be that led to the break down of hydroperoxides for the untreated flour, it suffices to say that the final reaction products were expected to be manifested as rancid off-flavours. This was indeed the case. The porridges of the fresh and stored flours of untreated grain were associated significantly with the rancid flavours (Figure 2.2). The PV of flour of toasted grain did not change during storage. This indicates that there was no further formation and break down or there was equal rate of formation and break down of hydroperoxides during storage. The fact that the porridges prepared using flour of toasted flour were not associated with rancid off-flavours, suggests that there was indeed no further formation and disintegration of hydroperoxides, which ultimately leads to the formation of volatile aldehydes that causes the rancid off-favours.

The stabilising effect of toasting by inhibiting the break down of hydroperoxides can be attributed to the thermal denaturation of the responsible enzymes. This agrees with what

was hypothesised. Furthermore, the stabilising effect can also be attributed to the radical scavenging of phenolic compounds such as ferulic acid and C-glycosyl flavones (Eskin and Przybylski, 2001). These phenolics (Fig. 3.1) occur naturally in pearl millet (Serna-Saldivar and Rooney, 1995). It has, however, been found that synthetic antioxidants such as butylated hydroxyanisole do not effectively prevent oxidation of pearl millet flour lipids (Kapoor and Kapoor, 1990). Nevertheless, scavenging of radicals can delay and even prevent the onset and propagation of autoxidation of unsaturated fatty acids (Eskin and Przybylski, 2001). Autoxidation involves the formation of a wide range of radicals that can initiate and propagate the deterioration of unsaturated fatty acids. This subsequently results in the formation of compounds associated with rancidity such as hexanal. Chelation of pro-oxidant cations such as copper and iron by reductones and melanoidins possibly formed through Maillard and caramelisation reactions (Yoshimura *et al*, 1997) can also be expected to delay and perhaps prevent the disintegration of hydroperoxides. Hence, they may also have been involved in the stability of toasted flour.

Presuming that wet thermal treatments inactivated lipoxygenase, the significant increases of about 7-fold of PVs of the flours of wet thermally-treated grain during storage indicate that autoxidation occurred. This was not expected in terms of the hypothesis originally formed, which simply assumed that thermal treatments would inhibit lipoxygenase-catalysed oxidation. Thus, autoxidation could be attributed to leaching of antioxidant flavonoids and phenolic acids that occur naturally in pearl millet (Serna-Saldivar and Rooney, 1995) during the boiling treatment. Moreover, boiling could have damaged the grain cell walls and membranes, thereby exposing cellular components including lipids to oxygen. As discussed, according to Galliard (1999) the use of heat to inactivate lipase could predispose lipids to oxidation by activating potential pro-oxidants. This could also have happened in this case. The PV increases may also indicate accumulation of hydroperoxides, presumably because only a small proportion of hydroperoxides were broken down into secondary oxidation products. This indicates that wet thermal treatments have the effect of delaying and probably preventing hydroperoxide break down. One of these effects was the inhibition of lipolysis. This means, as discussed before, that there was no or little unsaturated fatty acids available for oxidation in the wet

thermally-treated samples. Consequently, there was a delay in the onset of oxidation. Furthermore, Maillard and caramelisation products that may have antioxidant properties (Yoshimura *et al*, 1997) especially through chelation of pro-oxidants that favour hydroperoxides disintegration may have been formed. Hence, the accumulation of hydroperoxides. Conjugated diene and triene values, which similarly measure particularly long chain diketones and conjugated hydroperoxides, corroborate the PVs. Thus, the probable explanation for their change is the same as that for the PVs. In comparison with other researchers, Chavan and Kachare (1994) observed that there was no difference in the peroxides in oil extracted from untreated and heat-treated pearl millet during the same storage duration and conditions. These authors heated pearl millet grain in a hot air oven at 50°C for an hour and another grain at 100°C for 10 min. They also subjected another grain to boiling water (blanched) at 98°C for 30 s. Because Chavan and Kachare (1994) did not carry out any experiment that gives an estimate of secondary oxidation products that directly affect sensory quality, one can hardly make any meaningful conclusion with regard to the effect of their treatment on rancidity. Thus, it is highly probable that their observation indicated that their heat treatments were not effective to delay or prevent the oxidation of the oil that leads to rancidity.

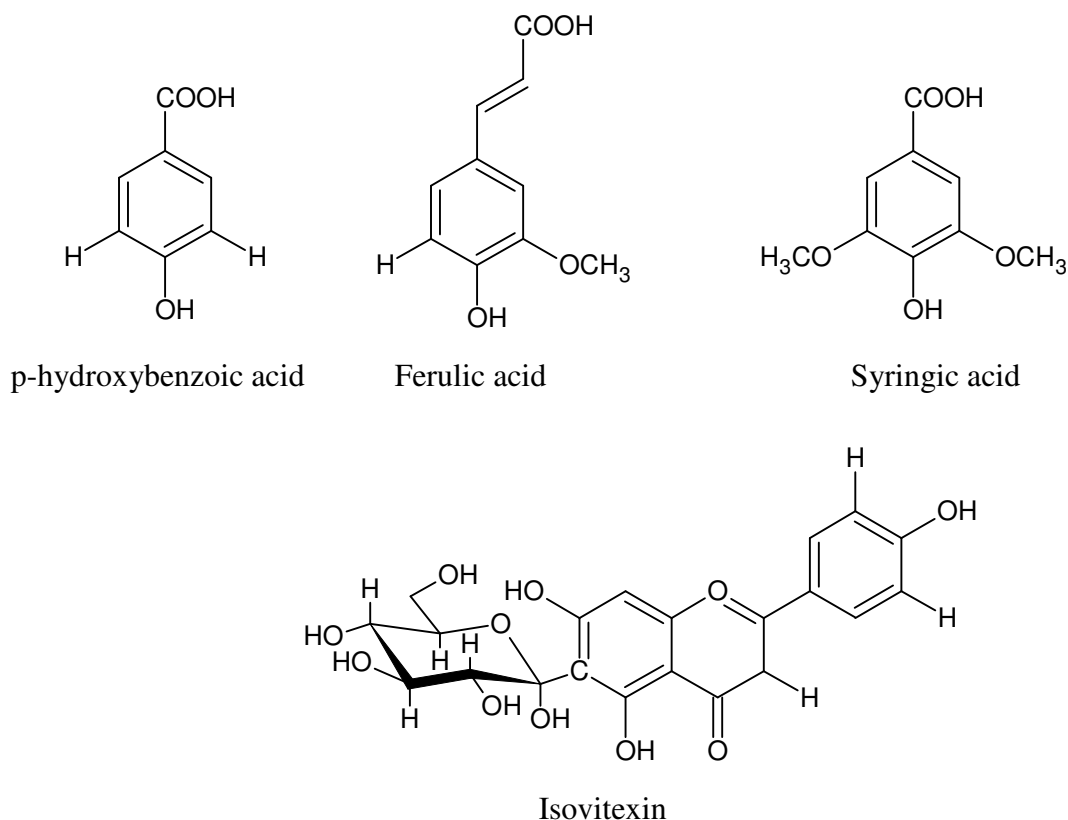


Figure 3.1: Some of the phenolic compounds that may exhibit antioxidant properties (Eskin and Przybylski, 2001) that are found in pearl millet (Serna-Saldivar and Rooney, 1995)

The degree of cook of starch (enzyme susceptible starch) of the wet thermally-treated grain (40%) (Table 2.1) indicate that the extent of starch gelatinisation of wet thermally-treated grain improved but was not complete. The incomplete gelatinisation of starch is probably due to the limited water penetration into the endosperm, presumably because there was slow diffusion of water into the grain. The slow diffusion of water into the grain would be due to the low surface area of whole grain, for example relative to flour particles. Among other factors, particle size of the flour granules influences the gelatinisation of starch (Mousia *et al*, 2004). Riva, Schiraldi and Piazza (1994) found that, under similar experimental conditions, gelatinisation of starch was delayed for the whole rice grains compared with the one for the ground rice.

Descriptive sensory analysis of porridges did not associate the porridges prepared using flours of thermally-treated grain with rancid off-flavours. This means that the panelists could not detect secondary products of unsaturated fatty acids oxidation, which are responsible for rancid off-flavours. This agrees with the fat acidity, PVs and conjugated diene and triene values, indicating that thermal treatments delayed and probably prevented the ultimate formation of carbonyls (aldehydes and ketones) responsible for rancidity in pearl millet. Due to insufficient material from different thermal treatments remaining after the sensory tests, it was not possible to determine the secondary oxidation products directly e.g. malonaldehyde. However, these data would have been particularly valuable for comparison with the descriptive sensory analysis results.

When the porridge was cooked for just 3 min, consumers showed preference for the porridge from flour prepared from boiled grain. The partial gelatinisation of the wet thermally-treated grain appears to have made it cook quicker than those that were not subjected to boiling. This is in agreement with the original hypothesis. This indicates that wet thermal (boiling) treatments not only stabilised the pearl millet flour but also substantially shortened the cooking time. It should be noted that cooking porridge in Namibia is normally done for at least 15 min. In this study it was envisaged to produce a pre-cooked flour that can be cooked into porridge within 3 min. Consequently, the flours produced from wet thermally-treated grain could be regarded as convenient, especially for consumers in urban areas. This is because they not only save time for cooking the porridges but in turn also reduce the energy cost arising from longer cooking time. Pre-cooking is also needed in rural areas. This is because in rural parts of Namibia deforestation is on the increase due to the use of wood for house construction and also for fuel. In some parts, firewood is no longer available. Consequently, people have resorted to using any energy source that can be found including cow dung, which should be used as a fertiliser for pearl millet cultivation.

3.3 Practicalities and energy demand estimation of thermal treatments as processing techniques in the production of whole pearl millet flour in rural areas of Namibia

The thermal treatments used in this study can be regarded as novel techniques for processing pearl millet for flour production, with potential application in the Namibian situation. These processing techniques would add value to pearl millet, thereby making it possible to produce and market a traditional food product that is more convenient for consumers. However, can these thermal-processing techniques be viable options for the manufacture of pearl millet flour in rural Namibia? The different thermal treatments will be examined in terms of the additional important equipment needed for each of them, over and above the standard equipment such as a hammer mill, and also in terms of safety of the products. For semi-commercial or commercial-scale production, toasting will require a semi-industrial or industrial size oven. This may be an additional economic burden. The cost of which will have to be recovered from sales of the product. With regard to safety of the flour, toasting is expected to inactivate microorganisms including pathogens that may be on the grain. Furthermore, the resulting grain and the subsequent flour will be of very low moisture content that will not support the growth of microorganisms. Hence, toasting can be expected to pose no safety risk to the end product. Unlike toasting, the boiling process takes a longer time relative to toasting. This is because it involves a drying step that takes about a day to complete. It will also require several utensils and equipment such as vessels for boiling, colanders to drain out the water, stoves and a drying oven. The initial cost of vessels, stoves and a drying oven will be expected to add more to the cost of the product. Moreover, the cost of water and also of electricity required to boil and to dry the grain could also be a major factor in determining the selling price of the product.

Namibia is a semi-desert country with plenty of sunshine and hot climate during the day for most of the year. As such, sun drying is the common method of drying steeped pearl millet grain and of flour in Namibia. Can the boiled grain be sun-dried? This would significantly reduce the energy costs. Unfortunately, it is a possibility with various risks, especially in terms of safety. Drying the grain in the sun in the open, subjects the grain to potential pathogenic contamination. This is because sun drying exposes the grain to dust, insects, birds and vermin, which are hosts to pathogens that may contaminate the grain.

Subjecting the grain to boiling is in itself expected to inactivate microorganisms. However, since the grain is a low acid product, there is a great safety risk at the time from draining the grain and through the drying step. If any contamination of microorganisms especially pathogens occurs, they are likely to grow during this period. Thus, there is great need to critically monitor and control the microbial quality of the flour of boiled grain. Since lactic acid fermentation is used traditionally in the milling process of pearl millet in Namibia, one could perhaps cook the grain in lactic acid to reduce the pH of the product. This could minimise the microbiological safety risk. The main bacterial pathogens in food are *Bacillus*, *Clostridium*, *Salmonella* species and *coliforms* (Hayes, 1992).

Energy in the form of electricity, wood and coal is becoming scarce in Namibia, as it is in most countries in southern Africa. Thus, it is valuable to estimate the energy demand for toasting, boiling and toasting then boiling processing methods, as the cost of energy will affect the cost of the flours. Flow charts of pearl millet processing involving the various thermal treatments are given in Figures 3.2 to 3.4.

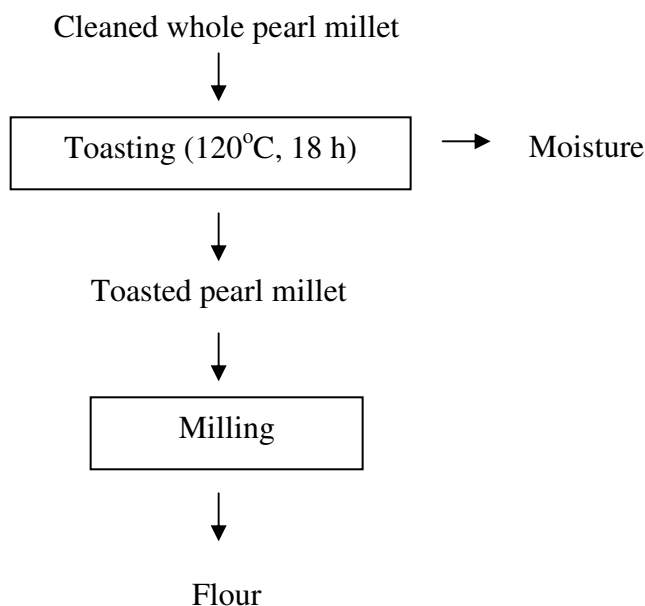


Figure 3.2: Flow chart of toasted pearl millet flour processing

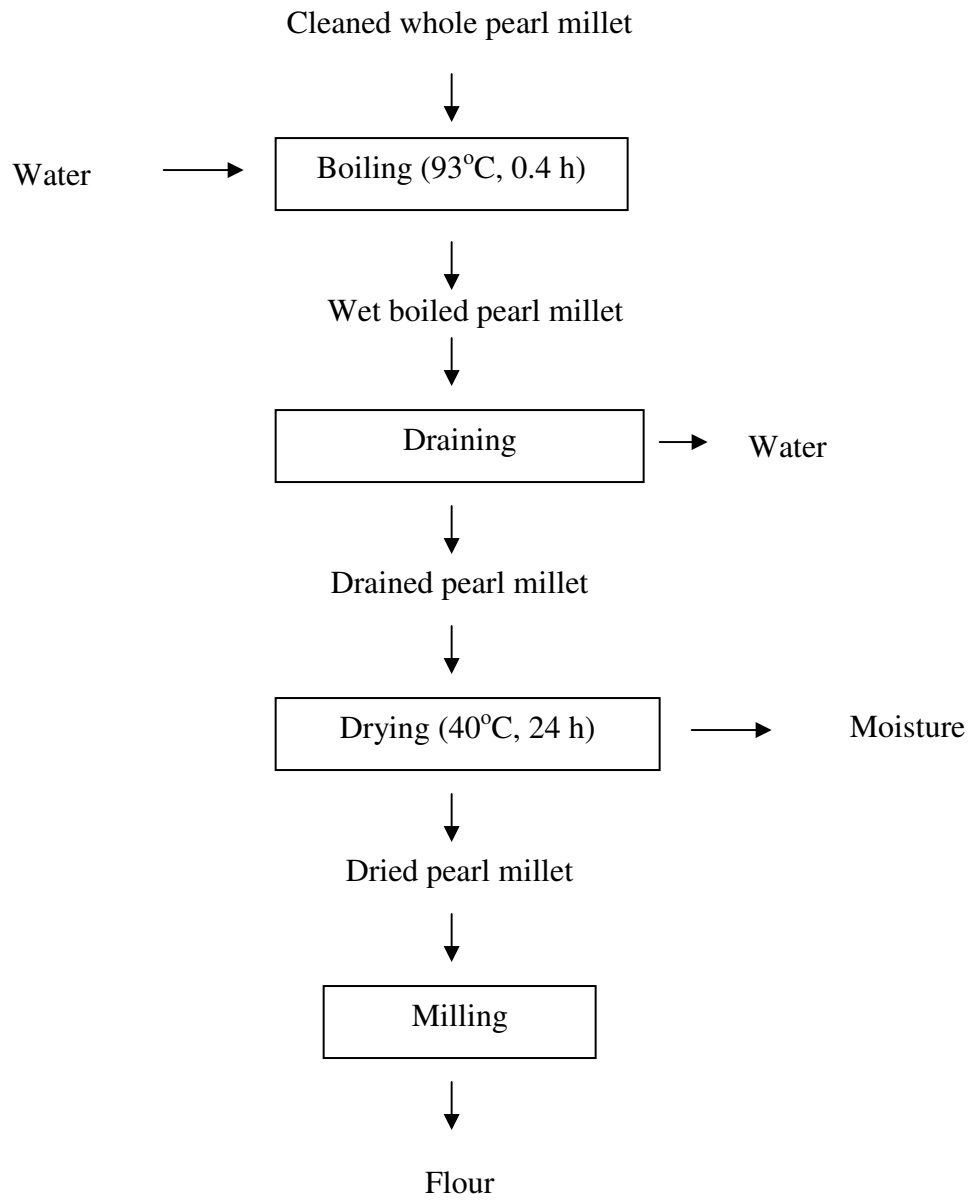


Figure 3.3: Flow chart of boiled pearl millet flour processing

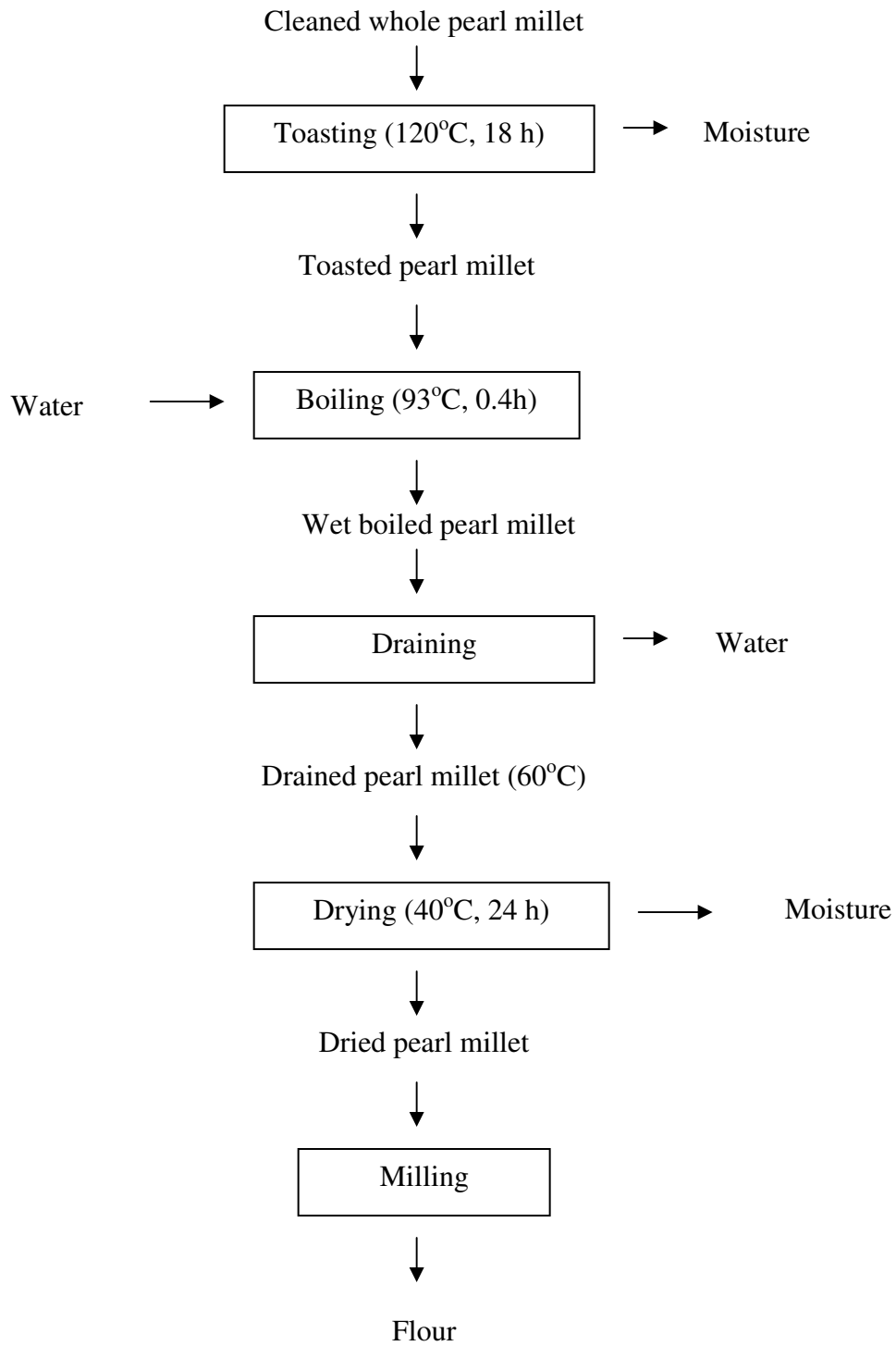


Figure 3.4: Flow chart of toasted then boiled pearl millet flour processing

The major unit operations that are energy demanding in processing pearl millet flour are toasting, boiling and drying. The energy demands were estimated using the following equations:

Energy (kJ) = $mc\Delta T$, or

Energy (kJ) = ml

where m = mass of substance

c = specific heat capacity of substance

ΔT = change in temperature

l = latent heat or heat of vaporization

The energy required for toasting (18 h) (Figure 3.2) was estimated as the sum of:

- The energy necessary to bring the temperature of the untreated grain (1 kg) from 23°C to 120°C.
- And the energy necessary to evaporate the moisture content of the untreated grain (90.3 g kg⁻¹ of grain) to moisture content of 8.6 g kg⁻¹ of the toasted grain (Table 2.1). This moisture loss represents 95% of untreated grain moisture.

Moisture of untreated grain = 90.3 g kg⁻¹

Moisture lost during toasting = $0.95 \times 90.3 \text{ g kg}^{-1} \times 1 \text{ kg} = 86 \text{ g} = 0.1 \text{ kg}$

Energy to heat the grain to 120°C = $1 \text{ kg} \times 1.50 \text{ kJ/kg}^\circ\text{C} \times (120-23)^\circ\text{C} = 146 \text{ kJ}$

Energy required to vapourise moisture from the untreated grain was estimated as follows:

Energy = ml , where l is the energy required to vaporize liquid water to steam at 120°C, [l = enthalpy of steam (vapour) - enthalpy of water (liquid), at 120°C]. The enthalpy values were obtained from Singh and Heldman (2001).

Thus, energy to vapourise moisture = $0.1 \text{ kg} \times (2706.3 - 503.71) \text{ kJ/kg} = 220 \text{ kJ}$

Sum = $146 \text{ kJ} + 220 \text{ kJ} = 366 \text{ kJ}$

Since Power = Energy/time (s), it follows that the power needed for toasting can be estimated as follows:

Power = $(366 \text{ kJ}) / 64800 \text{ s} = 0.006 \text{ kJ/s} = 6.0 \times 10^{-3} \text{ kW}$

Also, since we have estimated the power, the energy use required to toast 1 kg pearl millet grain can be estimated as follows:

Energy use = Power x hours of operation,

For toasting, energy use = $6.0 \times 10^{-3} \text{ kW} \times 18 \text{ h} = 0.1 \text{ kWh}$

With regard to boiling (Figure 3.3), water and pearl millet grain were brought and held at boiling temperature (93°C) for 0.4 h. The mass of water and the grain will be taken as 1 kg each. The specific heat of water is 4.187 kJ/kg°C (Singh and Heldman, 2001). The specific heat capacity of pearl millet grain was assumed to be the same with that of finger millet (*Eleusine corana*) of 1.50 kJ/kg°C reported by Subramanian and Viswanathan (2003). In all subsequent energy calculations the specific heat capacity of pearl millet is assumed to be 1.50 kJ/kg°C. It was assumed that no vapour was lost during boiling. The initial temperature of both the grain and water was 23°C. Thus, the energy required for the boiling unit operation is the sum of energy required to heat the grain and the water. It can be estimated as follows:

$$\text{Energy to heat and boil the grain: } 1 \text{ kg} \times 1.50 \text{ kJ/kg}^\circ\text{C} \times (93-23)^\circ\text{C} = 105 \text{ kJ}$$

$$\text{Energy to heat and boil the water: } 1 \text{ kg} \times 4.187 \text{ kJ/kg}^\circ\text{C} \times (93-23)^\circ\text{C} = 293 \text{ kJ}$$

$$\text{Sum} = 105 \text{ kJ} + 293 \text{ kJ} = 398 \text{ kJ}$$

The power needed for the boiling unit operation can be estimated as follows:

$$\text{Power} = (398 \text{ kJ}) / 1501 \text{ s} = 0.265 \text{ kJ/s} = 0.265 \text{ kW}$$

Also, since we have estimated the power, the energy use during this processing step can be estimated as follows:

$$\text{Energy use} = \text{Power} \times \text{hours of operation,}$$

$$\text{For boiling, energy use} = 0.265 \text{ kW} \times 0.4 \text{ h} = 0.11 \text{ kWh}$$

Energy required for the drying step (24 h) (Figure 3.3) was estimated as the sum of:

- The energy that has to be lost to bring the temperature of the 1 kg drained grain from 60°C to 40°C.
- And the energy necessary to evaporate the 0.7 kg water gained by the grain during the boiling step (mass of the drained grain (1.7 kg) minus mass of dried grain (1 kg)) at 40°C.

$$\text{Energy that the drained grain have to lose to reach } 40^\circ\text{C} \text{ from } 60^\circ\text{C} = 1.7 \text{ kg} \times 1.50 \text{ kJ/kg}^\circ\text{C} \times (40-60)^\circ\text{C} = -51 \text{ kJ}$$

Energy required to vaporize moisture from the grain was estimated as follows:

$$\text{Energy} = \text{ml}$$

where l is the energy required to vaporize liquid water to steam at 40°C , [$l =$ enthalpy of steam (vapour) - enthalpy of water (liquid), at 40°C]. The enthalpy values were also obtained from Singh and Heldman (2001).

$$\text{Energy to vapourise moisture} = 0.7 \text{ kg} \times (2574.3 - 167.57) \text{ kJ/kg} = 1.7 \times 10^3 \text{ kJ}$$

$$\text{Sum} = -51 \text{ kJ} + 1.7 \times 10^3 \text{ kJ} = 1.6 \times 10^3 \text{ kJ}$$

$$\text{Power} = (1.6 \times 10^3 \text{ kJ}) / 86400 \text{ s} = 0.019 \text{ kJ/s} = 1.9 \times 10^{-2} \text{ kW}$$

The energy use during this processing step can be estimated as follows:

$$\text{Energy use} = \text{Power} \times \text{hours of operation},$$

$$\text{For drying, energy use} = 1.9 \times 10^{-2} \text{ kW} \times 24 \text{ h} = 0.46 \text{ kWh}$$

Thus, the total energy use for boiling and drying 1 kg of pearl millet is estimated as the sum of the boiling and drying steps.

$$\text{For boiling, energy use} = 0.265 \text{ kW} \times 0.4 \text{ h} = 0.11 \text{ kWh}$$

$$\text{For drying, energy use} = 1.9 \times 10^{-2} \text{ kW} \times 24 \text{ h} = 0.46 \text{ kWh}$$

$$\text{Sum} = 0.11 \text{ kWh} + 0.46 \text{ kWh} = 0.57 \text{ kWh}$$

The energy use for toasting then boiling of 1 kg pearl millet grain processing (Figure 3.4) can be estimated as the sum of toasting, boiling and drying unit operations. This can be estimated as follows:

$$\text{For toasting, energy use} = 6.0 \times 10^{-3} \text{ kW} \times 18 \text{ h} = 0.10 \text{ kWh}$$

$$\text{For boiling, energy use} = 0.265 \text{ kW} \times 0.4 \text{ h} = 0.11 \text{ kWh}$$

$$\text{For drying, energy use} = 1.9 \times 10^{-2} \text{ kW} \times 24 \text{ h} = 0.46 \text{ kWh}$$

$$\text{Sum} = 0.10 \text{ kWh} + 0.11 \text{ kWh} + 0.46 \text{ kWh} = 0.67 \text{ kWh}$$

Regarding the energy use of the thermal treatments, the energy use for toasting is the lowest (0.10 kWh). The energy use for toasting then boiling is the highest (0.67 kWh). However, if sun drying will be used to dry the grain, the energy use for toasting and for boiling would become almost the same (0.10 kWh). Also the energy use for toasting then boiling would become significantly lower (0.21 kWh). Although consumers preferred the porridge of the flour of the boiled grain, toasting appears to be the best option in terms of energy demand and microbiological safety.

Extrusion cooking is a processing method that is used in the manufacture of pre-cooked breakfast cereal products (Bouvier, 2001). It will be compared with the thermal treatments

(toasting and boiling) in terms of throughput, energy demand and feasibility as a processing technique in rural areas of Namibia. Extrusion cooking is a high-temperature, short time process (HTST) where the raw materials are subjected to high temperatures and pressure over a relatively short time (20 to 150 s, residence time) (Bouvier, 2001). Ingredients are worked into dough by a screw shaft inside a barrel. Thermo-mechanical action during extrusion cooking gelatinises the starch and denatures the proteins.⁶¹ These transformations could be expected to pre-cook and stabilise pearl millet flour. Almeida-Dominguez, Gomez, Serna-Saldivar, Waniska, Rooney and Lusas (1993) used extrusion cooking to produce weaning foods containing pearl millet. Furthermore, Pelembe, Erasmus & Taylor (2002) used it to produce an instant composite porridge of sorghum-cowpea. Using Pelembe *et al* (2002) extrusion process conditions, the energy use for extrusion cooking will be estimated and then compared with that of the thermal treatments. The energy required for extrusion cooking of 1 kg of pearl millet will be estimated from:

The thermal energy required to heat the grain to 130°C, and

The mechanical energy required for shearing, conveying and pumping the product through the barrel to the die

Energy to heat the grain from 23°C to 130°C:

$$1 \text{ kg} \times 1.50 \text{ kJ/kg}^\circ\text{C} \times (23-130)^\circ\text{C} = 161 \text{ kJ}$$

The mechanical energy required for shearing, conveying and pumping the product through the barrel to the die will be estimated from the throughput and energy supplied by the motor (specific mechanical energy, SME) of the extrusion process described and used by Pelembe *et al* (2002). Their throughput was 1 kg per 0.04 h and the SME was 530 kJ/kg.

The mechanical energy required: $1 \text{ kg} \times 530 \text{ kJ/kg} = 530 \text{ kJ}$

Sum of energy for extrusion cooking = $161 \text{ kJ} + 530 \text{ kJ} = 691 \text{ kJ}$

Power for extrusion cooking = $691\text{kJ}/144 \text{ s} = 4.8 \text{ kW}$

Energy use for extrusion cooking = $4.8 \text{ kW} \times 0.04 \text{ h} = 0.19 \text{ kWh}$

The estimated energy use of extrusion cooking is probably an underestimation because the extrudates have to be dried to moisture level of ~10%. Like the boiling process, the

drying equipment cost will increase the cost of the product. In comparison with boiling treatment, extrusion cooking will require more energy if the boiled grain and extrudates will be dried by sun-drying instead of using electricity. In terms of throughput, extrusion cooking will have a throughput higher than that of any of the thermal treatments because its processing residence time is shorter. Although it appears that extrusion cooking has more advantages than the thermal treatments, the initial cost of the extruder can be prohibitive. An extruder is likely to cost ~N\$500,000. It would also require 3-phase electricity, which is not available in the area where Healthful Harvest is located. Although one can apply at the power supply utility for 3-phase electricity, this will be prohibitively expensive for a cooperative. A skilled technician would also have to be employed to operate an extruder. Therefore, the use of extrusion cooking may not be practical in rural areas where communities are poor and lack the skills to operate an extruder. However, the cooperative members can cope with the boiling process, which is surely the appropriate processing technology for this rural cooperative with limited financial resources and technical skills to afford and operate an extruder.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

Wet thermal treatments can inhibit hydrolytic de-esterification of the triglycerides. But they may subject unsaturated fatty acid to non-enzymatic oxidation. However, thermal treatments can significantly delay the break down of unsaturated fatty acid oxidation primary products into secondary oxidation products. Therefore, thermal treatments can be used to prevent the development of rancidity thereby stabilising whole pearl millet flour.

The flour of boiled grain can make a porridge that is preferred by consumers. This is probably because subjecting the grain to boiling partially gelatinises the starch before cooking. Consequently, boiling contributes to a substantial reduction of time required to cook pearl millet porridges. This can also reduce the amount of fuel required to cook pearl millet porridges. Boiling is therefore recommended as a pre-treatment method that can be applied to extend the shelf life of and partially pre-cook pearl millet flour. Boiling is also suitable as the appropriate processing technology in the Healthful Harvest situation, where there are limited financial resources and technical skills to afford and operate equipment such as an extruder.

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PRESENTATION ON THE RESEARCH

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