

Understanding the Relations Among the Storage, Soaking, and Cooking Behavior of Pulses: A Scientific Basis for Innovations in Sustainable Foods for the Future

Claire M. Chigwedere , Daniel M. Njoroge, Ann M. Van Loey, and Marc E. Hendrickx

Abstract: The world faces challenges that require sustainable solutions: food and nutrition insecurity; replacement of animal-based protein sources; and increasing demand for convenient, nutritious, and health-beneficial foods; as well as functional ingredients. The irrefutable potential of pulses as future sustainable food systems is undermined by the hardening phenomenon that develops upon their storage under adverse conditions of temperature and relative humidity. Occurrence of this phenomenon indicates storage instability. In this review, the application of a material science approach, in particular the glass transition temperature concept, is presented to explain phenomena of storage instability such as the occurrence of hardening and loss of viability under adverse storage conditions. In addition to storage (in)stability, application of this concept during processing of pulses is discussed. The state-of-the-art on how hardening occurs, that is, mechanistic insights, is provided, including a critical evaluation of some of the existing postulations using recent research findings. Moreover, the influence of hardening on the properties and processing of pulses is included. Prevention of hardening and curative actions for pulses affected by the hardening phenomenon are described in addition to the current trends on uses of pulses and pulse-derived products. Based on the knowledge progress presented in this review, suggestions for the future include: first, the need for innovation toward implementation of recommended solutions for the prevention of hardening; second, the optimization of the identified most effective and efficient curative action against hardening; and third, areas to focus on for elucidation of mechanisms of hardening, although existing analytical methods require advancement.

Keywords: cooking, hardening, pulses, texture, volatile compounds

Introduction

The world has evolved into a global village wherein common interests and goals are established, encouraged, and implemented. As concerns decisions on food production and consumption, crucial factors to be considered include universality, sustainability, affordability, versatility, convenience, nutrition, and health. Agronomists, food scientists, and nutritionists are searching for and focusing on foods that can meet these criteria while such actions are applauded by environmentalists. Pulses are such food crops and include lentils (*Lens culinaris*), chickpeas (*Cicer arietinum*), cowpeas (*Vigna unguiculata*), peas (*Pisum sativum*), and common beans

(*Phaseolus vulgaris*), among others. They (i) are widely grown and consumed worldwide, (ii) are of agronomic importance as they harbor rhizobia that fix nitrogen into the soil, thereby enhancing its fertility and facilitating a reduction in quantities of exogenous nitrogenous fertilizers required for plant growth, (iii) can be consumed at all stages of growth, and (iv) are of economic importance owing to their affordability and being a source of income for small-holder farmers.

Pulses have a rich composition of nutrients (Siddiq & Uebersax, 2012). Some of their components exhibit desirable health effects such as a decrease in incidences and multiplicity of cancer as was demonstrated using common beans by Bennink (2002) and reviewed by Luna-Vital, Mojica, González de Mejía, Mendoza, and Loarca-Piña (2015). Pulses also contain bioactive compounds, such as phenolic compounds, which exhibit antioxidant activity due to their conjugated systems as was shown for common beans (Chen et al., 2015). The divalent cation-chelating ability of phytic acid in (some) pulses qualifies it as an antioxidant given its high affinity for Fe^{2+} , which catalyzes many oxidation reactions (Oatway, Vasanthan, & Helm, 2001; Pokorný & Korczak, 2001).

CRF3-2019-0008 Submitted 1/7/2019, Accepted 5/10/2019. Authors Chigwedere, Van Loey, and Hendrickx are with Laboratory of Food Technology, Dept. of Microbial and Molecular Systems (M2S), Leuven Food Science and Nutrition Research Center (LFoRCe), KU Leuven, Kasteelpark Arenberg 22, Box 2457, 3001, Heverlee, Belgium. Author Njoroge is with Inst. of Food Bioresources Technology, Dedan Kimathi Univ. of Technology, Private Bag, Dedan Kimathi, Nyeri, Kenya. Direct inquiries to authors Chigwedere and Hendrickx (E-mails: clrchigwedere1@gmail.com and marceg.hendrickx@kuleuven.be).

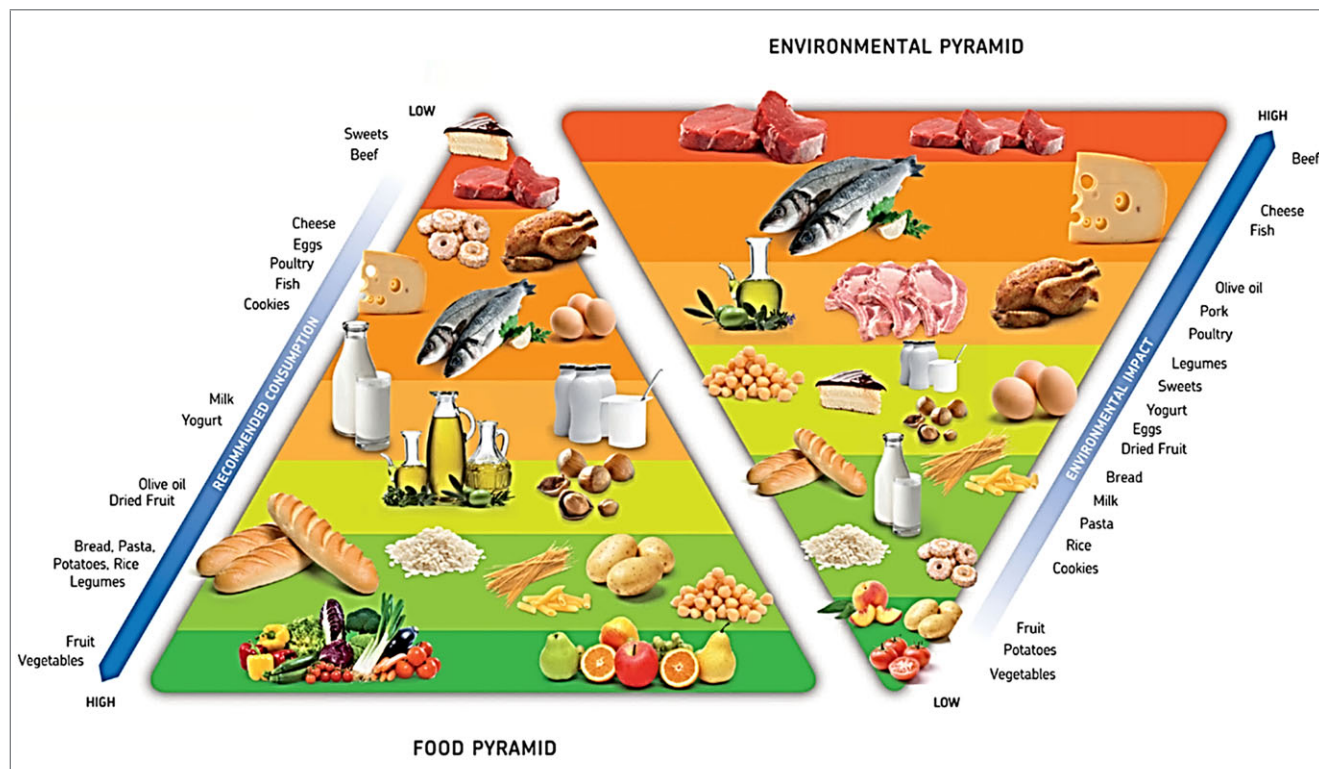


Figure 1–The double food and environmental pyramid. Reprinted, with permission, from Ruini et al. (2015). (Copyright 2019)

Other nutrition and health-related aspects associated with the consumption of pulses have been reviewed by Clark and Duncan (2017), Padhi and Ramdath (2017), and Ramdath, Renwick, and Duncan (2016). Moreover, Cuvelier, Storsley, Mollard, Thandapilly, and Ames (2017) reviewed the influence of whole pulses on glycemic response.

Pulses contribute significantly to the diet of populations of developing countries where poverty and hunger are ever-present, however, the consumption of pulses in developed nations, for example, North America, is rather low (Anderson et al., 2014). There is hope for increased consumption of pulses for two reasons: First, given the sustainability controversy surrounding meat production and consumption, as well as advocacy for animal rights by animal rights activists, pulses are the major protein substitute for meat products. Second, recent research reports that pulses and some of their extracts, such as hydrolysates and peptides, exhibit substantial bioactivity that is crucial with respect to (risk of) cardiovascular disease and various cancers, thereby rendering pulses nutraceutical foods. Efforts to raise awareness on the benefits of pulses in human health and nutrition, so as to encourage their production, utilization, and consumption, are heightening. Recently, the 68th United Nations General Assembly declared 2016 as the “international year of pulses, nutritious seeds for a sustainable future” to enhance their visibility by engaging governments, nongovernmental organizations, and other stakeholders. Therefore, they are potential crops for food and nutrition security given the information discussed above. The position of pulses in the modified double pyramid (Figure 1), which depicts the relative quantities for consumption of a variety of foods and their corresponding environmental impact, is not surprising. In fact, the global production of dry beans is increasing (Figure 2).

Diverse processing methods and technologies have been employed to enhance the utilization of pulses for consumption. These include boiling, baking, extrusion (Nosworthy et al., 2018), roasting, soaking, germination, fermentation, microwaving, autoclaving (Yin, Ma, Hu, Li, & Boye, 2018), high hydrostatic pressure (Lee et al., 2018), dehulling (Siva, Thavarajah, & Thavarajah, 2018), micronization (Bellido, Arntfield, Cenkowski, & Scanlon, 2006), and gamma irradiation (Dixit, Kumar, Rani, Manjaya, & Bhatnagar, 2011). However, the most common preparation method that facilitates palatability of pulses is presoaking the seeds followed by boiling in water, herein referred to as cooking, prior to application of sauces and condiments. Cooking is the most widely applied processing method for the consumption of pulses, and it is necessitated by consumer desires for soft textures (Ghasemlou, Gharibzadeh, & Emam-Djomeh, 2013). Therefore, this review is mainly based on this cooking process.

Postharvest drying of pulses lowers moisture content, thereby facilitating long-term storage and eradicating seasonality, albeit with a deterioration in cooking quality if storage is done under adverse conditions, that is, high temperature (>25 °C) and relative humidity (RH) (>65%). This loss of quality is caused by a hardening phenomenon that develops during the aforementioned storage conditions. The occurrence of this phenomenon has been reviewed by El-Tabey Shehata (1992), Liu and Bourne (1995), and Reyes-Moreno, Paredes-López, and Gonzalez (1993). In addition, Aguilera and Stanley (1985) reviewed the hardening phenomenon, soaking, and cooking, using kinetic approaches. Although these reviews focus on how hardening occurs, that is, the mechanisms involved, the current review explains why this phenomenon occurs, using the glass transition theory of (storage) stability. However, the current review also includes recently obtained insights on (some

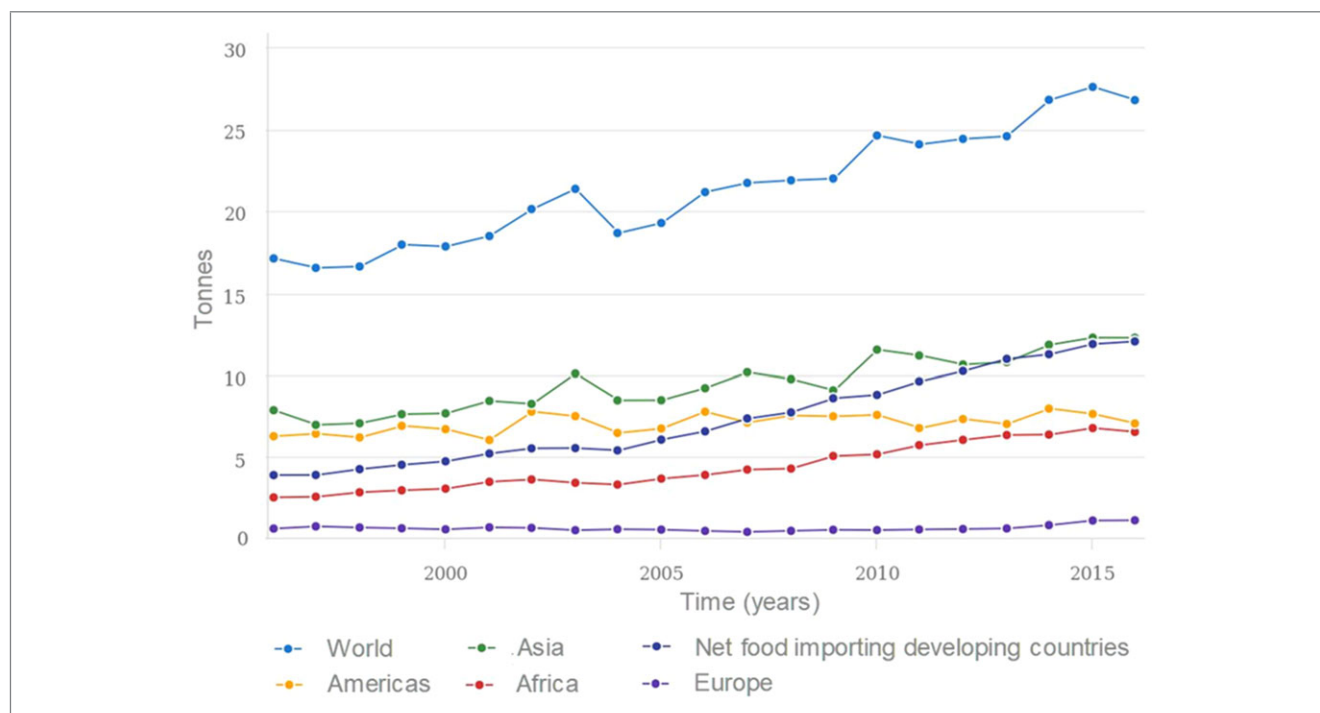


Figure 2—Production trends of dry beans for the 1996 to 2016 period (FAOSTAT, 2018).

of the) mechanistic explanations for the hardening phenomenon. Recommendations on prevention and curative actions for hardening are provided, as well as challenges that can be encountered in doing so.

This review also presents insights into the hydration and then texture evolution during the cooking-induced softening of pulses that has been attributed to starch gelatinization, protein denaturation, or pectin solubilization as described in some of the aforementioned reviews. Furthermore, this review provides the rate-limiting process for softening and how it is influenced by the hardening phenomenon. In addition to aspects on texture evolution, flavor generation during cooking of beans is reviewed with identification of chemical reactions from which the volatile compounds emanate. The contribution of this review emanates from its focus on mechanistic perspectives of all these processes.

Soaking and Cooking of Pulses

Soaking and cooking are the two universal methods applied during the preparation of pulses for consumption. It is interesting to understand the physicochemical changes including mechanistic aspects that occur during these two processes, which are reviewed in detail in this section.

Soaking

Soaking is a very crucial process that is an integral part of different preparation methods for pulses, such as domestic cooking and industrial canning where it facilitates faster cooking through sensitizing biopolymers to heat treatment (Bellido et al., 2006). It also facilitates germination and fermentation where biomembranes and biomolecules require hydration for active metabolism (Abu-Ghannam & McKenna, 1997; Kikuchi, Koizumi, Ishida, & Kano, 2006). During soaking, pulses attain equilibrium moisture content, which is pulse- and cultivar-dependent (Kaptso et al., 2008), increase in size and weight to a maximum, and soften to a constant value that is achieved long before moisture saturation, as

has been demonstrated in beans by Abu-Ghannam (1998) and in lentils by Joshi, Adhikari, Panozzo, and Aldred (2010). Mechanistic insight into water imbibition and distribution during soaking of pulses has been investigated over the past decades using various techniques and has been shown to involve different microstructural elements as discussed in the following section. Soybeans (*Glycine max*) are not considered pulses but rather as oilseeds because of their high oil content. However, since many studies on hydration have been conducted on soybeans, they are included in this review.

Transport of water in pulses during soaking. Hydration of a seed commences upon immersion in water (Mikac, Sepe, & Serša, 2015). However, there is controversy on the entry point of water in seeds with possible roles for the lens (strophiole) (Kikuchi et al., 2006), raphe (Koizumi et al., 2008) micropyle (Mikac et al., 2015), seed coat (Ma, Cholewa, Mohamed, Peterson, & Gijzen, 2004), hilum (Varriano-Marston, & Jackson, 1981), and combinations of these (Naviglio, Formato, Pucillo, & Gallo, 2013). Lentils on which the hilum, micropyle, and raphe were waxed (to seal them) exhibited a substantial hard-shell (HS) behavior after a 48-hr soaking period at 22 °C (Tang, Sokhansanj, & Sosulski, 1994), unlike the nonwaxed lentils, confirming the synergistic action of these microstructural components in moisture migration. Some of these structural components as well as the cell layers characteristic of *Phaseolus* seeds are shown in Figure 3.

In support of the micropyle being the port of water entry, an occluded micropyle as visualized by scanning electron microscopy (SEM) resulted in a suppressed water uptake rate and quantity in navy beans (Agbo, Hosfield, Uebersax, & Klomparens, 1987). The role of the hila in water transport is supported by reports on visualization of vascular bundles in hila of lima beans, using X-ray photography (McCollum, 1952), and later a honeycomb-like network structure containing cavities inside the hila of beans (De J. Berrios, Swanson, & Cheong, 1998). Permeability of water through the seed coat has been attributed to either presence of prominent pores as observed in beans (Agbo et al., 1987) or cracks

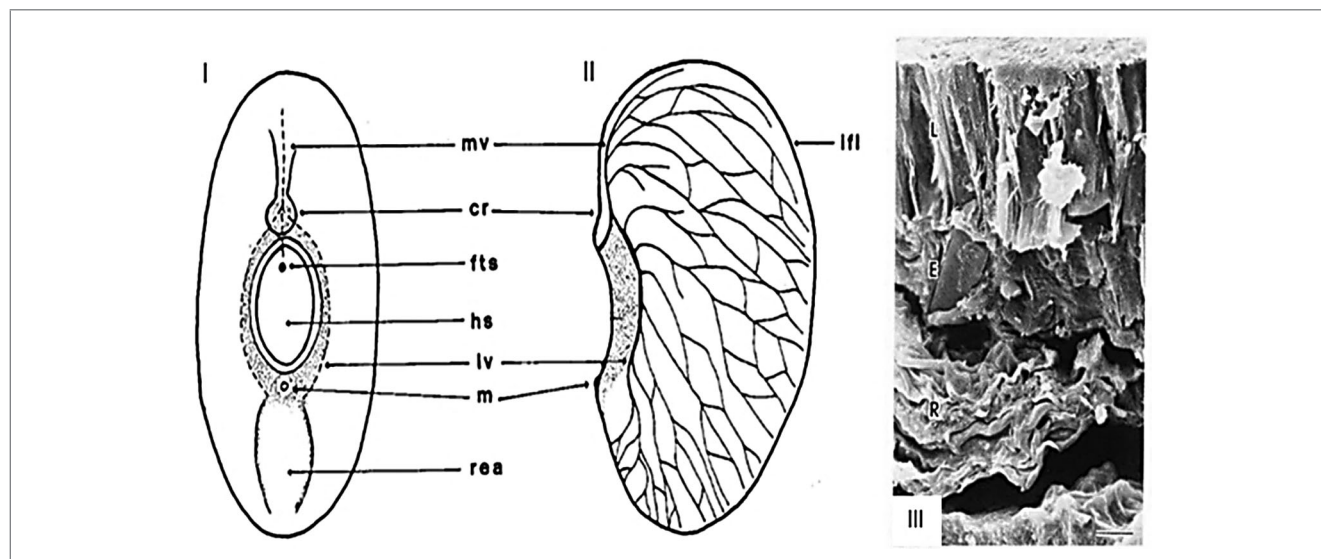


Figure 3—Morphology features of a *Phaseolus* seed coat showing surface features after removal of the funicle (I) (the chalazal region [cr], funicular trace scar [fts], hilum scar [hs], integument fusion line [ifl], lateral vein [lv], micropyle [m], median vein [mv], and region above embryonic axis [rea]) and the vascular network for transport of photosynthate into the cotyledons (II) (Offler & Patrick, 1984). (Copyright 2019). The cross-sectional view of the cell layers comprising the palisade (L), epidermal (E), and parenchyma (R) cell layers (III). The bar represents 10 μm (Hughes & Swanson, 1985). (Copyright 2019)

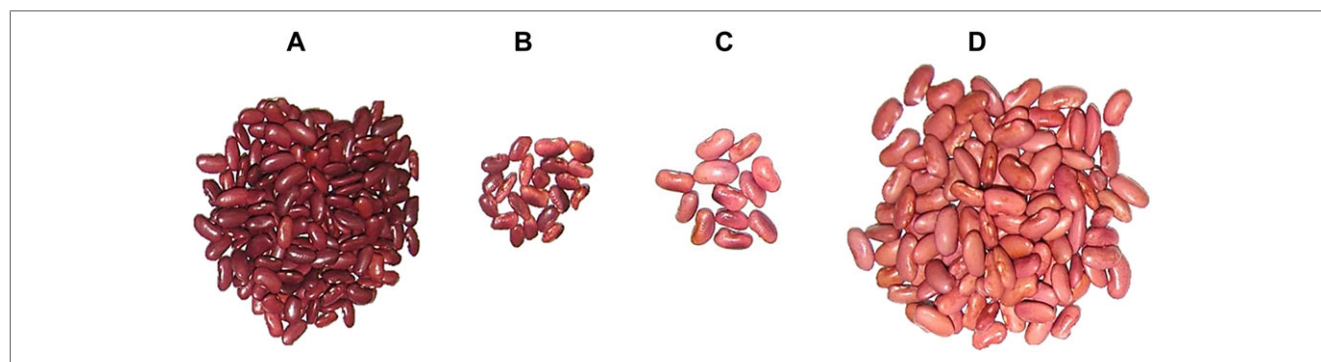


Figure 4—Nonhomogeneity of soakability showing nonhydrated (A), slightly hydrated (B), almost fully hydrated (C), and fully hydrated (D) beans after soaking in demineralized water at 25 °C for 16 hr.

in the hydrophobic cuticle layer, which covers the palisade cell layer of the seed coat, as observed in soybeans (Ma et al., 2004). In both reports, the hilum, micropyle, and raphe were not completely disregarded as water entry points. Tang et al. (1994) suggested that the sizes of the pores and cracks increase when surface area of the lentil increases during hydration. In addition to cracks in the cuticle, Shao, Meyer, Ma, Peterson and Bernards (2007) found its composition to be a factor determining water permeability. Soybean seeds whose seed coats had an unusually high quantity of hydroxylated fatty acids in the cuticle were water-impermeable. The impermeability was overcome by boiling in 0.1 M NaOH for 5 min. It is a challenge to isolate cutin, as was demonstrated by Ma et al. (2004) who failed to isolate it completely using several methods including a mixture of oxalic acid and ammonium oxalate (35 °C, 2 weeks) and 80% H₂SO₄ (24 hr). Impermeable pinto and navy beans had high levels of fatty acids and phenolics in the seed coats (Ross, Zhang, & Arntfield, 2010). According to Snykal et al. (2014), deposition of suberin, a complex lipophilic polyester, in the palisade layer of seed coats renders them water-impermeable. A delay (lag phase) in water uptake behavior, attributed to the seed coat, was demonstrated in common beans (Mikac et al.,

2015; Piergiorganni, 2011), adzuki beans (*Vigna angularis*) (Oliveira et al., 2013), and cowpeas (Kaptso et al., 2008). This lag phase was reportedly overcome by plasticization of the seed coat through a blanching treatment leading to an increased rate of water uptake by Abu-Ghannam and McKenna (1997). A high rate of water uptake for beans with damaged seed coats, as observed by Pan, Atungulu, Wei, and Haff (2010), may serve as attestation that seed coats act as barriers for water entry into the beans at the onset of hydration.

A batch of Canadian wonder common beans, which had fully soaking as well as partially and completely impermeable beans (soakability approximately 40%; Figure 4), was stored at 35 °C and 83% RH for 3 months in an aging experiment in our research unit (data unpublished). Surprisingly, the soakability of the beans increased to 100% after storage. From the perspective of the cracks and pores mentioned earlier, and the deposition of hydrophobic material such as suberin or lignin in the palisade layer, it seems logical that the deposited material seals off the pores and cracks, thereby enhancing the hydrophobicity of the seed coat. However, this hypothesis seems highly unlikely in light of our observations of storage-induced permeability. According to El-Tabey Shehata

(1992), HS in freshly harvested beans is reversible but that which is storage-induced is irreversible and this is what was exhibited by this batch of beans. However, the mechanism of this reversibility is not clear. A possibility would be that if the observed impermeability before storage was due to a hindrance of the crucial structural component(s) for water uptake, for example, an occluded micropyle or blocked hilum, storage under the stipulated conditions could have eliminated the obstruction. In fact, our observation of storage-induced permeability of seed coats further complicates the already complex situation of elucidating the structural component responsible for water uptake. There is no universally accepted structure denoted as the point of water entry into seeds. In fact, De J. Berrios et al. (1998) and Hu, Wang, Wu, and Baskin (2009) reported that the structural component responsible for water uptake in beans is cultivar-dependent. From this perspective, water uptake capacity under the same conditions can be cultivar-dependent as shown for three cultivars of lentils by Joshi et al. (2010).

Considering different studies on water uptake in pulses, it can be concluded that specific structural parts of the seeds constitute a complex integrated water absorption system. This was demonstrated using lentils by Tang et al. (1994) who showed that involvement of different structures in moisture absorption (from a humid environment) and water imbibition depends on initial moisture content of the lentils. At an initial moisture content of 12%, most lentils were characterized by impermeable seed coats and either closed or narrowly opened hila, thus they were categorized as exhibiting the HS defect. With an increase in initial moisture content or soaking temperature, the hila increased in width, as visualized by SEM, and seed coat permeability also increased. However, at 16% to 24% moisture, the major route for moisture uptake was the seed coat. Between 10% and 19% moisture, the raphe and micropyle were closed (Tang et al., 1994). From these results, it can be inferred that the hilum is the rate-limiting barrier for water/moisture uptake in lentils.

Treatment of pulses affected by the HS defect with methanol and ethanol overcomes the defect, leading to permeability of the seed coat as demonstrated for soybeans by Hsu, Kim, and Wilson (1983). To explain this observation, it was hypothesized that solvents, such as ethyl ether, chloroform, acetone, and alcohols decrease packing density of membrane components, thereby disrupting their interactions and enabling them to bind dormancy-breaking factors such as phytochrome and nitrate. This is termed as the membrane hypothesis of dormancy breakage.

After entering the seed, the water is either transported to the periphery of the cotyledons through the spongy parenchyma cells (Varriano-Marston & Jackson, 1981), thereby causing wrinkles that are observed during soaking (Naviglio et al., 2013) or channeled to the embryo through primarily the vascular system of the seed coat (Kikuchi et al., 2006; Koizumi et al., 2008). The latter was confirmed by microscopic visualization of the vascular bundle system between the germ (embryonic axis) and the periphery of the cotyledons in soaked lentils by Joshi et al. (2010). The vascular bundles were characterized by closely packed cells devoid of starch granules, with some containing nucleolus-like material. The seed coat directs and regulates water uptake by the embryo, suggesting that it acts as a water reservoir for the embryonic axis (McDonald, Vertucci, & Roos, 1988). As the water is distributed to the periphery of the cotyledons, it also enters into the void space between them before uptake by the cotyledons from both the abaxial surfaces and the void space (Mikac et al., 2015; Varriano-Marston & Jackson, 1981). Thereafter, water imbibition

by the cotyledons progresses toward the middle of the seed until full hydration is achieved. In soybeans, this is achieved through mainly the abaxial surfaces, thus forcing the adaxial surfaces apart, thereby increasing the void space between them (Koizumi et al., 2008). It was suggested that displaced gases may collect in the void that narrows later with progression of swelling of the cotyledons, but this hypothesis has not been evaluated.

Mechanistic insight into swelling of pulses during soaking. Imbibition is characterized by an initial phase of rapid inrush of water followed by a phase in which the rate of water uptake is steady until saturation. This was observed in studies on peas (Simon, 1974), common beans (Naviglio et al., 2013), soybeans (Koizumi et al., 2008), and cowpeas (Affrifah & Chinnan, 2006). This rapid inrush of water was associated with filling of capillaries on the surface of the seed coat and hilum (Abu-Ghannam and McKenna, 1997) and water uptake by the intracellular matrix (Zhang & McCarthy, 2013). In the latter study, the subsequent phase was associated with water uptake into the extracellular space.

During soaking, imbibed water displaces adsorbed gases as it wets the matrix. With advancement of the wetting front, the free and displaced gases become pressurized such that they exert backpressure resistance, which may impede further uptake of water. With increase in pressure, solubilization of the gases increases, thereby facilitating their escape and this is the rate-limiting step of the second phase (characterized by a steady rate of water uptake) (Parrish & Leopold, 1977). This gas desorption-backpressure process is suggested to lead to swelling of seeds during imbibition. Seeds with a higher initial moisture content have reduced quantities of adsorbed gases and hence experience delayed backpressure resistance leading to high initial rates of water uptake compared to drier seeds (Hincks, McCannel, & Stanley, 1987; Hincks & Stanley, 1986; Ibarz, González, & Barbosa-Cánovas, 2004; Parrish & Leopold, 1977; Tang et al., 1994). Regardless of maximum expansion, seeds can still incorporate more water and this is hypothesized to be due to progressive substitution of gases by water at small pores in cell constituents (Kikuchi et al., 2006). Enhancement of elimination of gas from the matrix can be achieved by repeated depressurization during vacuum-impregnation with soaking solution. Such a treatment reduced the soaking time of pinto beans (Zanella-Díaz, Mújica-Paz, Soto-Caballero, Welti-Chanes, & Valdez-Fragoso, 2014).

Soaking is a very slow (12 to 24 hr) process at ambient conditions, hence several methods have been devised to increase the rate of imbibition, thus accelerating soaking as discussed in the following section.

Improvement of soaking efficiency. Soaking efficiency can be improved by manipulation of properties of the pulses. For example, by mechanical decoating, as demonstrated on beans using a polishing machine (Kon, Brown, Ohannesson, & Booth, 1973), and by increasing initial moisture content as explained in the previous section. Enhanced elimination of adsorbed gases in the matrix through repeated vacuum-impregnation of soaking solution enhances water uptake as described in the previous section. Creation of new microscopic channels in the matrix, thereby diminishing internal resistance to mass transport, also enhances water uptake, and this can be achieved through cyclical pressure and ultrasound treatments. The efficiency of cyclical pressure soaking can be also attributed to enhanced plasticity of the seed coat (Naviglio et al., 2013), although this has not been confirmed in the literature. The efficacy of ultrasound treatment (16 °C, 47 kHz, 750 W) can be ascribed to its exertion of a rapid succession of alternating expansions and contractions leading to increased effective diffusivity

(by 61% in navy beans) (Ghafoor, Misra, Mahadevan, & Tiwari, 2014).

Also, heat treatments such as elevated temperature of the soaking medium (Kinyanjui et al., 2015; Mikac et al., 2015; Oliveira et al., 2013; Piergiovanni, 2011) and blanching (Joshi et al., 2010; Kapso et al., 2008) enhance soaking efficiency. Soaking at elevated temperature increases seed coat pore diameter and its water permeability, thereby increasing diffusivity. Blanching increases the initial moisture content and plasticizes the seed coat, thereby significantly enhancing the hydration rate, especially if soaking is conducted at temperatures <40 °C otherwise its influence is not pronounced (Abu-Ghannam & McKenna, 1997). After soaking at different temperatures in the same study, blanching prior to soaking decreased the activation energy of soaking by >50%, thus the temperature dependency of the rate of hydration was reduced.

Heat treatment methods are the most effective in reducing soaking time (Zanella-Díaz et al., 2014). The higher the soaking temperature, the greater the extent and rate of soaking-induced softening, as demonstrated by Abu-Ghannam (1998) during soaking of beans (at 20, 30, 40, and 60 °C) and by Joshi et al. (2010) during soaking of lentils (at 20, 50, and 80 °C). In the latter study, to achieve similar hardness of lentils, soaking at 50 and 80 °C was reported to be four to six times faster than at 20 °C. From these results, they deduced a link between texture and moisture content of soaked beans and moreover concluded that these parameters can be used for prediction of cooking quality. This link is not clear to envisage, given that water uptake capacity was lower with soaking at 80 compared to 50 °C, and yet the soaked beans were softer at the former temperature. Softening is based on mainly heat-induced changes of biomolecules, such as starch, pectin, and proteins, and the role of moisture is to sensitize these biomolecules to the applied heat. At 80 °C, most probably starch could have been gelatinized given that the temperature range for gelatinization of lentil starch is 67 to 82 °C (Chung, Liu, Hoover, Warkentin, & Vandenberg, 2008; Joshi et al., 2013). Thus, soaking at 80 °C could have imparted a cooking effect. Most probably, different phenomena were happening with change in temperature, hence the selected temperatures may not have been suitable for the objectives under study.

Hydration of pulses is crucial for protein denaturation, starch gelatinization, and, eventually, seed softening during the cooking process that is discussed in the next section.

Cooking

Pulses are cooked to facilitate palatability. According to Rodhouse, Haugh, Roberts, and Gilbert (1990), presence of phytohemagglutinin in beans necessitates adequate cooking otherwise they may become poisonous. Korte (1972) reported residual hemagglutinin activity in 22% of weaning food mixtures prepared from maize and bean flour. In the next sections, the process of cooking in terms of hydration and softening is described.

Hydration kinetics. Similar hydration kinetics as described for soaking can be observed also during subsequent cooking, except that for nonsoaked beans, cotyledons are hydrated from the outer surface only unlike for the cotyledons of presoaked beans that are hydrated also from the void between them (Mikac et al., 2015). The moisture gradient, which is the driving force due to differences in water content within the bean, decreases with the progression of cooking as observed from the wetting front during cooking of nonsoaked navy beans by Zhang and McCarthy (2013) using magnetic resonance imaging (MRI). During the initial phase (rapid water uptake), water is predominantly taken up

into the intracellular space concomitant with starch gelatinization and dissolution of the middle lamella, leading to creation of large intercellular spaces into which water is taken up during the subsequent linear phase. Mikac et al. (2015) realized increased water uptake into cotyledons after maximum volume (maximum expansion) of the beans was achieved, and they attributed it to water requirements for starch gelatinization and protein denaturation.

Evolution of texture. It was mentioned earlier (“Soaking” section) that precooking hydration sensitizes biopolymers (or their networks) to heat treatment. The biopolymers of interest for texture modification during cooking of pulses include proteins, starch, and pectin, whose structures have been thoroughly reviewed elsewhere (Pauling, Corey, & Branson, 1951; Sheldrick, Goddard, & Kruger, 1985; Voragen, Coenen, Verhoef, & Schols, 2009) and hence will not be covered in this review. Proteins, starch, and pectin are denatured, gelatinized, and solubilized during cooking. However, there are inconsistencies pertaining to the process that determines cooking time.

In several studies, cooking time of pulses was related to the extent of starch gelatinization (Arntfield et al., 1997; Bellido et al., 2006; Ndungu, Emmambux, & Minnaar, 2012; Taiwo & Akanbi, 1997). According to Aguilera and Stanley (1985), softening of pulses is a biphasic process wherein pectin solubilization precedes starch gelatinization. On the contrary, Zhang and McCarthy (2013) visualized swelling of starch granules and, consequently, cells, followed by creation of small intercellular spaces that were enlarged by the gradual dissolution of the middle lamella, eventually leading to cell separation. Therefore, in their study, starch gelatinization preceded pectin solubilization. del Valle, Cottrell, Jackman, and Stanley (1992) acknowledged that both pectin solubilization and protein denaturation contributed to softening of beans during cooking. However, the possibility of other mechanisms contributing to bean softening was highlighted. Enhanced softening, leading to reduced cooking times, was related to protein insolubilization due to denaturation in lentils and beans according to Arntfield et al. (1997) and Garcia-Vela, del Valle, and Stanley (1991), respectively.

Due to this controversy, the authors of the current review explored the rate-limiting step for softening of common beans. Cotyledons of Canadian wonder common beans cooked in demineralized water and sodium bicarbonate (NaHCO₃) solution for different times were disintegrated to simulate mastication prior to microscopic and calorimetric analyses. The summary of the evolution of microstructure, texture, and pectin solubilization during cooking of Canadian wonder common beans from our previous work (Chigwedere et al., 2018; Chigwedere, Nkonkola, et al., 2019) is shown in Figure 5. Three phases, namely, cell breakage, cell breakage and cell separation, and then cell separation, were visualized as shown by the micrographs in Figure 5 (for beans cooked in demineralized water), highlighting progressive solubilization of pectin. Similar observations were made after cooking in NaHCO₃ solution, except that the transitions occurred much faster than when the beans were cooked in demineralized water. After cooking in demineralized water for 120 min, Njoroge et al. (2016) also visualized cell separation.

Calorimetry results showed that proteins were denatured and starch was gelatinized early (within 30 min) during cooking, yet the beans still retained hardness (Chigwedere et al., 2018). It is clear from Figure 5 that with progression of cooking there was residual birefringence, highlighting residual molecular order in the darker micrographs (observed under polarized light to

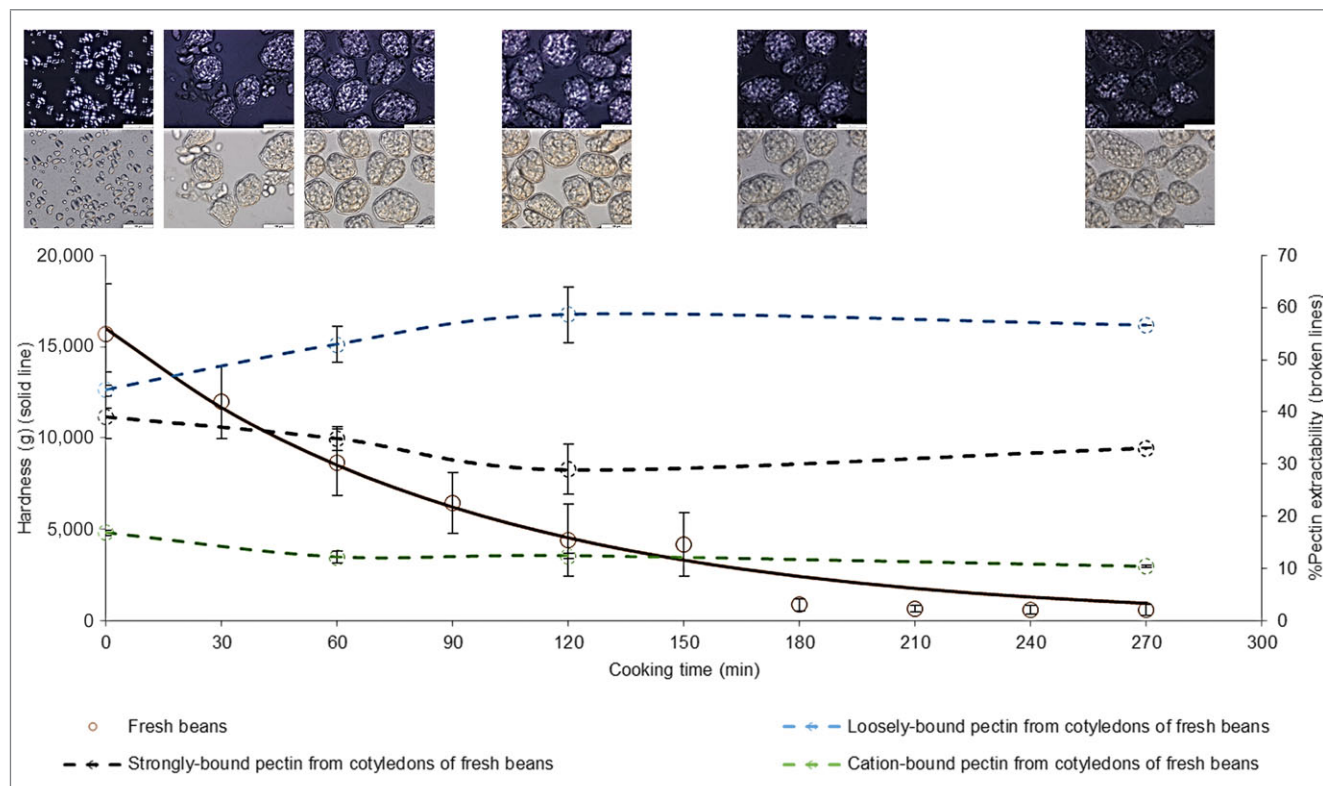


Figure 5—Evolution of microstructure (from micrographs), texture (indicated by hardness), and pectin solubilization (highlighted by pectin extractability) in cotyledons of (fresh) Canadian wonder common beans during cooking in demineralized water. Darker micrographs were visualized under polarized light to assess the extent of starch gelatinization. Pectin extractability data were not modeled, the broken lines are to show trends clearly. All scale bars on micrographs represent 100 μm (Chigwedere et al., 2018; Chigwedere, Nkonkola, et al., 2019). (Copyright 2019)

qualitatively assess the extent of starch gelatinization). To investigate this residual birefringence, starch was released from the enclosing cell walls through cryomilling. Micrographs A and B represent the cryomilled sample (fresh beans cooked for 120 min) in Figure 6. Micrograph C shows swollen and distorted starch granules that lost the semicrystalline structure of native granules after heat treatment (95 °C, 5 min) as confirmed under polarized light by absence of birefringence (micrograph D), thereby indicating complete starch gelatinization. By comparing micrographs of powdered fresh bean cotyledons obtained from beans cooked for 120 min after cryomilling (A and B), with those of bean cotyledon flour cooked in demineralized water (95 °C, 5 min) (C), it can be unequivocally stated that the morphology of starch granules is similar, but the size differs with the latter being bigger due to unhindered swelling during the heat treatment. Therefore, cell walls restricted uncoiling of gelatinized starch and not starch hydration as suggested by Berg, Singh, Hardacre, and Boland (2012) and Brummer, Kaviani, and Tosh (2015). These changes in protein denaturation, starch gelatinization, and pectin solubilization during cooking of beans indicate that pectin solubilization is the rate-limiting process (Chigwedere et al., 2018). Therefore, texture decay during the cooking process in beans is related to pectin changes in the cell walls and middle lamellae.

Profound understanding of the softening process necessitated deeper insight into the pectin solubilization process, hence we extracted and quantified pectin from the cotyledons of beans cooked for different times. With an increase in cooking time, hence softening, the proportion of loosely bound (water extractable) pectin increased concomitantly with a decrease in strongly bound

(sodium carbonate extractable) pectin (Figure 5), considered up to now as ester-bound to other cell wall components. Moreover, this solubilization process was not accompanied by depolymerization (Chigwedere et al., 2019). No great changes in cation-crosslinked (chelator extractable) pectin were observed and this supports the interconversion of pectin fractions as the mechanism by which pectin is solubilized rather than breaking of the cation-mediated cross-links.

The effect of different individual processing technologies, such as extrusion, high-pressure processing, pulsed electric field, and use of microwaves, as well as their combinations on pectin solubilization, can be explored in the same way as in our previous work (Chigwedere et al., 2019). This is important considering that these technologies are used in many food processing industries.

Evolution of volatile compounds: toward generation of flavor.

Flavor and its development in plant-based food systems depend on interdependent factors, such as maturity level at harvest, postharvest handling, composition, industrial and/or domestic processing, and mastication during consumption. Odor and aroma emanate from perception of volatile compounds through ortho- and retronasal means, respectively. It is challenging to differentiate first, flavor-active and flavor-inactive volatile compounds and second, flavor-active volatile compounds according to the mode of perception (ortho- and retronasal) (van Ruth, 2001). In this review, flavor (in)activity or mode of perception are disregarded, hence all such compounds are referred to as volatile compounds.

Influence of the food matrix on flavor development and perception. Food composition and structure influence the release of volatile compounds leading to partition coefficients due to the multiplicity

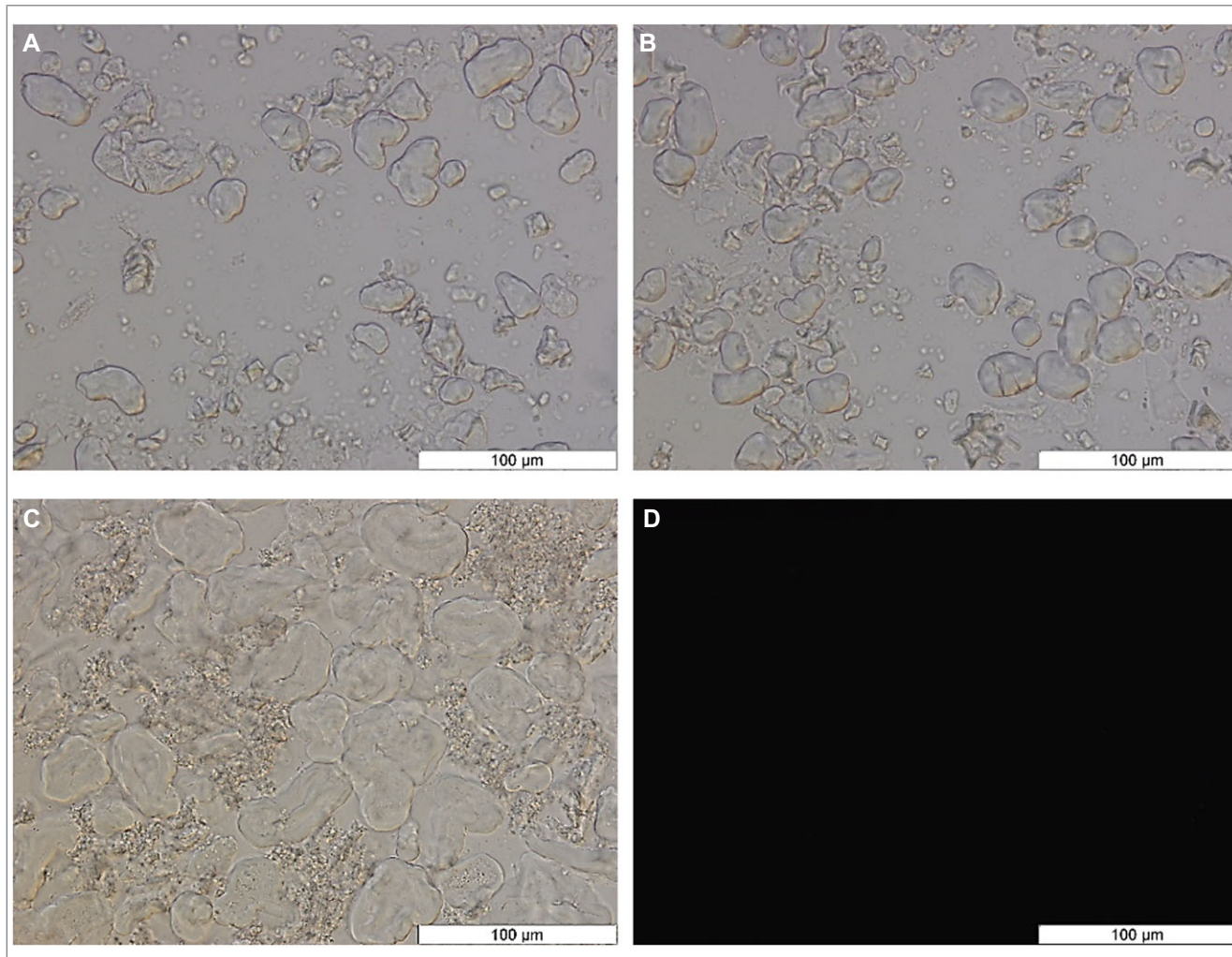


Figure 6—Cell wall–enclosed starch granules of fresh bean cotyledons from beans cooked for 120 min after cryomilling (A and B). Micrographs C and D show microstructure of bean cotyledon flour cooked in demineralized water (95 °C, 5 min) and cooked cotyledon flour under polarized light, respectively.

of complex interactions between the matrix constituents and volatile compounds. Moreover, such interactions can lead to partition coefficients for release, thereby influencing flavor perception. Factors that influence retention and perception of flavor due to these interactions were reviewed by Guichard (2002). Proteins bind volatile compounds through either covalent or hydrophobic interactions. Lipids retain (hydrophobic) volatiles to a greater extent than do proteins, and this is interesting in light of flavor release from emulsions wherein proteins are involved at the oil/water interface. However, other characteristics of the emulsions, such as droplet size, contribute significantly to retention and perception of flavor. Phenolic compounds influence flavor retention through either hydrophobic interactions or weak noncovalent interactions, especially hydrogen bonding (Guichard, 2002). Formation of complexes between phenolics and proteins may influence flavor retention and perception.

In the presence of polysaccharides, hydrocolloids that increase viscosity of food systems, diffusion of volatile compounds is limited leading to flavor retention. The effect of increased viscosity plays a more significant role in retention and perception of flavor, compared to molecular interactions between the polysaccharides and the volatile compounds. Carbohydrates are popular encap-

sulation materials for volatile compounds for flavor delivery. As reviewed by Goubet, Le Quere, and Voilley (1998), retention increases with increased molecular weight of the carbohydrate but decreases beyond an optimum size. The state of the carbohydrates influences retention in this order: amorphous > collapsed > crystallized. On the other hand, properties of the volatile compounds that enhance retention include a high molecular weight, while high relative volatility and polarity diminish it. Addition of salt to aqueous food-based systems facilitates release of volatile compounds, and this is more pronounced for alcohols than aldehydes and esters (Guichard, 2002). Upon processing, especially thermal, these macromolecules undergo changes and the enormous effect of such on flavor development is not a surprise.

Influence of processing on flavor development. The flavor of fresh foods is highly influenced by primary aromas, which are mainly produced due to enzymatic activity during maturation. In addition to enzyme-catalyzed oxidation, β -oxidation and autoxidation of unsaturated fatty acids generate volatile esters, alcohols, ketones, and acids during ripening. Physical damage facilitates autoxidation and increased enzymatic activity, thereby enhancing formation of volatile compounds (Christensen, Edelenbos, & Kreutzmann, 2007). Lipoxigenase activity on linoleic and α -linolenic fatty

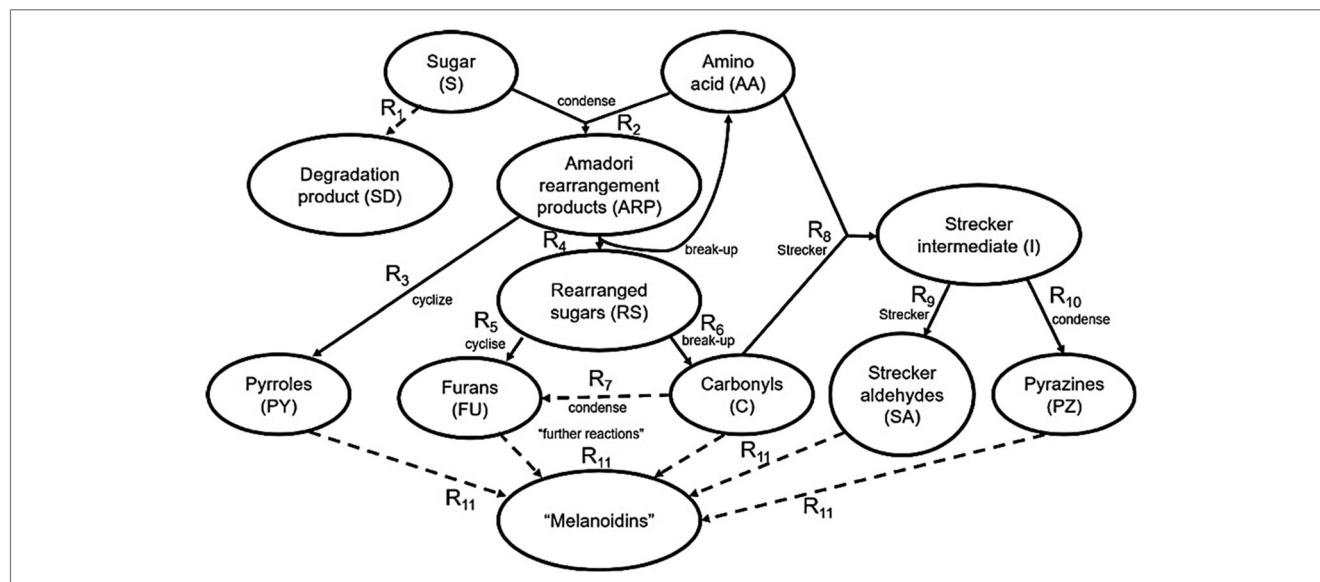


Figure 7—Illustration of flavor generation by the Maillard reaction with reaction steps R_1 , R_3 , R_4 , R_5 , R_6 , R_9 , and R_{11} representing unimolecular reactions while R_2 , R_7 , R_8 , and R_{10} represent bimolecular reactions (Jousse et al., 2002). (Copyright 2019)

acids leads to the generation of volatile alcohols or aldehydes with possible enzymatic esterification of the latter to produce sweet and fruity sensory notes (Salas, García-González, & Aparicio, 2006). According to Stevenson and Chen (1996), most aldehydes with at least six carbon atoms emanate from lipid oxidation and can, together with alcohols, be oxidized to acids through free-radical reactions (Marteau et al., 2013).

At low moisture content, the diffusivity of organic molecules is subdued, hence for aromatic molecules the aroma can be entrapped in glasses (for example, carbohydrates and proteins; Le Meste, Champion, Roudaut, Blond, & Simato, 2002). Therefore, glass–rubber transitions due to temperature and moisture content abuse can lead to release of the glass-encapsulated aroma. Structure collapse, which is characterized by reduction in porosity and volume, reduces sensitivity of materials to oxidation, but it facilitates escape of aroma (Le Meste et al., 2002). This can occur during air- or freeze-drying as well as during storage of dried products. Secondary aromas that are process-induced contribute immensely toward the flavor of processed food products. According to Jaeger, Janositz, and Knorr (2010) and Jousse, Jongen, Agterof, Russell, and Braat (2002), the greatest contribution of thermal processing to the flavor profiles of foods is accredited to mainly the Maillard reaction, which can be illustrated schematically by 11 reaction steps as shown in Figure 7.

The Maillard reaction is characterized by a series of chemical reactions that are initiated by condensation of an amino acid and a reducing sugar. A side-reaction of the Maillard reaction called the Strecker degradation leads to formation of flavor-active aliphatic aldehydes that are termed Strecker aldehydes (Jousse et al., 2002). Such aldehydes include 3-methylbutanal, 2-methylbutanal, and 2-methylpropanal that emanate from leucine, isoleucine (Cremer, Vollenbroeker, & Eichner, 2000; Estévez, Ventanas, & Heinonen, 2011), and valine (Cremer & Eichner, 2000), respectively. Amino acids undergo Strecker degradation to form Strecker aldehydes, whereas lipids and polyphenols can undergo the same degradation to yield uncommon flavors (Yaylayan, 2003; Zamora, Gallardo, & Hidalgo, 2007, 2008). Temperature, time, and the nature of the metabolites are the variables that influence the Maillard reaction.

Generation of flavor during processing of pulses. Assessment of cooking quality of pulses involves mainly texture. However, flavor is among other quality attributes of importance for consumer acceptance of pulses. Studies that have been published on generation of flavor from pulses are few and limited in scope, encompassing either the raw or fully cooked pulses only, as summarized in Table 1. From this table, it is clear that the evolution of volatile compounds during the process of cooking has been neglected. Realizing that knowledge gap, Chigwedere et al. (2019) studied the evolution of volatiles by analyzing headspace components from beans cooked in demineralized water for different times using headspace solid phase microextraction gas chromatography linked with mass spectrometry. Some of the compounds found in the studies listed in Table 1 were obtained.

The distinction between noncooked and cooked beans, as well as differences in volatile profiles of beans cooked to different extents (Figure 8), demonstrates the influence of cooking time on evolution of volatile compounds (Chigwedere et al., 2019). As opposed to only listing the obtained volatile compounds, as was done in most of the earlier studies, our data analysis approach enabled selection and identification of significantly changing volatile compounds. They included ketones (2-propanone, 2-butanone), aldehydes (2-methylbutanal, 3-methylbutanal, benzaldehyde), a furan compound (2-ethylfuran), an ester (ethyl acetate), sulfur compounds (dimethyl sulfide and dimethyl disulfide), and a benzopyran derivative (2H-1-benzopyran). Kinetic modeling of these marker compounds was done to quantitatively describe their formation/production, as was thoroughly discussed in our work (Chigwedere et al., 2019). Most of the selected marker compounds were linked to the Maillard reaction, and this is not surprising given that beans are rich in proteins and starch. Different aroma and flavor attributes for sensory analysis of the volatile fraction of beans were established by Malcolmson et al. (2014) and Mishra et al. (2017).

Flavor perception during oral processing. Flavor perception during food consumption is a dynamic experience, from the initial impact to the residual flavor after chewing. During mastication, mass transport of volatile compounds between the solid matrix and the

Table 1—Studies conducted on volatile profiles of pulses.

Source	Pulse	Processing	Analytical technique
Buttery, Seifert, and Ling (1975)	Kidney beans	Cooking: steam distillation continuous extraction	Capillary gas chromatography and mass spectrometry (GC-MS)
Lovegren, Fisher, Legendre, and Schuller (1979)	Common beans, lima beans, lentils, mung beans, and split peas	Grinding of nonsoaked noncooked pulses	Flame ionization GC-MS-data system
Del Rosario et al. (1984)	Winged beans	Grinding of soaked seeds	GC-MS-data system
van Ruth, Dings, Aprea, and Odake (2005) and van Ruth, Dings, Buhr, and Posthumus (2004)	Kidney beans	Cooking: 190 °C, 20 min Commercially canned	GC-MS and proton transfer reaction-mass spectrometry
Oomah, Liang, and Balasubramanian (2007)	Black, dark red kidney, and pinto beans	Grinding of nonsoaked noncooked beans	Headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS)
Azarnia et al. (2011)	Field peas	Dehulling, dry milling, cooking (20 min, temperature not specified)	HS-SPME-GC-MS
Malcolmson et al. (2014)	Field peas	Cooking (20 to 30 min, temperature not specified)	Sensory analysis
Ma, Boye, Azarnia, and Simpson (2016)	Common beans, lentils and peas	Grinding of raw and roasted seeds, roasting of flour, mashed precooked seeds, slurries from precooked seeds, freeze-drying of slurries flours, precooked spray-dried flours	HS-SPME-GC-MS
Mishra, Tripathi, Gupta, and Variyar (2017)	Kidney beans	Preparation of slurry from raw and cooked (through simultaneous distillation/extraction) beans	HS-SPME-GC-MS and sensory analysis

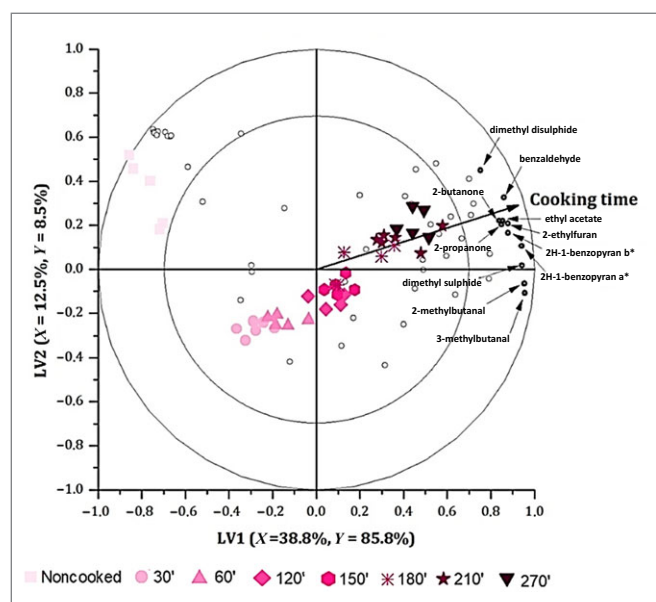


Figure 8—Biplot depicting the evolution of volatile compounds during cooking of fresh beans in demineralized water. Symbols represent the samples and open circles represent volatile compounds but those with thicker edges represent marker compounds. These marker compounds were selected based on variable identification coefficient (VID) procedure ($VID > |0.80|$) and identified based on retention index and mass spectra. *The two benzopyran derivatives were identified as the same compound regardless of different elution times (Chigwedere, Tadele, et al., 2019). (Copyright 2019)

liquid phase of the material determines the rate of release of the volatiles. This mass transport is dependent on mastication rate, type of compound, and resorption/retention of volatiles by the mouth mucosa (van Ruth et al., 2005; van Ruth et al., 2004). All these factors lead to different sensory experiences and impressions with which different foods are associated among consumers,

due to differences in physiology, mouth temperature, presence of saliva, and oral processing of the food. Moreover, structure and initial concentration of odorants influence flavor perception, and mixing of odorants can result in enhancement or suppression of the perception of some of the odorants (Buettner & Schieberle, 2000).

Leaching during soaking and cooking of pulses

Leaching/loss of solids from a matrix is influenced by seed damage, temperature, soaking solution, and type of processing applied, and these factors are discussed in this section. A high rate of imbibition leads to nonuniform swelling of cell constituents in cotyledons, creating an imbalance of forces, thus giving rise to tensions among local tissues, resulting in seed damage if the seed coat is damaged or absent (Kikuchi et al., 2006; McCollum, 1952). Consequently, this leads to increased loss of solids (Pan et al., 2010). Duke and Kakefuda (1981) demonstrated occurrence of seed damage using Evan's blue solution that cannot permeate differentially permeable cells, hence its uptake and retention indicates cell rupture. In the same study, they found leaching of cytosol enzymes or those common to the cytosol and the organelles, thereby indicating damage of internal membranes. In fact, in addition to limiting release of solutes from the embryo to the soaking medium, the seed coat actually protects the embryo from damage since it regulates water transport to it, thus lowering the extent of leakage from it (Koizumi et al., 2008; Simon, 1974). Seeds with a higher initial moisture content experience delayed backpressure resistance ("Mechanistic insight into swelling of pulses during soaking" section) and hence reduced loss of solutes in the initial phase of rapid inrush of water compared to drier seeds (Hincks et al., 1987; Hincks & Stanley, 1986; Parrish & Leopold, 1977; Tang et al., 1994).

Temperatures ≥ 60 °C modify the permeability of cells leading to high losses and beans soaked at such temperatures incurred a three- to fourfold increase in loss of total soluble solids (Bellido et al., 2006; Kon, 1979). Soaking temperatures of around 60 °C are

advantageous in beans with regard to oligosaccharides because they are hydrolyzed by bean α -galactosidase that has an optimal activity temperature of 55 °C, resulting in 50% loss of oligosaccharides. Temperature and soaking duration are important for leaching, when increased they exacerbate leaching (ElMaki et al., 2007; Rehman, Salariya, & Zafar, 2001). In addition, the higher the soaking temperature, the lower the equilibrium moisture content at maximum water absorption capacity (Bellido et al., 2006; Joshi et al., 2010). This could be attributed to the interplay between loss of solids during the initial phase of soaking, which reduces the water holding capacity of the seed, and the influence of pressurized gases entrapped in the beans, as described earlier (“Mechanistic insight into swelling of pulses during soaking” section), which is exacerbated at elevated temperatures.

Soaking and cooking of beans leads to leaching of antinutrients including phytates, tannins, flatulence-causing oligosaccharides, lectins, saponins, and protease inhibitors, and this is more pronounced during cooking of presoaked rather than nonsoaked beans, with the least extent in noncooked soaked beans (ElMaki et al., 2007; Jood, Bishnoi, & Sehgal, 1998; Mikac et al., 2015; Rehman et al., 2001). Using MRI, Mikac et al. (2015) found more dissolved solids in unbound water in the void between the cotyledons of presoaked (soaked at 20 °C for 15 hr, then cooked at 98 °C for 1.5 hr) than nonsoaked (cooked at 98 °C for 3 hr) beans during cooking. Leaching of a particular antinutrient may be pulse-dependent as was demonstrated by Shi, Arntfield, and Nickerson (2018) who found no influence of both soaking and cooking on phytic acid content in common beans, but it was reduced in lentils, chickpeas, and peas.

The soaking medium can also influence leaching as shown for phenolic compounds when pigeon peas were soaked in (individual or combined) salt solutions (NaHCO_3 , Na_2CO_3 , citric acid), instead of demineralized water (Devi, Chaudhary, Jain, Saxena, & Shilpa, 2018), and for total soluble sugars and starch during soaking of beans in NaHCO_3 solution (Rehman et al., 2001). Devi et al. (2018) hypothesized that the salt solution creates an ionic environment, thereby altering seed coat permeability, leading to enhanced loss of solids from the matrix, but this hypothesis has not been fully elucidated. Next to the soaking medium, the type of processing can influence the extent of leaching/loss of antinutrients from the matrix. Extrusion of flour from cowpeas and beans resulted in significant decreases in phytic acid, lectin, and also α -amylase and trypsin inhibitors (Batista, Prudêncio, & Fernandes, 2010a, 2010b; Martín-Cabrejas et al., 1999). Compared with dehulling, soaking, and germination, which could be regarded as conventional methods of processing, extrusion reduced the activity of amylase, chymotrypsin, and trypsin inhibitors as well as lectin content to a greater extent (Alonso, Orúe, & Marzo, 1998). Canning also greatly reduced trypsin inhibitors and inactivated the thermostable lectins (Pedrosa et al., 2015).

In this section, we have so far reviewed leaching of antinutrients because of their negative role in nutrition. Phenolic compounds form complexes with proteins via hydrogen, hydrophobic, and ionic bonds, thereby inhibiting enzyme activity, lowering protein solubility and digestibility, and hindering bioavailability of amino acids (Kardum & Glibetic, 2018). In addition, polyphenols have been implicated in reductions of vitamin and carbohydrate metabolism as well as influencing the bioavailability of divalent mineral cations (Buitimea-Cantúa, Gutiérrez-Urbe, & Serna-Saldívar, 2018; Devi et al., 2018; Kardum & Glibetic, 2018; Kaspchak, Mafra, & Mafra, 2018). Phytic acid is an antinutrient due to its chelating ability of divalent mineral cations, which

renders them unavailable for absorption into the blood stream. Enzyme inhibitors hinder digestion of nutrients, thus rendering the digestion products unavailable for absorption. However, other components also leach out of the matrix. After cooking, protein and pectin constituted <5% of the total leached solids and the rest was suggested to consist of minerals, starch, sugars, amino acids, and other low-molecular-weight compounds (del Valle et al., 1992). In addition to solids, pigments are also leached into the soaking medium (Paredes-López, Carabez-Trejo, Palma-Tirado, & Reyes-Moreno, 1991).

The extent to which selected ions (Ca^{2+} , Mg^{2+} , Fe^{2+} , and Zn^{2+}) were leached was investigated by exploring the change in their distribution in the cotyledons, seed coats, and cooking water during cooking of Canadian wonder common beans (Chigwedere et al., 2019). Unlike other minerals, Mg^{2+} was leached out of the bean matrix to a large extent and this is attributable to its electronegativity and effective hydrated diameter differences in comparison with the other minerals under study (Chigwedere et al., 2019). This study showed that despite prolonged cooking, beans can provide minerals although this necessitates exploring their bioaccessibility. This is especially given the chelating ability of pectin and phytic acid inherent in the beans as well as the ability of intact cotyledon cell walls to act as barriers that limit transfer of iron outside the cell as demonstrated by Glahn, Tako, Cichy, and Wiesinger (2016).

Defects that Influence Soaking and Cooking of Pulses

The utilization of pulses is greatly challenged by development of the HS and hard-to-cook (HTC) defects. Literature sources do not fully agree on the definitions and, hence, the difference(s) between them. However, most sources report HS as partial or complete failure of pulses to imbibe water due to partial or complete impermeability of the seed coats, while HTC is defined as the inability to attain desirable texture, a crucial quality attribute for consumer acceptability, within a reasonable time due to delayed softening of the cotyledons. According to El-Tabey Shehata (1992), HS in freshly harvested beans is reversible, but that which is storage-induced is irreversible. In one case, HS and HTC developed concurrently during storage of beans (Hentges, Weaver, & Nielsen, 1991).

Factors that influence development of defects in pulses

Development of both defects in pulses can be hereditary, that is, dependent on variety/cultivar as demonstrated for beans (Njoroge et al., 2015; Nyakuni et al., 2008), cowpeas (Jombo, Minnaar, & Taylor, 2018), and chickpeas (Reyes-Moreno, Okamura-Esparza, Armienta-Rodelo, Gomez-Garza, & Milan-Carrillo, 2000). It can also be dependent on seed size, with smaller seeds being more prone to HTC as demonstrated for beans (De J. Berrios, Swanson, & Cheong, 1999; Nyakuni et al., 2008). Small seeds of a black bean variety exhibited both HTC and HS characteristics because they did not hydrate even after 24 hr of soaking, and they neither cooked nor germinated (De J. Berrios et al., 1999). After storage-induced aging of beans with 13.3% to 15.6% moisture at ambient conditions (23 to 27 °C and 63% to 74% RH) during which moisture content decreased, Nyakuni et al. (2008) found smaller seeds more prone to HTC development than larger seeds of different varieties. The authors attributed this to a higher moisture loss (35.56%) due to a higher volume-to-surface ratio compared to larger seeds, for example, NABE11 that incurred a loss of 24.4%, the lowest in the study. A period of 6 months is expected to be a long enough time for all seeds to have

attained equilibrium, thereupon assuming comparable moisture content albeit at different rates of water loss due to differences in volume-to-surface ratios. Actually, their moisture content compared with storage figure depicts this and does not reflect differences that would be clearly significant apart from the starting values. Statistical tests for significant differences for the data in that figure were not reported, they would have given more confidence on their interpretations. Mkanda, Minnaar, and de Kock (2007) found no relation between seed size and cooking time. Paredes-López et al. (1991) found moisture gain in beans during storage, whereas De J. Berrios et al. (1999) found loss of moisture. From these findings, it can be concluded that loss or gain of moisture during storage most likely depends on the water activity of the pulses in comparison with that of the storage environment.

Other factors that influence defect development, particularly HTC include agronomic conditions, such as temperature as demonstrated for beans (Mkanda et al., 2007), storage conditions and time as shown for beans (Njoroge et al., 2015), and growing location (differing in calcium and magnesium contents) as demonstrated for beans (Paredes-Lopez, Reyes-Moreno, Montes-Rivera, & Carabez-Trejo, 1989). Calcium is more effective in inducing hardness in beans than magnesium (Garcia-Vela et al., 1991).

It was long ago established that moisture content of pulses and temperature, oxygen, and RH of the storage space are fundamental for the development of the HTC defect. Storage of pulses in enclosed environments may lead to accumulation of respiration products, namely, carbon dioxide, water vapor, and heat, thereby modifying the internal atmosphere (Aguilera & Rivera, 1992). Accumulation of water vapor results in increased RH, thus making the enclosed space a conducive environment for HTC development (Aguilera & Rivera, 1992). In the same study, it was shown that low temperatures and moisture content are important for reducing the rate of HTC development in beans. In developing countries, after postharvest drying, pulses are either sold in heaps at local markets, totally exposed to ambient conditions, or packaged in woven polypropylene bags for long-term storage.

Aguilera and Rivera (1990) stored beans (10% moisture) underground (18 to 22 °C, approximately 11 months) using a woven polypropylene bag lined with a 150- μm -thick layer of low-density polyethylene to obtain a moisture-proof bag. These beans exhibited the least hardening behavior; hence these researchers demonstrated the worthwhile benefit of a low initial moisture content combined with low-storage temperature and protective packaging. Although this experimental setup is a simple and economically sound approach, it may not be a practical solution due to larger space requirements after high crop yields. In the same study, modified atmosphere packaging using air, nitrogen, and carbon dioxide in laminated polyester-aluminum foil-polyethylene bags failed to suppress hardening rates of beans (14% moisture) after storage at either 31 or 35 °C for 11 months. Based on the authors, residual oxygen in the bean matrix could have facilitated some deleterious reactions that can thrive at low oxygen concentrations. In this perspective, it would be interesting to evacuate oxygen before filling the bag with either nitrogen or carbon dioxide and also to incubate beans at low moisture content, for example, 10% and then evaluate HTC development. Therefore, packaging considerations for pulses may be crucial for the preservation of cooking quality.

It is widely known that HTC development, herein referred to as hardening, influences the cooking behavior of pulses to a greater extent than does HS, therefore, in this review, the focus is on HTC. In addition to storage-induced hardening, chemical

solutions, such as 0.1 M acetate buffer, can induce hardening to a similar extent as storage-induced hardening by soaking at specific pH-temperature-time conditions (Paredes-López et al., 1991). However, in this review, the focus is on storage-induced hardening.

Hypotheses for hardening of pulses: current insights

Several hypotheses have been put forward to try to obtain mechanistic insight into HTC development that involves biomolecules such as pectin, phytate, phenolic compounds, proteins, starch, and lipids. In this section, we review the current knowledge on the mechanisms of HTC development without providing an in-depth account of each as this has been thoroughly covered elsewhere (El-Tabey Shehata, 1992; Reyes-Moreno, Paredes-López, & Gonzalez, 1993). Rather, a short explanation of each is given in this review with the aim of highlighting new insights on the state-of-the-art.

Pectin-cation-phytate hypothesis. The classical hypothesis for the hardening phenomenon involves changes in pectin (El-Tabey Shehata, 1992), a complex heteropolysaccharide whose functionality is based on its structure-related properties such as degree and pattern of methylesterification (Voragen et al., 2009). Pectin methylesterase activity on pectin demethylesterifies it, thereby enabling its cation-mediated cross-linking that reinforces adhesion of cells at the middle lamellae and consequently enhances texture. The cations that facilitate the aforementioned ionic interactions are reportedly released from phytate hydrolysis by phytase (El-Tabey Shehata, 1992; Paredes-López et al., 1991). Studies supporting this hypothesis reported phytase activity coupled with a decrease in phytate content and eventual decrease in pectin solubility (Hentges et al., 1991; Hincks & Stanley, 1986; Ndungu et al., 2012) as well as in the degree of methylesterification (DM) of pectin (Jones & Boulter, 1983). In addition, phytic acid content was related to susceptibility to HTC development in chickpeas (Reyes-Moreno et al., 2000) but not in beans (Martin-Cabrejas, Esteban, Perez, Maina, & Waldron, 1997). Irradiation of HTC cowpeas leading to reduced cooking time was associated with changes in pectin solubility (Jombo et al., 2018).

In the context of this hypothesis, an increase in hardening of pulses is expected during soaking of fresh beans (usually done for 12 to 24 hr) in demineralized water since mobility will be enhanced. Surprisingly, this has not been demonstrated in the literature, except for when soaking is done in solutions containing divalent cations as mentioned earlier in this section. Rather, soaking pulses in demineralized water decreases hardness of pulses (Abu-Ghannam, 1998; Joshi et al., 2010). In fact, it is known that the optimum temperature for phytase activity is 40 °C, thus soaking at this temperature for 12 to 24 hr would be expected to impart some hardness on the pulses. Instead, the extent of decrease in hardness increases with an increase in soaking temperature (Mikac et al., 2015; Oliveira et al., 2013; Piergiovanni, 2011). However, hardening is induced at this temperature at pH 3 to 4.8 as demonstrated for beans soaked in acetate buffer (Kilmer, Seib, & Hosney, 1994; Kinyanjui et al., 2015).

Since the influence of HTC on cooking behavior is related to cell wall and middle lamella microstructure wherein pectin is involved, the same (cell wall and middle lamella) should be involved in its development. From our evaluation, the role of pectin in HTC development of beans is undeniable, necessitating deeper insights into changes in pectin characteristics due to aging. We extracted, fractionated, and quantified pectin from cotyledons and seed coats of noncooked fresh (without HTC) and aged (with

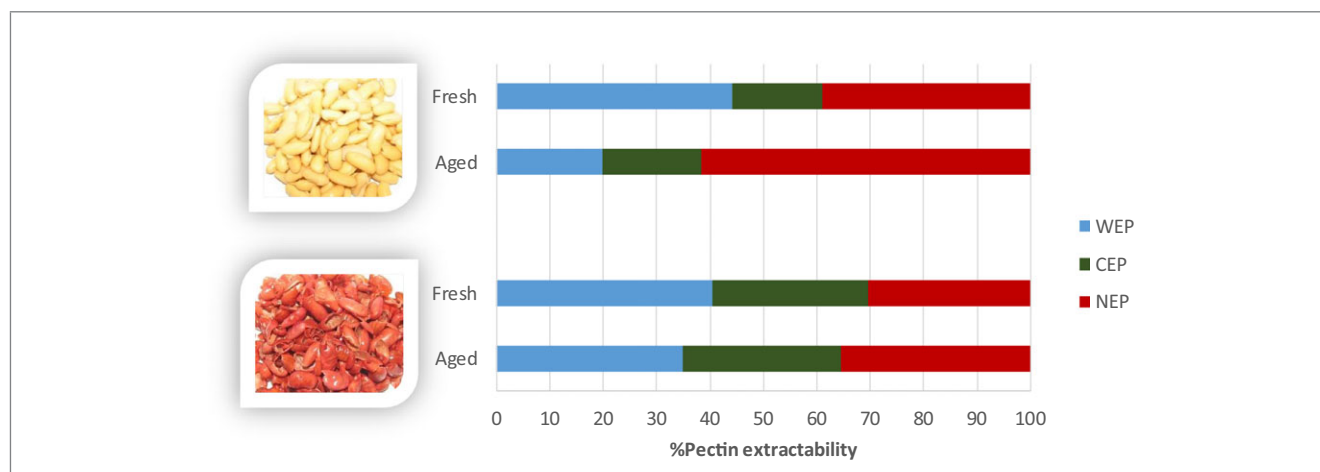


Figure 9—Profiling of water-extractable pectin (WEP), chelator-extractable pectin (CEP), and sodium carbonate-extractable pectin (NEP) fractions extracted from cotyledons and seed coats of fresh and aged noncooked beans (Chigwedere, Nkonkola, et al., 2019). (Copyright 2019)

HTC) beans. Despite major contributions to hardening during adverse storage being attributable to changes in cotyledons rather than seed coats (Chigwedere et al., 2018; Yi et al., 2016), we analyzed pectin from both to obtain deeper insights into localized changes. A decrease in loosely bound pectin paralleled an increase in strongly bound pectin highlighting interactions of the former with other matrix components upon aging (Figure 9; Chigwedere et al., 2019). These interactions may include (i) esterification of ferulic acid dehydrodimers to appendages of the rhamnogalacturan I substructure of pectin chains, (ii) uronyl ester formation between carboxyl and hydroxyl groups of homogalacturonan chains of pectin, (iii) cross-linking of homogalacturonan chains due to dimerization of rhamnogalacturan II that is facilitated by borate diester bonds, (iv) homogalacturonan and xylan cross-links, and (v) formation of cross-links between xyloglucan and neutral side chains of rhamnogalacturan I, as reviewed by Caffall and Mohnen (2009) and Voragen et al. (2009).

The extent to which the pectin interconversion occurred upon aging of beans was greater in cotyledons than in seed coats, confirming a more significant role of the former in bean-hardening than the latter (Chigwedere et al., 2018; Chigwedere et al., 2019). For both the cotyledons and seed coats, the proportion of cation-crosslinked pectin remained rather constant, but it was greater in seed coats than cotyledons. In corroboration with this result, the DM of seed coat pectin was approximately half that of cotyledons, even though no significant changes were observed for both upon aging as shown in Figure 10 (Chigwedere et al., 2019). Therefore, seed coat pectin is much more sensitive to cation-mediated pectin cross-linking compared to cotyledon pectin, especially because of the higher quantity of inherent Ca^{2+} ions in seed coats than in cotyledons (Chigwedere et al., 2019). In this way, migration of cations to the cotyledons for pectin cross-linking is futile since seed coat pectin has a higher cation-binding capacity than cotyledon pectin due to its lower DM. In fact, the pectin-cation-phytate hypothesis is more plausible for seed coat pectin. However, our previous results showed that the contribution of seed coats to HTC development is insignificant, unlike that of cotyledons (Chigwedere et al., 2018) as mentioned earlier in this section.

All these findings provide a far more complete picture of pectin changes in beans. The nonsignificant changes in both the DM and cation-crosslinked pectin fraction, and the molecular

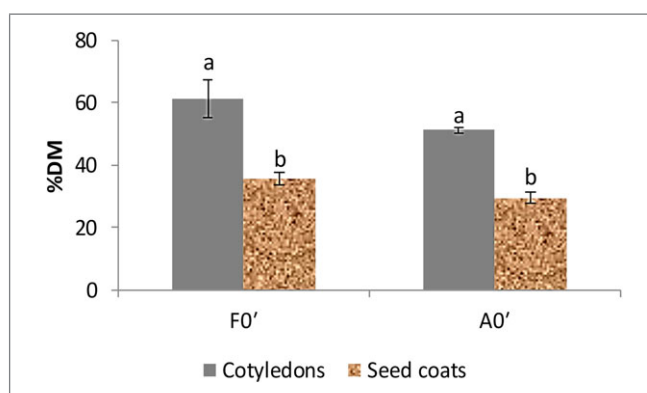


Figure 10—Degree of methylesterification (DM) of pectin in alcohol insoluble residue extracted from cotyledons and seed coats of fresh and aged noncooked beans. FO' and AO' represent fresh and aged soaked noncooked beans, respectively. Different small letters above the bars represent significant differences in %DM (Chigwedere, Nkonkola, et al., 2019). (Copyright 2019)

interconversions of pectin fractions undermine the classical pectin-cation-phytate hypothesis according to which the DM of pectin is expected to decrease with a concomitant increase in cation-mediated pectin cross-linking. Since the proportion of cation-mediated pectin did not increase, we hereby propose a more plausible explanation for the pectin-related mechanism of bean hardening. The reformulated hypothesis is: The inherent DM of cotyledon pectin (approximately 60) facilitates cation-mediated pectin cross-linking in the presence of the divalent cations released from phytate hydrolysis by phytase in the cotyledons, thereby contributing to HTC development.

In their review on the HTC defect, Liu and Bourne (1995) reported the occurrence of HTC during cooking and ascribed it to reduced pectin degradation. High pH of the matrix and/or the cooking medium and high DM of pectin facilitate pectin degradation through the β -elimination reaction, thus leading to faster cooking. Upon aging, the pH of the matrix decreases, thereby suppressing this reaction and prolonging the cooking process. However, changes in the DM of pectin upon aging of pulses are not consistent in the literature, with decreases (Jones & Boulter, 1983) and no changes (Chigwedere et al., 2019; Liu, Hung, &

Phillips, 1993) being reported. In our opinion, the idea of HTC development occurring due to a retardation of the β -elimination reaction is difficult to fathom because the β -elimination reaction is a mechanism through which pectin solubilization and hence softening occurs. Therefore, a single reaction cannot take part in opposing phenomena simultaneously. In beans, the extent of the β -elimination reaction as a cause of HTC during cooking would be highly undermined by the rather low (for such a reaction) DM of both cotyledon and seed coat pectin as shown in Figure 10 (Chigwedere et al., 2019).

Lignification hypothesis. According to the lignification hypothesis, lignin-like compounds are deposited in cell walls and middle lamellae of cotyledons due to reactions involving aromatic amino acids and polyphenolic compounds, some of which migrate from the seed coats (Hincks & Stanley, 1986; Hohlberg & Stanley, 1987; Martin-Cabrejas et al., 1997; Reyes-Moreno et al., 2000; Stanley, 1992). In a study on lentils, storage under adverse conditions led to seed coat color changes from green to brown, paralleled by reduced leaching of proanthocyanidins into the soaking water, and this was attributed to their polymerization into higher molecular weight polymers (Nozzolillo & Bezada, 1984). Similar seed coat darkening was observed in chickpeas (Reyes-Moreno et al., 2000).

In some studies, lignin quantification (Martin-Cabrejas et al., 1997) was reported, while in others, changes in polyphenols (Nozzolillo & Bezada, 1984) were used to make inferences in relation to this hypothesis. Quantification of lignin is a challenge due to its heterogeneity and hydrophobicity that renders it insoluble (Plhak, Stanley, Hohlberg, & Aguilera, 1987). Although not much credibility is placed on lignin quantification, in support of this mechanism, Hincks and Stanley (1987) presented histological evidence of lignin deposition in stored beans. Using transmission electron microscopy and potassium permanganate as a stain, they visualized lignin in intercellular spaces and middle lamellae. In comparison with fresh beans, secondary walls of aged beans were clearly defined with positive stain indications of lignin deposition. In the same study, indications of cellulose depositions, described as lamellated appearance of cell walls, were visualized using SEM, and it was suggested to be a process that preludes lignification.

It is known that lignin is deposited in cellular junctions, middle lamella, primary wall, and secondary wall, in that order regardless of ignorance on molecular explanations for this order (Vance, Kirk, & Sherwood, 1980). It forms impenetrable networks with hemicellulose in the cell wall, with possibilities of covalent linkages. However, true lignin is defined as having p-coumaryl, coniferyl, and sinapyl alcohols as precursors because oxidation of phenolic compounds produces polymers with properties similar to those of lignin. Therefore, suitability of the term “lignification hypothesis” for this mechanism is debatable. Although Srisuma et al. (1989) observed an increase in hydroxycinnamic acids, especially ferulic acid due to aging of beans, no storage-induced lignin formation occurred.

This hypothesis points toward a contribution of both the cotyledons and seed coats to HTC development, but the extent of contribution of each had not been assessed until we investigated this through storage-induced aging of fresh whole beans and cotyledons obtained therefrom. Poststorage texture analysis revealed a similar behavior of aged whole beans and cotyledons aged as such when cooked in demineralized water (Chigwedere et al., 2018). These results provide evidence that cotyledons play a major role in the development of HTC, with seed coats making a minor contribution (Chigwedere et al., 2018).

Hypotheses involving proteins, starch, and lipids. Oxidation and polymerization of lipids, as well as structural changes in starch and proteins contribute to HTC development. Citing increased proportions of saturated membrane lipids and high membrane phase transition temperatures, which are characteristic of increased membrane permeability, Richardson and Stanley (1991) hypothesized that membrane deterioration may be a primary event in the initiation of HTC development. Aging led to a decrease in the pH of beans that is usually around neutral (6.3 to 6.5), with the largest decrease (pH 6.42 to 5.85) being exhibited in Canadian wonder beans, which is one of the varieties with the highest proneness to HTC development (Martin-Cabrejas et al., 1997). Hydrolysis of lipids with release of fatty acids may lower the pH of beans during storage leading to insolubilization, reversible denaturation, and decreased extractability of proteins, as reported for cowpeas by Hentges et al. (1991) and Liu, McWatters, and Phillips (1992). However, Thomas et al. (1989) did not relate the reduced protein extractability with decrease in pH. Liu et al. (1992) hypothesized that network formation by intracellular proteins during cooking influences starch behavior, thereby retaining hardness in cooked cowpeas. This retention of hardness implies that starch is involved in HTC development at the stage of cooking. In a review on the HTC phenomenon, El-Tabey Shehata (1992) concluded that starch can be considered a “victim” of HTC development and not a cause. In some studies, pseudo-retrogradation reactions were hypothesized to contribute to HTC development (El-Tabey Shehata, 1992), but in others (Hohlberg & Stanley, 1987) such changes in starch characteristics were not associated with this defect.

However, from our investigation of the rate-limiting step for softening of beans (Chigwedere et al., 2018), it is clear that the extent of protein denaturation and starch gelatinization during cooking is not influenced by the presence of HTC unlike pectin solubilization. In fact, neither intracellular proteins nor starch are “victims” of HTC. Therefore, we regard the lipids, starch, and protein hypotheses less plausible to explain HTC development. However, any contribution(s) of membrane proteins cannot be ruled out since this is lacking in the literature.

Microstructure changes associated with hardening

Degradation of lipids in cell membranes of pulses during aging depends on membrane integrity (Richardson & Stanley, 1991), and this is exhibited by a greater extent of leaching for aged than for fresh pulses (De J. Berrios et al., 1999; Hentges et al., 1991; Liu, Phillips, & McWatters, 1993). Aging-induced membrane damage leads to denaturation of the adenylypyrophosphatase (ATPase) of the membrane-associated H^+ -ATPase that restricts the transmembrane passive influx of cations (Liu et al., 1993). Liu et al. (1993) induced cell membrane damage and hence electrolyte leakage by freezing, then thawing cowpeas, and with two cycles, but not more, the leakage increased. The extent of increase of leakage was higher for fresh cowpeas than preaged cowpeas because for the latter, damage to cell membranes already occurred during storage-induced aging. Bewley (1986) attributed solute leakage to a reorganization of membrane constituents as a result of instantaneous hydration.

Cotyledon cells of aged beans are characterized by larger adhesion regions and smaller intercellular spaces compared with fresh beans (De J. Berrios et al., 1998). Development of HTC is associated with withdrawal of the plasmalemma from the cell wall as well as fission of organelles in the cytoplasm (Varriano-Marston & Jackson, 1981). Similar results were observed by Garcia, Lajolo and

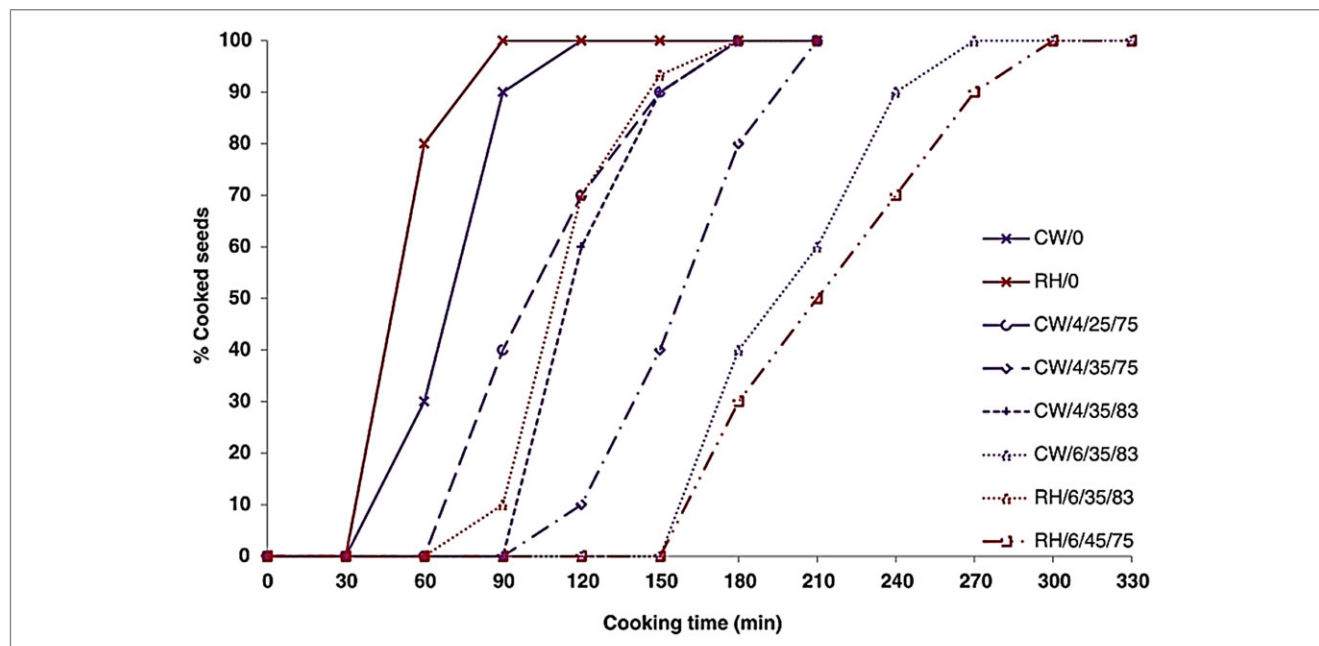


Figure 11—Influence of hardening on cookability of Canadian wonder and Red haricot common beans. CW/0 means nonstored Canadian wonder beans and CW/4/25/75 means Canadian wonder beans stored for 4 months at 25 °C and 75% relative humidity (Njoroge et al., 2015). (Copyright 2019)

Swanson (1993) who described cotyledon cells of HTC beans as having compact cell walls with contracted cell contents. However, De J. Berrios et al. (1998) highlighted possibilities for the introduction of artifacts during microscopic analyses involving fixation of samples using glutaraldehyde or formaldehyde that were used by Varriano-Marston & Jackson (1981) and Garcia et al. (1993).

Influence of hardening on soaking and cooking of pulses

There are inconsistencies concerning hydration capacity of fresh and aged pulses during soaking. One reason pertains to differences in methods applied in the measurement of hydration capacity. Most studies in which similar hydration capacity was reported involved simple gravimetric analysis. However, in some studies, a layer of bulk water was observed between the seed coat and the periphery of cotyledons of aged but not fresh beans. It was argued that the water to be considered is that which is absorbed by the cotyledon matrix, therefore the water-holding-capacity method was introduced by Plhak, Caldwell and Stanley (1989) so as to exclude the bulk layer. With this method, they reported aged beans to absorb 25% less water than fresh beans. Paredes-López et al. (1991) and Richardson and Stanley (1991) also found a lower water-absorption capacity of aged compared to fresh beans. Another reason for the inconsistencies is lack of correction for solids lost during soaking as suggested by Parrish and Leopold (1978). Despite taking this into account, results were still inconsistent with no difference (Jackson & Varriano-Marston, 1981) and higher hydration capacity for aged beans (Hincks et al., 1987) being reported. This disagreement in findings has consequently led to disagreements in the description of manifestation of HTC.

Considering equal hydration between fresh and aged beans, HTC is described as failure of affected seeds to cook within a reasonable timeframe. Cookability is used as the classic indicator of the extent of HTC development in pulses through change in cooking behavior in comparison with freshly harvested pulses of the same variety. Pulses that are affected by HTC take longer time to cook due to the proposed biochemical changes discussed

in “Hypotheses for hardening of pulses: current insights” section and as reported by dos Santos Siqueira, Vianello, Fernandes and Bassinello (2013), Machado, Ferruzzi and Nielsen (2008), Njoroge et al. (2016), and Wu, Feng and Kojima (2015). The influence of hardening on cookability of two varieties of beans stored for different times under different conditions of temperature and RH is shown in Figure 11 (Njoroge et al., 2015). Canned beans are a convenient option for consumers, but not for the canning industry because the extent of hardening may vary with batches, thus necessitating adaptation of the process for each batch to attain and maintain similar texture quality.

Influence of hardening on flavor generation

A study on evolution of volatiles during cooking of beans demonstrated the influence of hardening on flavor development (Chigwedere et al., 2019). Aging of beans leads to a higher number of volatiles in aged than fresh beans as illustrated in Figure 12. This can be attributed to chemical and/or biochemical reactions that produce volatile compounds and/or their precursors due to mobility in the bean matrix during storage. Notably, most volatile compounds characteristic of the HTC beans can be linked to the oxidation reactions that have been implicated in hardening reactions (“Hypotheses for hardening of pulses: current insights” section). Surprisingly, during cooking most of the marker (significantly changing) compounds identified in both fresh and aged beans had similar evolution rate constants despite having distinct starting points. Therefore, the abundance of the volatiles in the beans depends on their prehistory. Fresh and aged beans exhibited different volatile profiles regardless of similarities or differences in texture as highlighted in Figure 13 (Chigwedere et al., 2019). Therefore, processing of fresh and aged beans to a similar texture level as is done for canned beans does not imply that the processed beans will have similar flavor. In this section, there is no comparison of these results with those in the literature because, to the best of our knowledge, no studies on volatile compounds from aged beans have been published apart from those of our research.

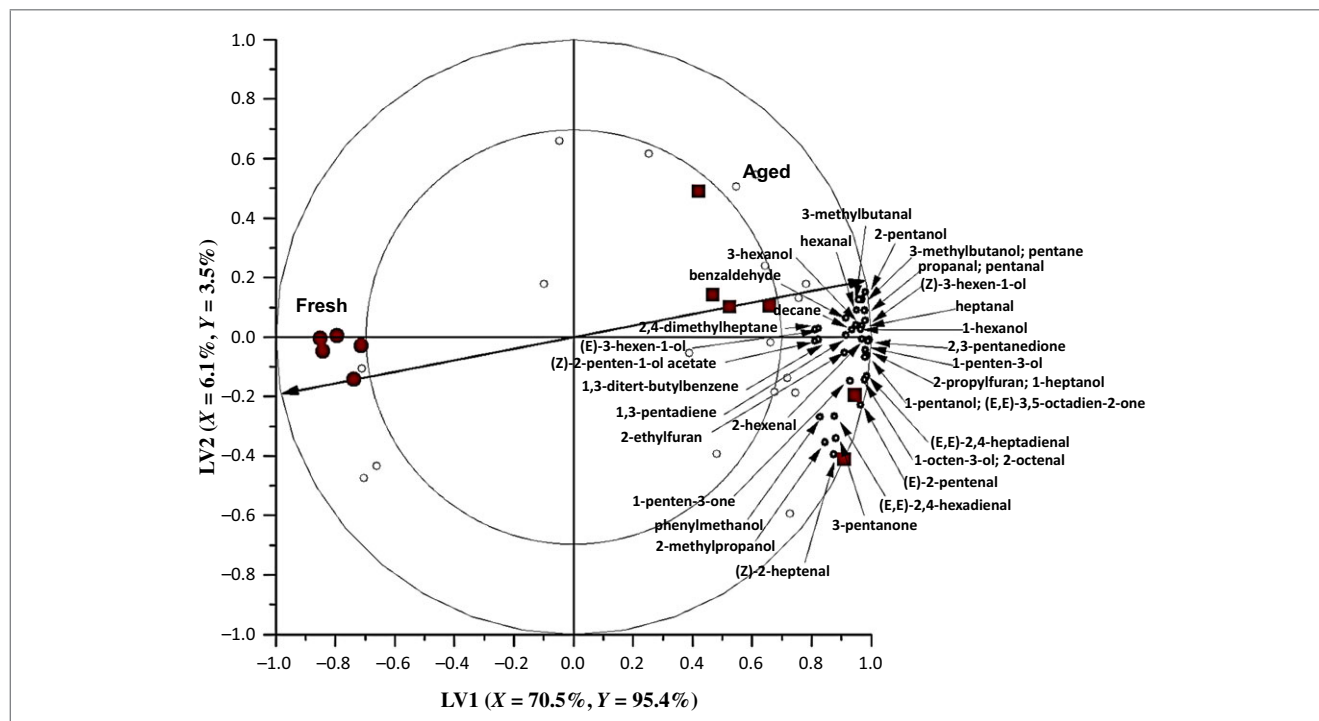


Figure 12—A comparison of volatile profiles of fresh and aged noncooked beans. Symbols represent the samples and open circles represent volatile compounds but those with thicker edges represent discriminant compounds. Discriminant volatiles labeled in black had higher peak areas in the class close to their projection than the other class. Volatiles labeled in maroon were present only in the class close to their projection. These compounds were selected based on variable identification coefficient (VID) procedure ($VID > |0.80|$) and identified based on retention index and mass spectra.

Influence of hardening on nutrients

Development of HTC in beans is unlikely to affect the quantity of nutrients. For example, a proximate analysis of HTC and fresh beans revealed that crude protein, crude fat, and ash concentrations were not influenced by the aging process (De J. Berrios et al., 1999). However, HTC has been shown to influence nutritional quality. After storage under adverse conditions (conducive for HTC development), decreases in *in vitro* protein digestibility in chickpeas (Reyes-Moreno et al., 2000) and common beans (Nyakuni et al., 2008), and *in vitro* starch digestibility in common beans (Nyakuni et al., 2008) were noted. These findings can be explained by the presence of antinutrients, such as phytic acid and amylase inhibitors, and storage-induced interactions (Nyakuni et al., 2008). In all the aforementioned studies, pulses with and without HTC received the same treatment, for example, the same cooking time. Therefore, given the reported polymer changes that occur in pulses during HTC development, these observations are logical. It would be interesting to explore this at the same level of treatment, for example, treating the pulses (with and without HTC) to a similar texture level.

In vitro protein digestibility increased after extrusion of flour from HTC cowpeas due to possibly a combination of partial inactivation of trypsin inhibitors and protein denaturation that occurs during extrusion (Batista et al., 2010a). Therefore, from a nutrition perspective, extrusion has the potential to contribute toward increased utilization of HTC pulses.

Preventive and Curative Solutions for Hardening

Different storage and processing methods and/or technologies with the potential to prevent HTC development, lower

susceptibility of pulses to it, or to (partially) reverse it have been suggested. Some of them are discussed in the following sections.

Storage conditions

The need for suitable storage conditions, in terms of temperature and RH, for the prevention of HTC development in pulses has been overemphasized in the literature. Storage conditions, including combined refrigeration and hypobaric storage (De J. Berrios et al., 1999) and very low temperatures ($-18\text{ }^{\circ}\text{C}$) (Liu, Phillips, Hung, Shewfelt, & McWatters, 1992), prevented the development of HTC defect in pulses. The cooking time of aged cowpeas and beans decreased following storage under low temperature ($6.5\text{ }^{\circ}\text{C}$) and medium RH (71%) for 18 months (Hentges et al., 1991). It was suggested that the same components involved in hardening are possibly also involved in its reversal, but possibly through different mechanisms.

Evolution of storage stability concepts from moisture content to glass transition temperature. The storage stability of food materials has long been considered as being dependent on moisture content. Thus, a decrease in moisture content through drying was conducted primarily to decrease perishability. However, some different foods with the same moisture content exhibit differences in their storage stability. Thus, the relationship between moisture content and storage stability was proven to be imperfect. As such, it was concluded that moisture content alone is an unreliable indicator of storage stability of some food materials, prompting introduction of the water activity (a_w) concept. Water activity takes into account differences in the intensity with which water interacts with the nonaqueous components. These interactions are illustrated through a moisture sorption isotherm, a relationship between moisture content and water activity that is determined

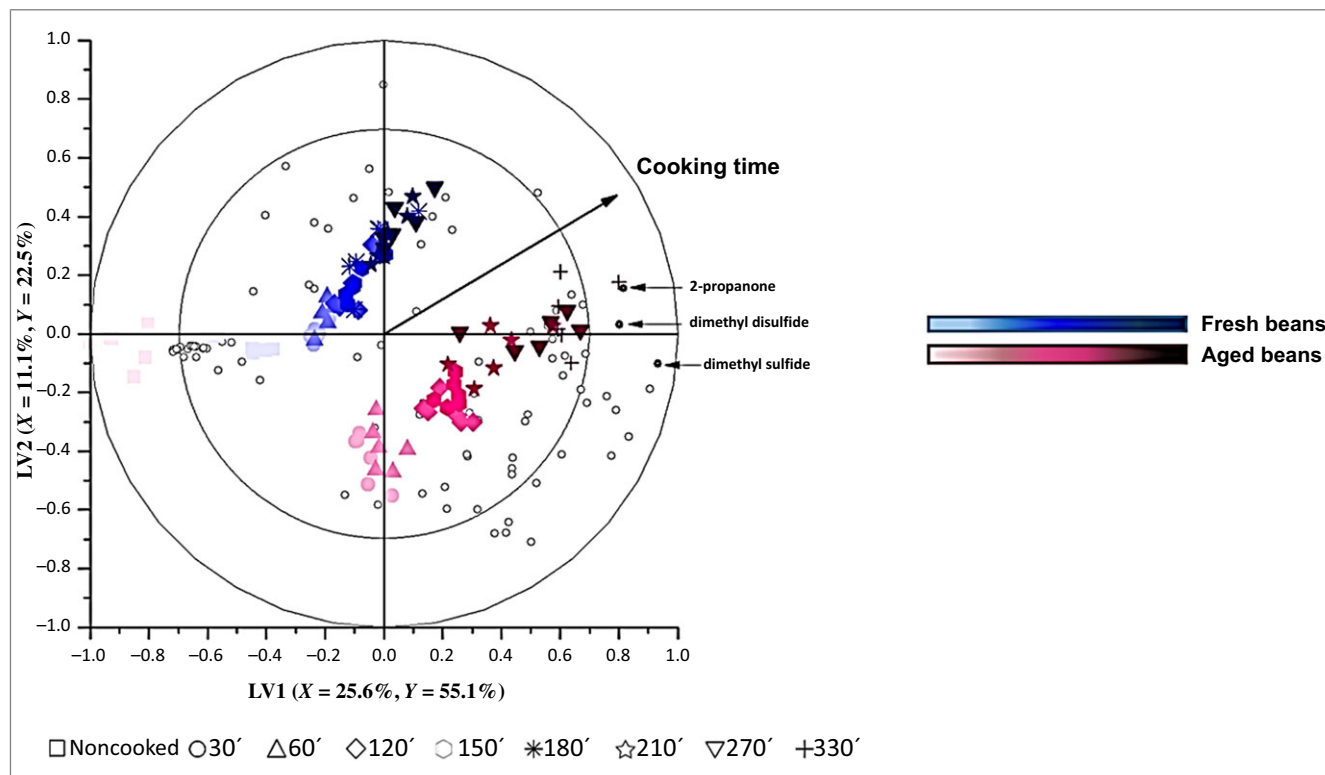


Figure 13—Evolution of volatile compounds during cooking of fresh and aged beans as represented by score symbols that are colored gradually in blue and pink, respectively. Scores representing fresh and aged beans cooked for the same time have similar shapes and can be identified by the open symbols below the biplot.

at constant temperature. Water activity is expressed in terms of relative vapor pressure (RVP), a ratio of the chemical potential of water in the food (p) to that of free water (p_0), measured at the same temperature. The RVP is related to percent equilibrium relative humidity (%ERH) of the environment to which the food is exposed. These relations are shown in the following equation:

$$\text{RVP} = p/p_0 = \%ERH/100$$

Food quality, as determined by the extent of microbial, nonenzymatic and enzymatic activity, as well as lipid oxidation, has been evaluated successfully by the a_w concept using the monolayer moisture content as the basis for stability. Using moisture sorption isotherms, the a_w concept has been used to design food stability maps such as the one shown in Figure 14. Despite this concept being more reliable than moisture content, it also lacks perfection. Foods at the same water activity can exhibit different levels of stability from a chemical and/or microbial point of view, hence this concept was superseded by another concept based on mobility within the food system and termed as the glass transition temperature concept (Fennema, 1996).

The glass transition temperature concept. The glass transition theory has been studied extensively in plant physiology, material science, and food science research, hence it is shortly summarized in this review. During cooling, the aqueous phase of a food matrix assumes a very viscous state eventually leading to a nonequilibrium noncrystalline state resembling a solid, which is termed a glass. This state is achieved at the glass transition temperature (T_g). According to Leprince and Walters-Vertucci (1995), glass formation (vitrification) does not prohibit molecular rearrangements. There is consensus regarding lack of long-range order, lack of co-

operative motions, and residual molecular motions of molecules in a glass. In this regard, T_g can be considered as the initiation point of molecular mobility restrictions given that at lower temperatures, molecular diffusion-limited reactions, which are mainly responsible for degradation in foods, are suppressed, thereby ensuring physicochemical stability. Molecular mobility greatly influences storage stability of biological tissues due to its suppressive effect on deleterious reactions that curtail storage life (Murthy, Kumar & Sun, 2003).

Based on research findings from Leopold, Sun, and Bernal-Lugo (1994), molecules in a glass are restricted to localized rotations and vibrations only. According to Walters (2004), molecular mobility in a glass is severely limited (considered practically nil) to an extent where it assumes the level found in a crystal at a temperature called the Kauzmann temperature (T_K). In fact, it would be better to target the T_K rather than the T_g as the benchmark for storage stability despite residual molecular motion below T_K . In agreement with this, it was recommended not to consider T_g as an absolute threshold for molecular motion by Le Meste et al. (2002) due to possible occurrences of relaxations at sub- T_g temperatures. The tendency of a glass to revert to a supercooled liquid is termed relaxation (Walters, 2004) and there are three types of molecular relaxations, the γ , β , and α relaxations characterized by vibrational, rotational, and sliding motions, respectively (Figure 15). Rotational motions in β relaxations can trigger molecular rearrangements leading to microstructural changes and are thus undoubtedly more relevant for storage stability considerations rather than α relaxations that are considered synonymous with the glass-rubber transition (Ballesteros & Walters, 2011).

The relaxation phenomenon of a glass implies that its formation process prohibits immediate attainment of equilibrium, hence

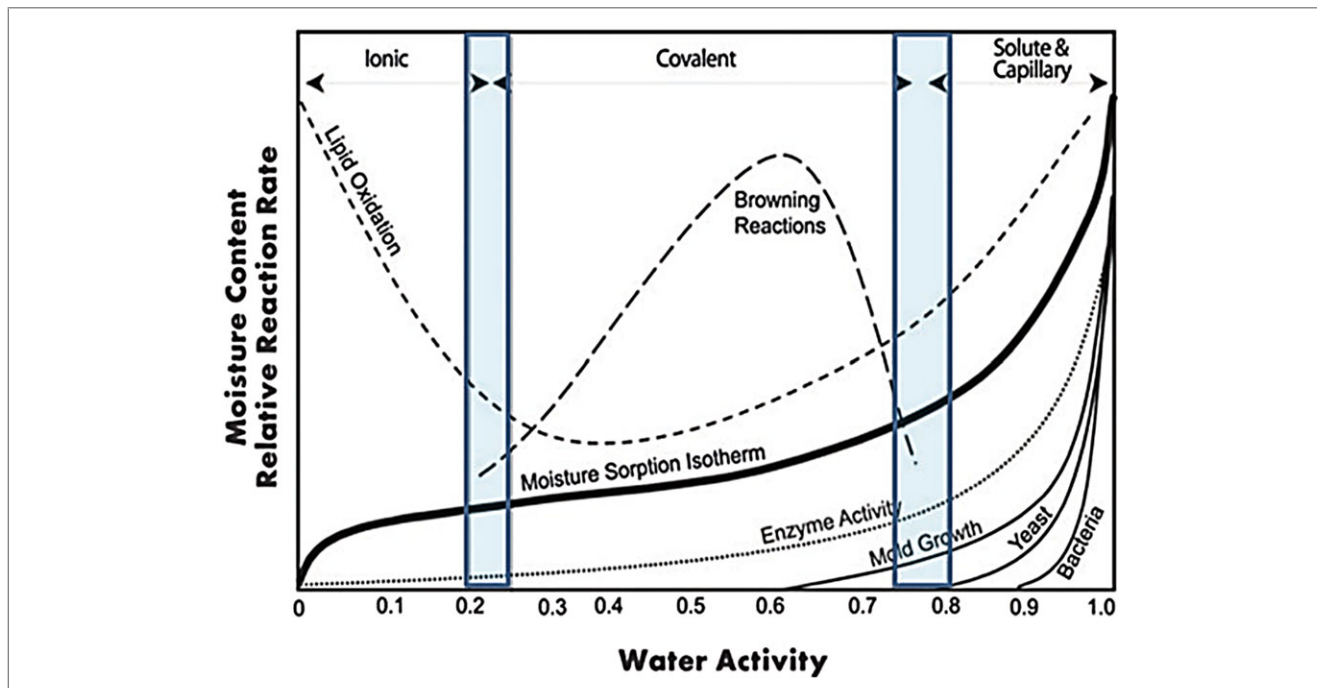


Figure 14—Storage stability determined by relative rates of reactions as a function of water activity (Finley, Hurst, & Lee, 2018). (Copyright 2019)

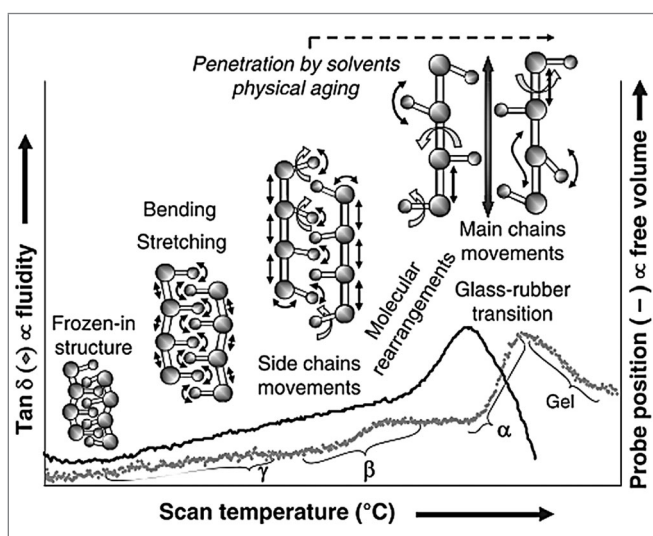


Figure 15—Illustrations of different structural relaxations and their characteristic molecular motions (Ballesteros & Walters, 2011). (Copyright 2019)

a glass is kinetically but not thermodynamically stable due to existence of the force driving the relaxation process (Leprince & Walters-Vertucci, 1995). Glass transition temperatures provide a better understanding of the influence of temperature and moisture content in food technology applications that include control of texture and various technological operations, as thoroughly reviewed by Le Meste et al. (2002) and Roos (2010). Benefits of formation of the glassy state include protection of proteins from denaturation, suppression of tissue collapse, prevention of crystallization of cytoplasmic components upon withdrawal of water, as well as increased resistance to water loss (Leopold et al., 1994).

Factors that influence the glass transition temperature. The composition of a system and presence of plasticizers influence T_g . Of all the plasticizers including low molecular weight solutes, water is the most ubiquitous and its content in a system greatly influences T_g (Leopold et al., 1994). Water interacts with components of an amorphous matrix, thus being adsorbed onto it, thereby forming a monolayer. Progression of adsorption culminates into formation of a multilayer causing diffusional forces to overcome the binding forces and this leads to absorption of water into the matrix. Water absorption by the matrix causes plasticization, which can be described by lowering of the viscosity of the matrix, thus promoting molecular motion.

At high temperatures, water can exert its plasticizing property at very low amounts because high temperatures enhance molecular mobility (Ross, Arntfield, & Cenkowski, 2013). The variation of T_g with addition of a plasticizer, among other factors that influence it, can be explained using the free volume concept. Free volume can be defined as the available space for molecular movement (Roos, 2010). Therefore, molecular motion due to plasticization by water and heating increases the free volume of the system while cooling and drying decrease it leading to restoration of rotational and vibrational motion (Ballesteros & Walters, 2011) as depicted in Figure 15. The relation between T_g and moisture content is crucial in food technology because it facilitates characterization and prediction of behavior of food materials and it is often illustrated in the form of state diagrams. A state diagram depicting the changes in T_g due to variation in moisture content (and hence proportion of solids) is shown in Figure 16 for sucrose.

The molecular weight of components, especially sugars, plays a significant role in determining the T_g , with higher molecular weight elevating it. Moreover, mixtures of sugars in a system enhance its stability due to elevation of T_g as well as suppression of proneness to crystallization of the mixture. Furthermore, presence of irregularly shaped molecules, such as polyols, hinders efficient molecular packing, thereby also suppressing crystallization and thus

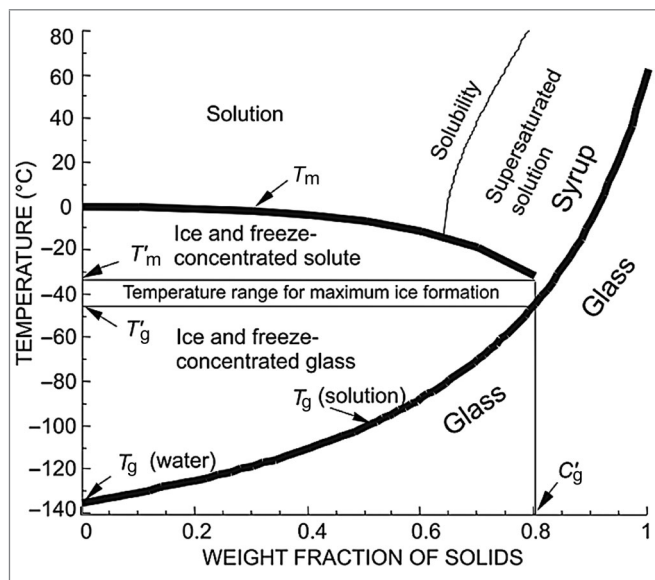


Figure 16—Dependence of T_g on water content for sucrose showing the equilibrium melting temperature curve for ice (T_m), onset glass transition temperature (T_g), and onset temperature for ice-melting (T'_m) in a maximally freeze-concentrated solution (Roos, 2010). (Copyright 2019)

favoring glass formation (Leopold et al., 1994). This is interesting for pulses given that, as orthodox seeds, they contain a mixture of sugars such as raffinose and stachyose among others but the possibility of components other than sugars influencing T_g cannot be ruled out.

Measurement of glass transition temperatures. There are several methods used to measure T_g of systems that have been described well in the literature (Leopold et al., 1994; Roos, 2010; Williams, 1994). The method of choice should be dependent on application. For collapse and agglomeration studies, the relevant method would involve measurement of change in Young modulus or viscosity (Le Meste et al., 2002). However, deeper insights into glass transition-related phenomena necessitate utilization of different techniques, since for some the measurements are on a macroscopic level (for example, differential scanning calorimetry [DSC]), while for others they are on a molecular level (for example, nuclear magnetic resonance, electron spin resonance, and solute translational diffusion). However, the heat capacity change during analyses using the DSC mainly explores the mobilization of principally translational and rotational degrees of freedom, allowing chain flow in the case of polymers, although specific motions in the structure cannot be precisely identified (Bizot et al., 1997).

Water activity concept and glass transition concept. Although these concepts both relate to stability of food systems, a considerable disaccord between them was noted by Sablani, Kasapis, and Rahman (2007). For example, the glass transition concept resulted in underestimation of the temperature required for stability of sugar-rich products such as apples and strawberries. Walters (1998) suggested that critical moisture levels that are reflected by monolayer moisture content in the a_w concept should be reflected in terms of viscosity or porosity rather than the glass-rubber transition in the glass transition phenomenon concept. This was reiterated by Buitink, Claessens, Hemminga, and Hoekstra (1998) who suggested prediction of ideal storage stability from molecular mobility measurements rather than state diagrams. Some physicochemical and structural processes, such as stickiness, crispness,

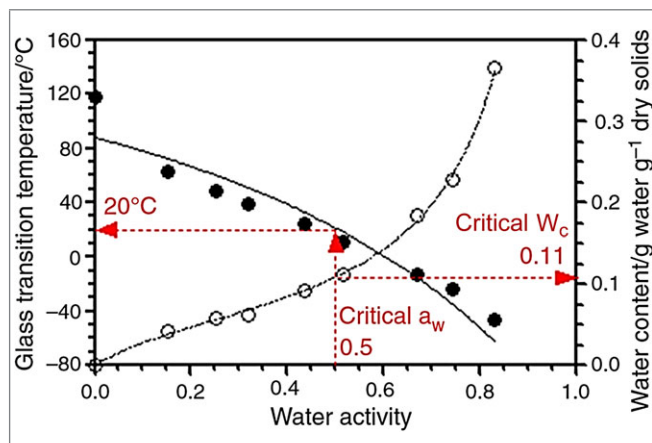


Figure 17—The state diagram of agavin, a fructan showing water plasticization at various water activities (a_w) and a water adsorption isotherm at 20 °C. W_c is water content; the solid markers show glass transition temperatures, whereas the open ones show water adsorption behavior (Espinosa-Andrews & Rodríguez-Rodríguez, 2018). (Copyright 2019)

collapse, and amorphous-crystalline conversions are not related to a monolayer moisture content in the a_w concept but rather to T_g through temperature changes and plasticization by water (Sablani et al., 2007).

Findings from several studies provide evidence that the storage stability of materials is dependent on molecular mobility. Intracellular molecular mobility was found to regulate reaction kinetics, thus governing aging of desiccated organisms (Walters, Hill & Wheeler, 2005). In a related study, the critical temperatures for storage stability of orthodox seeds (for example, peas) were near or below their T_g values and the effects of plasticization of intracellular glasses were correlated with effects of moisture content on storage stability (Sun, 1997). In yet another study on pea seeds, minimum mobility corresponded to maximum stability and both occurred at the same moisture content (Buitink et al., 1998). In the same study, it was revealed that at moisture contents below that which corresponded to maximum stability, mobility increased (before stabilizing) in parallel with decrease in stability. Walters et al. (2005) found longevity of seeds to increase with decrease in moisture content to a certain critical moisture content beyond which longevity decreases.

Although insights into storage stability of foods evolved from a moisture content perspective through a_w to the T_g concept, they can be used together as presented in a state diagram to make inferences on storage stability. Such a state diagram is shown in Figure 17 for a fructan, agavin. The critical water content is the quantity of water that depresses T_g to its storage temperature condition. The critical a_w is then the a_w that corresponds to the critical water content (Espinosa-Andrews & Rodríguez-Rodríguez, 2018).

Longevity of seeds. Aging is characterized by deterioration processes that mainly involve hydrolytic and oxidative reactions, and causes loss of viability and finally death (Murthy et al., 2003; Walters, 1998). The longevity of seeds can be hereditary and the rate of aging depends on the storage conditions of the seeds (Walters et al., 2005). Since the rate of deteriorative reactions is a function of moisture content, aging can be regarded as desiccation injury (Vertucci & Farrant, 1995). As described earlier, pulses undergo aging during which physiological and/or biochemical changes

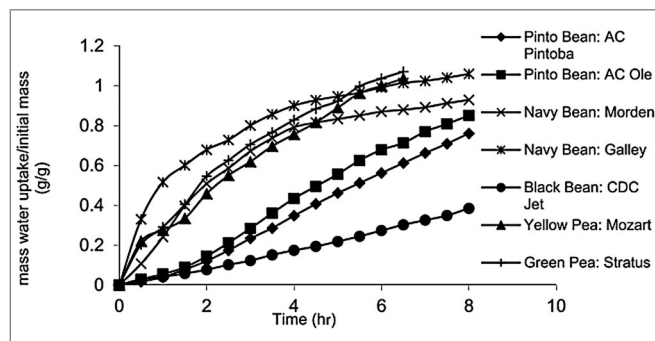


Figure 18—Water uptake behavior of native/unprocessed whole seed peas and beans (Ross et al., 2013). (Copyright 2019)

occur (“Defects that influence soaking and cooking of pulses” section). The moisture content and temperature of seed tissues govern the mobility and thermal properties of water within cells and their interdependency influences seed longevity. Specific combinations of moisture content and temperature at which changes in properties of the intracellular water occur can be described by either equilibrium (water sorption and chemical potential measurements) or nonequilibrium (glass transition phenomena) thermodynamic principles (Leprince & Walters-Vertucci, 1995). In seeds, vitrification is strategic for desiccation tolerance, quiescence, and storage stability, especially because changes to cellular structures are minimal (Leprince & Walters-Vertucci, 1995). Orthodox seeds undergo programmed desiccation at the end of the maturation phase of seed development during which they acquire desiccation tolerance to lose it upon germination. Desiccation tolerance implies that the seeds are capable of preventing, slowing down, or repairing any effects of water removal (Vertucci & Farrant, 1995).

The glass transition concept: application to pulses.

Water uptake. There is substantial evidence that the seed coat plays a role in hydration, although the exact mechanism(s) and stage of involvement are still disputable (“Transport of water in pulses during soaking” section). In a quest to better understand water uptake behavior in pulses, Ross et al. (2008) characterized the glass transition temperature of seed coats of pea and bean varieties. These pulses exhibited two different behaviors in terms of water uptake. Some took up water immediately upon soaking, while others exhibited a lag phase. The former had T_g values close to ambient temperatures (20 to 34 °C), with a narrow range of 10 °C about the T_g value unlike the slow-hydrating pulses that exhibited much higher T_g values (37 to 81 °C) with wider ranges (30 °C). The water uptake behavior of some of the pulses and the corresponding T_g values of their seed coats as measured using DSC, are shown in Figure 18 and Table 2, respectively. Although the seed coats of the fast-hydrating pulses were thinner than those of the slow-hydrating pulses, this could not explain the observations.

There are inconsistencies in the literature concerning water uptake behavior and seed coat thickness/thinness. For example, Sefa-Dedeh and Stanley (1979) found cowpeas with thicker seed coats that imbibed water much faster than those with thinner seed coats. Therefore, Ross et al. (2008) concluded that T_g can be related to water uptake behavior. Later, based on these results, the same authors put forward a hypothesis to explain water uptake from a T_g context based on the temperature- and solvent-driven glass transition, (T_g) and a_g , respectively.

If the glass transition of a seed coat of a pulse is below the soaking water temperature, the time taken for plasticization, which is the attainment of a saturated surface solvent (water) concentration, depends on water content of the seed coat and the temperature of the soaking water. This time is the lag phase observed for the slow-hydrating pulses. Upon achievement of solvent saturation, water uptake becomes exponential. Due to the propensity of high temperatures to enhance molecular mobility, it speeds up attainment of solvent saturation, thereby reducing the lag phase. On the fast-hydrating pulses, it was hypothesized that if soaking is done at temperatures around ambient (T_g of the seed coats of these pulses), they may have a short relaxation time and hence exhibit an instantaneous saturated solvent concentration and, consequently, rapid initial solvent uptake. Therefore, pulses with such T_g values exhibit no lag phase due to immediate exponential water uptake behavior (Ross et al., 2013). In a study on lentils by Tang et al. (1994), effective diffusivity measurements revealed that the seed coat was more resistant to moisture migration compared to the cotyledons. Although it was not included in their study, it could be possible that their result can be explained in terms of the T_g concept.

Dehulling quality. Some pulses are often dehulled as part of processing, especially red lentils that are milled to produce dehulled whole lentil products. The types of lentils used by Ross et al. (2013) to study the role of T_g on dehulling are usually harvested with very high moisture content (16% to 18%) due to their region of production. High-quality products are characterized by minimal splitting, breakages, and powder formation, hence milling efficiency during dehulling is crucial for good quality. The processing involves drying and postdrying equilibration (also called tempering) prior to dehulling. In their study, Ross et al. (2013) applied different regimes involving drying and equilibration temperatures with respect to the T_g values of the lentils. Regardless of the drying temperature (above or below T_g), more splitting of lentils was observed upon equilibration at a temperature below T_g unlike at a temperature above T_g . This can be explained in terms of moisture gradients in the seeds, with change in temperatures relative to the T_g .

According to Ross et al. (2013), drying above T_g creates temperature and moisture gradients, with the latter being rate-limiting with progression of drying. Upon equilibration below T_g , that is, cooling, the remaining moisture gradient causes different parts of the seed to transition to the glassy state at different moisture contents, thus introducing differential stress to the seeds. The

Table 2—Characterization of the glass transition temperature (T_g) of seed coats of varieties of beans and peas (Ross et al., 2013).

Pulse	Seed coat thickness (mm)	Seed coat moisture content (%)	T_g range (°C)	T_g midpoint (°C)
Mozart (yellow pea)	0.11	8.3	19 to 23	21.4
Stratus (green pea)	0.11	8.6	33 to 37	33.3
AC Pintoba (pinto bean)	0.23	9.7	43 to 65	45.2
AC Ole (pinto bean)	0.18	9.6	33 to 66	51.6
Galley (navy bean)	0.11	9.7	24 to 48	26.2
Morden (navy bean)	0.11	9.2	20 to 30	22.2
CDC Jet (black bean)	0.19	9.3	22 to 57	40.2

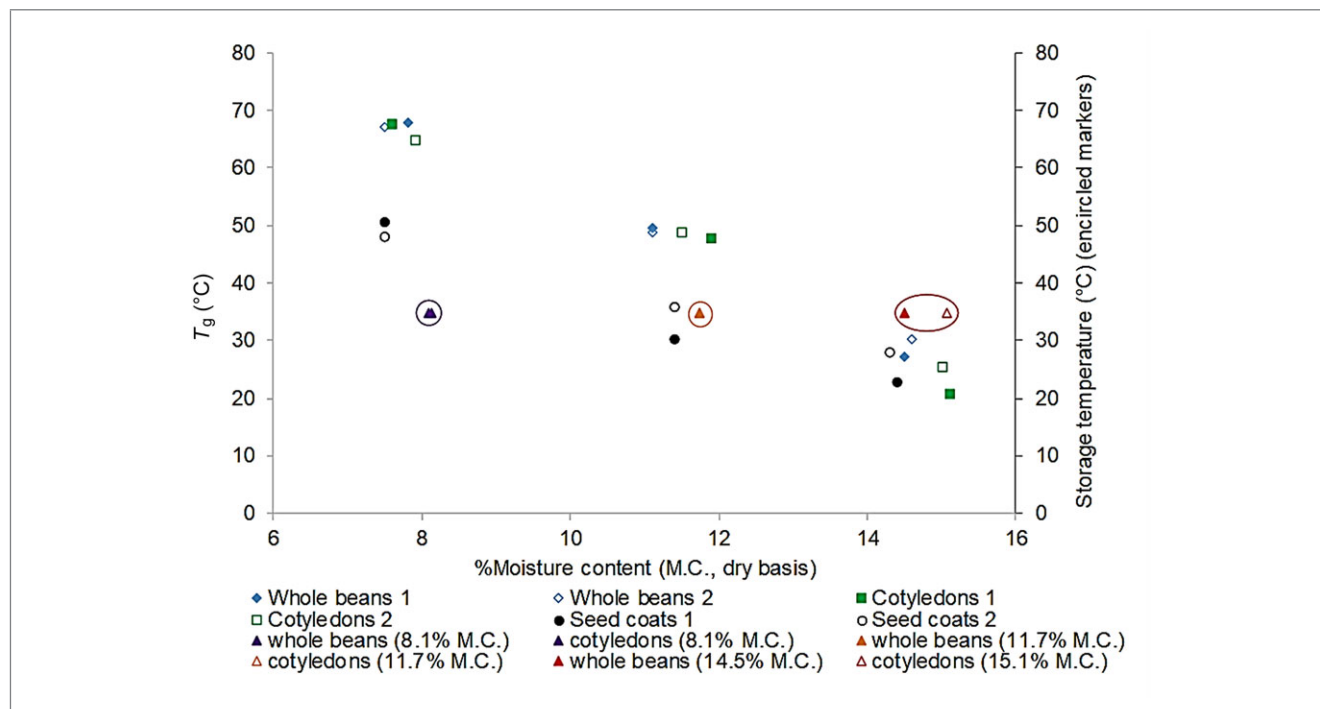


Figure 19—Variation of glass transition temperature with moisture content (symbols not encircled) of whole bean, cotyledon, and seed coat powders. The materials were analyzed in duplicate from independent treatments, hence the results are presented in duplicate for each material. Encircled colored triangular symbols represent the conditions of whole beans and cotyledons stored at different moisture content (shown in the legend) at 35 °C for 3 months to determine relevance of T_g data (Chigwedere, Humerez Flores et al., 2019). (Copyright 2019)

damage, splitting, or powder formation observed during milling is due to the presence of these differential stresses. However, when equilibration is conducted above T_g , moisture will equilibrate in all regions of the seed, thus eliminating any moisture gradients. Upon cooling to room temperature, the seed undergoes the glass transition at a uniform moisture content, thereby suppressing formation of differential stresses and, consequently, show propensity for damage, splitting, or powder formation. Instead of moisture gradients, their results can be explained in terms of material properties with respect to T_g . Below T_g , materials are brittle unlike above it, hence such a brittle material is prone to breakage upon milling. This explains why samples that were equilibrated below T_g had more breakage.

Loss of viability. It has been recommended to properly store the pulses to avoid not only hardening, but also loss of viability. Viability is critical from both an agronomic and a food processing perspective since some preparation methods involve germination of the pulses. Germination is used to assess viability and hence quality of seeds. Pulses stored under adverse conditions have a lower germination capability than their nonstored counterparts (De J. Berrios et al., 1999; Murthy & Sun, 2000; Varriano-Marston & Jackson, 1981). Loss of viability in mung beans was attributed to Maillard reactions by Murthy et al. (2003) who demonstrated the role of the glass transition phenomenon in retarding the rate of primary biochemical reactions involved, that is, lipid peroxidation and nonenzymatic protein glycosylation with reducing sugars. The longevity of seeds is attributed in part to their ability to form glasses upon drying, but, unfortunately, seeds can lose this ability of glass formation as demonstrated by Sun and Leopold (1993). The role of the T_g concept in preserving seed viability was demonstrated by Sun (1997) and Walters et al. (2005). These results demonstrate that the glassy state suppresses deleterious reactions that cause quality

losses, such as loss of viability, hence it can be considered as a physical stabilizer.

It seems unclear to some researchers whether biomolecular changes occurring in beans under inappropriate conditions are responsible for both HTC development and reduced seed viability or whether HTC development causes reduced viability. They either declare this uncertainty, as was done by Varriano-Marston and Jackson (1981), or it is exhibited by their interpretation of results. The suggestion by Parrish and Leopold (1978) that the low germination rates they found were caused by HTC development indicates a causal relationship. Since development of the HS defect in seeds also decreases their viability, we propose that occurrence of defects and loss of viability are correlated but without a causal relationship. It is clear that both HTC defect and loss of viability develop and occur simultaneously because the conditions that are conducive for them are unequivocally similar.

Loss of cooking quality. The concept of T_g has been studied, on seeds in general and pulses in particular, in the context of loss of viability after storage. Germination capacity has been used as a viability indicator, while products of lipid peroxidation, Maillard reactions, and Amadori reactions have been used to monitor deterioration reactions. We found it imperative to explore the concept of T_g in the context of aging and loss of cooking quality. It was intended to obtain temperature and moisture content conditions that would prevent HTC development, thereby ensuring long-term storage stability and hence preservation of cooking quality. Whole bean, cotyledon, and seed coat powders were equilibrated above different saturated salt solutions to generate bean materials having different moisture contents. In all our previous work on hardening and softening of common beans during storage and cooking, respectively, cotyledons played a more significant role than seed coats. Therefore, in the exploration of the T_g of beans,

we also analyzed these materials in isolation (Chigwedere et al., 2019).

The T_g values were determined using an approach based on change in compressibility (Boonyai, Bhandari, & Howes, 2006) and the obtained T_g -moisture data in our study are shown in Figure 19 (Chigwedere et al., 2019). It is clear that increase in moisture content was coupled with a decrease in T_g . This relation is attributed to the plasticizing effect of water as discussed earlier (“Factors that influence the glass transition temperature” section). This property is facilitated by the low molecular weight of water that increases the free volume of the system, thus enhancing its mobility (Al-Muhtaseb, McMinn, & Magee, 2002).

Similar results for whole beans and cotyledons at all moisture contents indicate that the physical state of cotyledons (whether below or above T_g) has a critical contribution for storage stability of whole beans. The data were evaluated for practical relevance by subsequent storage of whole beans and cotyledons at 35 °C at different RH values. The strategy was to store beans below, close to, and above their T_g , followed by an assessment of (any) change in their cooking quality using HTC defect development as a stability indicator. Beans stored below T_g did not develop HTC unlike those stored in its vicinity or above it. These results supported the hypothesis of stability below T_g . It is clear from Figure 19 that, at the same storage temperature, as moisture content increases, the storage temperature approaches and even surpasses T_g . Increase in moisture content facilitated mobility in the matrix, leading to deteriorative reactions that led to an increase in the extent of HTC development and hence the lowest cooking quality. Therefore, the established T_g data were proven to be of practical relevance, hence they can be used as a stability map for storage of common beans (Chigwedere et al., 2019). Based on a material science approach, the appropriate storage conditions, that is, moisture content and temperature, that ensure storage stability of common beans in the context of aging and cooking quality were explicitly revealed.

After harvest, the moisture content of the beans can be determined and the temperature below which they should be stored to ensure preservation of cooking quality can be read-off from the stability map (T_g -moisture relation). The lower the moisture content of the beans, the higher the T_g values, hence postharvest drying would increase the T_g . This is an advantage for common bean farmers in temperate regions because they can store their beans at room temperatures, but not so much for those in tropical regions who may require cool conditions for bean storage during the summer period (Chigwedere et al., 2019).

Variations in ease of processing of pulses are influenced by differences in intrinsic (for example, differences in variety) and extrinsic properties (type and intensity of processing). To a large extent, storage conditions and duration facilitate changes in biomolecular interactions and microstructural integrity on which mechanisms of soaking and cooking are dependent, thereby affecting ease of processing.

Pretreatments

Usually, pretreatments are performed to enhance processing, for example, to reduce cooking time. However, the type and intensity (including duration) of pretreatments in combination with other factors such as level of moisture may lead to undesirable physical, nutritional, and sensory changes in pulses (Arntfield et al., 1997; Taiwo & Akanbi, 1997; Zhao & Chang, 2008). Splitting, bursting, cracking, shedding of seed coats, breaking, and “butterflying” (split cotyledons attached at one end of the bean) are some of the common physical damages occurring in preprocessed beans

(Pan et al., 2010; Schoeninger, Coelho, Christ, & Sampaio, 2014; Zhao & Chang, 2008). These occurrences are problematic to the bean processing industry (Aguilera & Rivera, 1990). Splitting and butterflying are caused by differences in drying rates between seed coats and cotyledons leading to accumulation of vapor pressure in the cotyledons that then ruptures the seed coat (Zhao & Chang, 2008).

Soaking and blanching of beans in salt solutions followed by subsequent drying, in an effort to produce dry beans with reduced cooking time, led to damage in the form of cracking or shedding of seed coats and breaking of the beans (Schoeninger et al., 2014). Damage increased with increase in soaking and drying temperature, and this has implications on the appearance of the product and, consequently, consumer acceptance. Although Zhao and Chang (2008) found increased damage to bean seeds with an increase in soaking time, no influence of soaking time was observed by Schoeninger et al. (2014). The greater the incidence of splitting, the higher the seed coat peeling and, consequently, the thicker the broth due to unhindered leaching of bean components into the cooking water (Mkanda et al., 2007; Taiwo & Akanbi, 1997). Transverse splitting of beans from the hilum/micropyle region during processing exacerbates leaching of solids from the beans and their subsequent sedimentation in canned beans. This spoils the appearance of the product and may reduce its quality and, consequently, consumer acceptance (Forney, Halseth, & Kelly, 1990).

To reduce the extent of splitting of beans during processing, especially canning, beans are soaked in a solution of calcium chloride to retain firmness (Ghasemlou et al., 2013). Attempts on predicting postprocessing quality and, hence, acceptability of processed beans using raw beans proved to be a challenge as demonstrated by Forney et al. (1990). They found that the measurable attributes, such as seed and soaked seed weight as well as harvest and canning moisture, accounted for only 59% of total variability. Later, Pan et al. (2010) developed impact acoustic detection and density separation techniques to eliminate damaged raw beans or those with a higher probability of being damaged during processing to improve the quality of dehydrated precooked beans. Beans with low-impact acoustic signals or low density, as evaluated by steeping beans in salt solutions of known densities, had more skin damage. There is potential for online evaluation of the sensory quality of canned beans by using machine vision (Mendoza, Kelly, & Cichy, 2017).

Most pretreatments that are done prior to storage are targeted at inactivating enzymes that are possibly involved in HTC development, especially phytase. Phytase activity is implicated in the pectin-cation-phytate hypothesis of HTC development described earlier (“Pectin-cation-phytate hypothesis” section). Steaming (121 °C, 4 min, 13% moisture), hot-air roasting (150 °C, 5 min, 25% moisture), and micronization (150 °C, 5 min, 25% moisture) pretreatments prior to storage under conditions that are conducive for hardening only partially inactivated phytase activity in cowpeas (Affrifah & Chinnan, 2006; Ndungu et al., 2012). In addition, despite micronization and hot-air roasting pretreatments of cowpeas, pectin extractability decreased during subsequent storage under conditions conducive to HTC development (Ndungu et al., 2012). Although steaming prevented hardening, micronization minimized greatly the extent of HTC development compared to hot-air roasting. During micronization, the infrared waves penetrate the beans and induce molecular vibrations that generate heat that is of a much higher intensity compared to convective heat. Therefore, a better phytase inactivation was realized

with micronization than with hot-air roasting (Ndungu et al., 2012). In relation to the lignification-like reaction mechanism, residual activity of peroxidase was found after a dry hot roast of beans in a sand roaster (200 °C) pretreatment (Rivera, Hohlberg, Aguilera, Plhak, & Stanley, 1989).

Beans were either steamed (98 °C) or retorted (121 °C, 15 psi) for different times and, surprisingly, treatments for the minimum time, 10 and 2 min, respectively, completely prevented hardening after storage at room temperature and 75% RH for 9 months unlike at longer times where hardness increased during storage (Molina et al., 1976). In yet another study on beans, of all the applied pretreatments including sun-drying (with and without pods), roasting, solar drying, and irradiation, irradiation led to a significantly lowered cooking time compared to other pretreatments (Plhak et al., 1987). Therefore, it minimized the extent of hardening during posttreatment storage under adverse conditions. Over the years, no implementation of such technologies on an industrial scale has been documented, demonstrating that it is a challenge for most bean farmers and consumers who reside in developing countries due to economic infeasibility.

Soaking and subsequent cooking in salt solutions

Soaking of pulses is widely employed to reduce the extent of HTC. Unlike demineralized water, solutions of high pH, chelating agents such as ethylenediaminetetraacetic acid (EDTA), and monovalent cations such as sodium (Na^+) reduce the cooking time of beans (del Valle & Stanley, 1995; Hincks & Stanley, 1986; Kinyanjui et al., 2015; Njoroge et al., 2016; Paredes-López et al., 1991; Pirhayati, Soltanizadeh & Kadivar, 2011; Varriano-Marston & Omana, 1979), lentils (Pirhayati et al., 2011), and cowpeas (Liu et al., 1992). We also demonstrated this in our previous work (Chigwedere et al., 2018) using demineralized water and 0.1 M NaHCO_3 solution as shown in Figure 20. Figure 21 shows the 90% joint confidence regions (JCRs) for the estimated parameters, softening rate constant, and lag phase for each cooking curve in Figure 20.

Systems with vertically aligned JCRs are not significantly different in lag phase as is the case for all the JCRs, except for aged cotyledons cooked in demineralized water. Likewise, systems with horizontally aligned JCRs are not significantly different in softening rate constants as is the case for aged whole beans and cotyledons cooked in demineralized water. If two systems are not significantly different in both parameters, their JCRs would overlap. Upon cooking in NaHCO_3 solution, enhanced cooking was observed, as can be visualized by the shift of their cooking profiles toward the left (Figure 20) and their higher softening rate constants compared to the ones for bean materials cooked in demineralized water (Figure 21). Dis(similarity) in the cooking behavior of aged whole beans and aged cotyledons depended on the cooking medium. In NaHCO_3 solution, the dissimilarity in cooking behavior may be attributed possibly to hindrance of pH adaptation and/or uptake of Na^+ ions by the seed coat (Chigwedere et al., 2018). In our previous study (Njoroge et al., 2016), the influence of Na_2CO_3 solution on pectin solubilization was investigated on whole aged (35 °C, 83% RH, 6 months) Canadian wonder beans cooked for 270 min. The results showed unequivocally that more sodium carbonate extractable pectin (84.5%) was solubilized due to this solution than demineralized water (3.7%).

A popular rock salt known as *kanwa*, *trona*, or *magadi* in east, central, and west Africa tenderizes beans and other food crops considered to retain toughness during domestic cooking. This salt contains NaHCO_3 and Na_2CO_3 , so its tenderizing effect is no

surprise. The rock salt is contaminated by fluoride ions that originate from the weathering of volcanic rocks, especially those in the eastern Rift Valley area (Minka, Mbofung, Gandon, & Bruneteau, 1999; Nielsen, 1999). Although fluoride ions may pose health risks in high concentrations, they were shown to inhibit hardening in beans during soaking, even at low pH and high temperatures, supposedly by inhibiting phytase action on phytate (Kilmer et al., 1994; Vindiola, Seib, & Hosene, 1986). This was postulated in relation to the pectin-cation-phytate hypothesis discussed earlier (“Pectin-cation-phytate hypothesis” section).

Chelating agents sequester divalent cations from divalent cation-crosslinked pectin, thereby enhancing pectin solubilization, consequently decreasing cooking time (Aguilera & Rivera, 1992; Varriano-Marston & Omana, 1979). There is controversy pertaining to the effect of solutions containing monovalent cations on softening of beans, with some studies concluding a positive effect and others no effect. Increased water-holding capacity due to presence of monovalent cations has been suggested by de León, Elías, and Bressani (1992). This is plausible because the entrapped water sensitizes biomolecules to heat treatment. X-ray microanalysis spectra have revealed monovalent-divalent cation exchange during cooking (in demineralized water) of beans presoaked in a solution of mixed salts (pH 9.32) consisting of 1% NaCl (pH 7.08), 0.75% NaHCO_3 (pH 8.58), 0.25% Na_2CO_3 (pH 11.25), and 0.5% $\text{Na}_5\text{P}_3\text{O}_{10}$ (pH 9.91) (Varriano-Marston & Omana, 1979). Although the beans presoaked in a combination of the aforementioned salts were cooked in demineralized water, pectin solubilization during cooking was in most cases double than that during soaking. According to these authors, chelation of divalent cations facilitates hydrogen bonding (thermolabile) between pectinic acid moieties, thereby enhancing pectin solubilization. In addition, they reported more pronounced leaching of pectin when beans were soaked in high-pH solutions. Surprisingly, this result was explained in terms of chelation and ion exchange, disregarding the influence of pH. However, the influence of pH was acknowledged with regard to protein solubilization and leaching only.

Later, in a related study, the contribution of salt solutions to the softening of beans was suggested to be due to type (but not charge) of anions rather than cation exchange as suggested by Varriano-Marston and Omana (1979). Efficiency was in the order $\text{CO}_3^{2-} > \text{EDTA}^{2-} = \text{NO}_3^- > \text{SO}_4^{2-} = \text{Cl}^-$ and with increased ionic strength of the salt solution (Garcia-Vela et al., 1991). In their discussion, the CO_3^{2-} ions lowered the denaturation enthalpy and temperature of proteins, and microscopic evidence suggested that monovalent salt solutions do not play a role in cell separation but rather in the promotion of protein solubilization. They concluded, “In summary, the data presented in this work can be interpreted as supportive of a mechanism for the action of salts on bean softening dependent upon protein solubilization.”

It is widely known that CO_3^{2-} ions confer a high pH, especially in comparison with the listed anions, but this was not considered in their study. In addition, the beans were cooked in salt solutions unlike in the study by Varriano-Marston and Omana (1979); thus the influence of a high pH in the solution containing CO_3^{2-} ions is expected to play a critical role in softening. Unfortunately, pectin analysis was done qualitatively using microscopy, and not quantitatively because it is interesting how its solubilization would be explained disregarding cation exchange and influence of pH. It is also known that starch gelatinization and pectin solubilization contribute to texture modification, but this was not considered in their proposed mechanism of softening. Although del Valle et al.

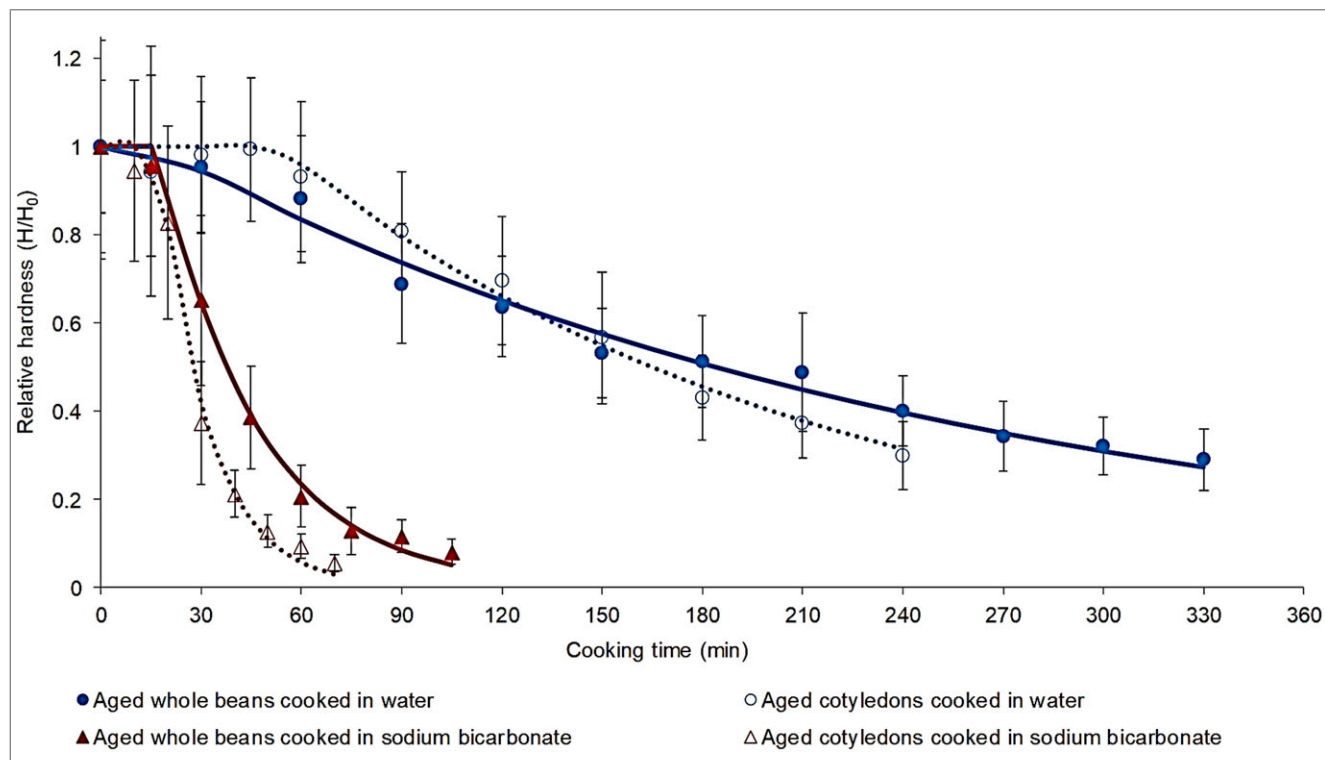


Figure 20—Cooking profiles of aged whole beans and cotyledons cooked in demineralized water (blue) and 0.1 M NaHCO_3 (maroon). Markers represent mean values of 20 hardness measurements from 20 cotyledons (whole beans were peeled before hardness measurements) expressed as a ratio of the initial hardness (H/H_0). Error bars represent standard deviations associated with mean hardness. Solid and dashed lines denote modeled data for whole beans and cotyledons, respectively (Chigwedere et al., 2018). (Copyright 2019)

(1992) acknowledged the influence of high pH (solutions) on both pectin and protein solubilization, they did not find a significant contribution of each of these processes on the texture of cooked beans from regression analysis. However, due to the influence of pH on denaturation temperature and enthalpy of proteins, they concluded that protein destabilization contributed more to softening than pectin solubilization. The possibility of other mechanisms contributing to bean softening was highlighted. Reduced cooking times were also related to protein insolubilization due to denaturation in lentils by Arntfield et al. (1997) and in beans by Garcia-Vela et al. (1991).

We noted that inconsistencies in mechanisms by which softening occurs may be mainly due to not focusing on effects of the treatments on characteristics of all the biomolecules involved in texture modification simultaneously. Having noted this, we applied an inclusive approach to our study on investigating the rate-limiting step for softening of beans and found it to be pectin solubilization (Chigwedere et al., 2018) as described earlier (“Evolution of texture” section).

After cooking beans aged for different times in demineralized water, NaHCO_3 (0.05 M, pH 8), sodium phosphate buffer (0.1 M, pH 7), and NaEDTA (0.1 M, pH 7) for 2 hr, Aguilera and Rivera (1992) found that, up to 2 months of storage, only NaEDTA could facilitate softening of aged beans to the level of fresh beans. This was assessed by expressing hardness associated with beans stored for a particular period relative to that of nonaged beans. For longer aging times, hardness was not overcome, leading to a postulation on reversible and irreversible hardening during storage. This hypothesis was later supported by del Valle and Stanley (1995) who ascribed the reversible hardness to the pectin-cation-

phytate mechanism and the irreversible hardness to the mechanism involving lignification-like reactions. In addition, they found that the rate of the former was dependent on water activity, whereas that of the latter was mainly temperature-dependent. These results corroborated a postulation earlier by Hincks and Stanley (1986) that hardening of beans is due to multiple mechanisms. It was hypothesized that the pectin-phytate mechanism plays a significant role when hardening commences, and then, upon prolonged storage, the mechanism involving lignification-like reactions plays the major role. The multiple-mechanism nature of the hardening process of pulses was also reiterated by Liu et al. (1993) who reported changes in proteins, starch, and components of the middle lamella.

Although these salt solutions greatly enhance the bean-softening process, they can also influence sensory and nutritional properties of the cooked beans. In terms of sensory perception, soaking and blanching of beans in NaHCO_3 produces a darker color of the seed coats, thereby altering the visual appearance of the product (Schoeninger et al., 2014). In addition, beans cooked in salt solutions were less acceptable than those cooked in demineralized water, regardless of the salt used during soaking in both cases. With regard to nutrition, cooking of pulses in monovalent salt solutions characterized by high pH (>8) can lead to racemization of some amino acids and reduced availability of the already limiting sulfur amino acids (de León et al., 1992).

Toward Increased Utilization of Pulses: Current Trends

Not only have consumers become extremely conscious of food quality, nutrition, and health, they are influencing research in the

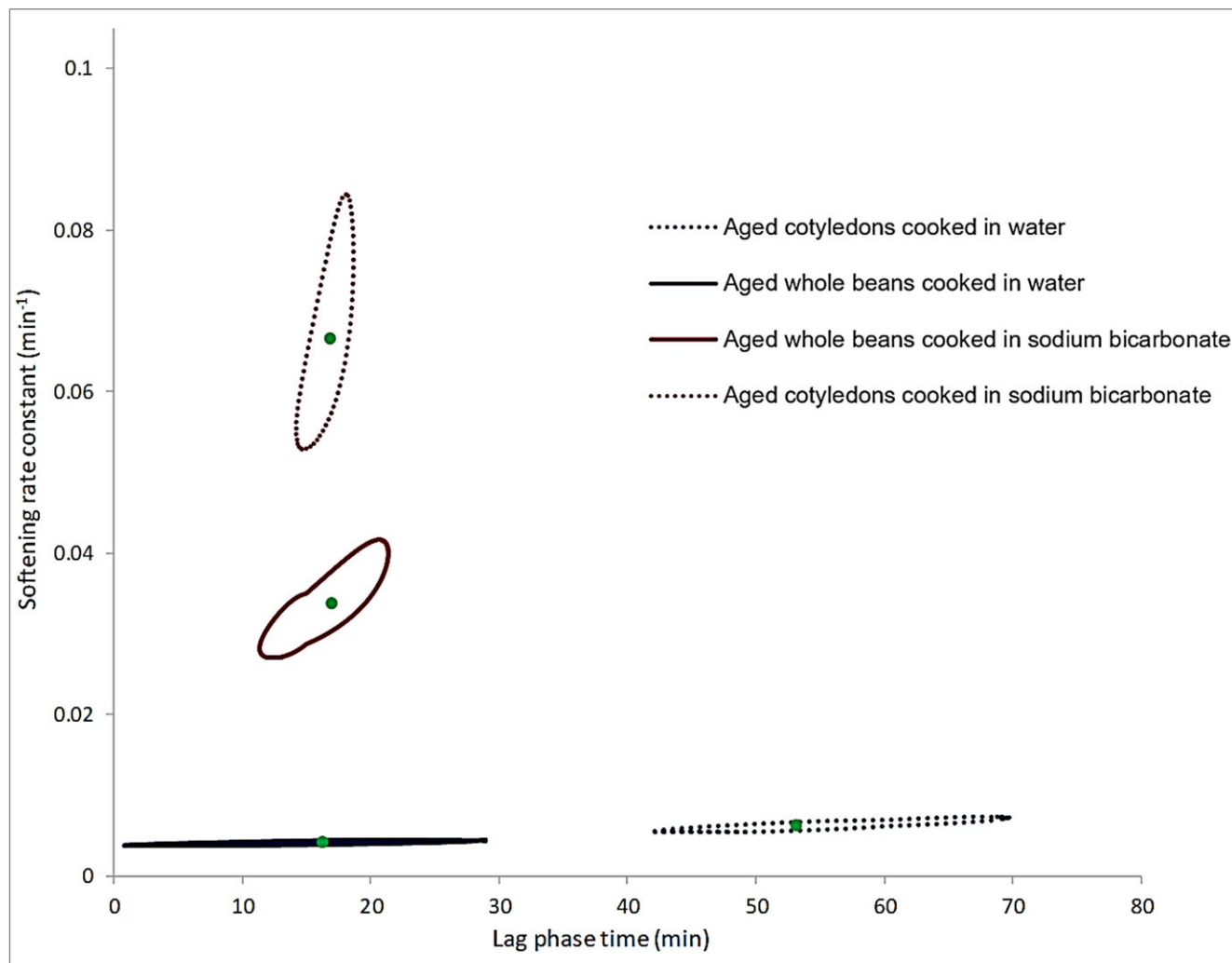


Figure 21—Ninety percent joint confidence regions (JCRs) for the rate constant for softening and the lag phase as determined from the 95% confidence intervals of each. The green markers in all JCRs represent the rate constant for softening and the lag phase values for each cooking curve.

food industry. This explains the attempts to increase utilization of pulses by incorporating them into formulations with other foods as well as to extract components for bioactivity or other functionalities. Incorporation of bean flour in formulations of cereal-based products, such as corn-based snacks, improved nutritional but not physical properties of the product (Anton, Gary Fulcher, & Arntfield, 2009). Other products that have flour from pulses incorporated into the formulations include wheat bread (Coda, Varis, Verni, Rizzello, & Katina, 2017), gluten-free cookies (Simons & Hall, 2018), corn pasta (Giménez et al., 2013), gluten-free rice pasta (Bouasla, Wójtowicz, & Zidoune, 2017), and pasta formulated entirely from pulse flour (Laleg, Cassan, Barron, Prabhasankar, & Micard, 2016; Rosa-Sibakov et al., 2016). Giuberti, Gallo, Cerioli, Fortunati, and Masoero (2015) formulated spaghetti with reduced *in vitro* glycemic index (GI) from rice flour and flour from a bean cultivar characterized by low phytic acid content and no lectins. The use of pulses as functional ingredients in gluten-free bakery and pasta products was recently reviewed by Foschia, Horstmann, Arendt, and Zannini (2017).

Apart from the incorporation of flours and/or powders of pulses in food formulations, current research trends are on the nutraceutical functionalities of pulses (Chávez-Mendoza &

Sánchez, 2017; Díaz-Sánchez, Guajardo-Flores, Serna Guerrero, Gutierrez-Urbe, & Jacobo-Velázquez, 2018; Jamdar, Deshpande, & Marathe, 2017; Jing et al., 2018) as influenced by different processing methods (López-Martínez, Leyva-López, Gutiérrez-Grijalva, & Heredia, 2017) or, more specifically, bioactivity of peptides and hydrolysates (Carbonaro, Maselli, & Nucara, 2015; Luna-Vital et al., 2015) as well as hydrolyzability of the proteins and related physicochemical characteristics (Ghribi et al., 2015; Jamdar et al., 2017; Torres, Rutherford, Muñoz, Peters, & Montoya, 2016; Worku & Sahu, 2017). Other studies involve *in vitro* starch digestion (Bhattarai, Dhital, Wu, Chen, & Gidley, 2017; Dhital, Bhattarai, Gorham, & Gidley, 2016; Edwards et al., 2015; Ma, Wang, Wang, Jane, & Du, 2017; Pallares Pallares et al., 2018; Rovalino-Córdova, Fogliano, & Capuano, 2018).

Implications of Cooking-Induced Structural Changes: Industrial Relevance

Pulses are characterized by a low GI owing to the factors reviewed by Cuvelier et al. (2017). From a structural point of view, inference on why pulses in general have low glycemic indices can be drawn from the results discussed in “Evolution of texture” section. The low GI of cooked pulses can be attributed, to a greater

extent, to the encapsulation of starch by the cell wall in soft bean tissue, making it less accessible to starch-degrading enzymes during digestion. Raw bean flour would expose the gelatinized starch to amylolytic enzymes much more effectively due to absence of the cell wall, thus there is a high probability of differences in GI due to microstructural differences. Another explanation could be that the residual molecular order of starch observed after cooking, leading to its retrogradation can pose challenges for starch digestion.

The pectin solubilization process can be manipulated leading to different microstructures. This is crucial for food engineering since some products can be tailored for specific groups with special caloric needs, for example, diabetics for whom powdered beans characterized by separated cells and absence of free starch granules would be more suitable. This notion is supported by findings from Dhital et al. (2016) and Pallares Pallares et al. (2018) who demonstrated that the degree to which starch is encapsulated influences the extent of its hydrolysis during subsequent digestion.

Using *in vivo* experiments, Anderson et al. (2014) studied the effect of whole canned, pureed canned, and powdered pulse products on blood glucose response, and concluded that, overall, there were no significant differences due to various treatment methods. Therefore, they recommended incorporation of pulse powders as ingredients in commercial products to increase intake of pulses in the diet in their respective region. However, microstructures of the differently treated pulses were not analyzed in their study. The preparation of their commercially available powders involved heating steps such as cooking and micronization before grinding, although the conditions were not specified. In our opinion, the applied heat treatments could have softened the beans enough to cause cell separation upon grinding, in which case the microstructure would be similar for all samples. Interestingly, starch and protein hydrolysis of a processed matrix with an open microstructure, such as milled raw pulses, can be modulated to obtain unique functional and nutraceutical characteristics. This was demonstrated by Chávez-Murillo, Veyna-Torres, Cavazos-Tamez, de la Rosa-Millán, and Serna-Saldívar (2018) through hydrothermal treatment-modulated reduction of starch hydrolysis with a concomitant increase in protein hydrolysis to obtain a low-GI characteristic.

Conclusions and Future Outlook

Water that is imbibed during hydration plays a pivotal role in the cooking of pulses, to a lesser extent during soaking where it hydrates biopolymers such as proteins, starch, and pectin, or their networks, thereby sensitizing them for denaturation, gelatinization, and solubilization, respectively, during the subsequent cooking process. Cooking causes texture changes, with pectin solubilization being the rate-limiting process for softening and heat-induced chemical reactions such as the Maillard reaction that produces volatile compounds that are important for flavor development. It is necessary to quantify the significantly changing (marker) volatile compounds and thereafter to evaluate their sensory consequences on flavor, taking into consideration their odor thresholds. Moreover, texture and flavor optimization can be explored using sensory analysis. The effect of different individual processing technologies, such as extrusion, high pressure processing, pulsed electric field, and microwave technologies, as well as their (sequential) combinations on pectin solubilization and flavor development can be explored. This is important considering that these technologies are used in food manufacturing industries.

The hardening of pulses upon storage emanates from mobility of the matrix as explained by the glass transition temperature

concept, with moisture content and temperature being critical variables. This facilitates chemical and/or biochemical reactions that reinforce cell-cell adhesion through enhanced binding of pectin polymers (from being loosely to covalently bound) to other cell wall components, among reactions involving other polymers. Other chemical and/or biochemical reactions can produce volatile compounds and/or their precursors that can be crucial for flavor development. During subsequent cooking, changes due to the aforementioned reactions among others influence texture by delaying cell separation through delayed pectin solubilization. From a pectin perspective, hardening and softening of pulses occurs through interconversion of pectin polymers. Flavor is influenced through changes in composition of volatile compounds emanating during the hardening process.

The mechanistic insight into the hydration of fresh beans has been reported extensively in the literature, but it is lacking for aged beans. It would be interesting to visualize any differences in hydration kinetics due to the aging process.

It is clear from this review that solutions of high pH containing monovalent cations play a pivotal role in enhancing softening of pulses during cooking. This necessitates optimization of concentrations of such solutions during processing to achieve consumer-acceptable products while reducing cooking time to a great extent. The development of the HTC defect can be prevented by storage under specific moisture-temperature combinations as obtained from the storage stability study described in this review. In the future, it would be interesting to conduct similar storage stability studies for other pulses that are critical in human nutrition and that also undergo storage-induced hardening, and these include bambara groundnuts (*Vigna subterranea*) and cowpeas (*Vigna unguiculata*). Another prevention method lies in breeding for varieties that are less susceptible to the defect. However, breeding should be informed on the target biomolecules that would be manipulated. Therefore, there is still need to elucidate the biomolecules that play the key roles in HTC development and from this review, it is clear that this research should focus on the cotyledons rather than seed coats. The current methods of investigating biomolecular changes are mainly based on extraction than characterization of the polymers. The extraction processes may influence the interactions under investigation. Therefore, the most appropriate method to understand interactions among biopolymers would be to visualize them *in situ*, a clear future challenge in this field.

The minimal leaching of minerals during soaking and cooking of beans is interesting from a health perspective. Unfortunately, most of the calcium is found in seed coats wherein the pectin is highly demethylesterified. This necessitates studies on bioaccessibility and/or bioavailability of minerals in pulses, based on *in vitro*, *in silico*, and *in vivo* approaches.

Author Contributions

All authors contributed to this work. Claire M. Chigwedere wrote the manuscript and the co-authors critically evaluated and approved it.

Conflict of Interest

The authors declare no conflict of interest.

References

- Abu-Ghannam, N. (1998). Modelling textural changes during the hydration process of red beans. *Journal of Food Engineering*, 38(3), 341–352.

- Abu-Ghannam, N., & McKenna, B. (1997). Hydration kinetics of red kidney beans. *Journal of Food Science*, 62(3), 520–523.
- Affriah, N. S., & Chinnam, M. S. (2006). The effect of drying conditions on the development of the hard-to-cook defect in steam-treated cowpeas. *International Journal of Food Science and Technology*, 41(8), 867–877.
- Agbo, G. N., Hosfield, G. L., Uebersax, M. A., & Klomprens, K. (1987). Seed microstructure and its relationship to water uptake in isogenic lines and a cultivar of dry beans (*Phaseolus vulgaris* L.). *Food Structure*, 6(1), 91–102.
- Aguilera, J. M., & Rivera, J. (1990). Storage and handling of black beans. *Journal of Food Processing and Preservation*, 16(6), 423–435.
- Aguilera, J. M., & Rivera, R. (1992). Hard-to-cook defect in black beans: Hardening rates, water imbibition and multiple mechanism hypothesis. *Food Research International*, 25(2), 101–108.
- Aguilera, J. M., & Stanley, D. W. (1985). A review of textural defects in cooked reconstituted legumes—the influence of storage and processing. *Journal of Food Processing and Preservation*, 9(3), 145–169.
- Al-Muhtaseb, A. H., McMinn, W. A. M., & Magee, T. R. A. (2002). Moisture sorption isotherm characteristics of food products: A review. *Food and Bioprocess Processing*, 80(2), 118–128.
- Alonso, R., Orúe, E., & Marzo, F. (1998). Effects of extrusion and conventional processing methods on protein and antinutritional factor contents in pea seeds. *Food Chemistry*, 63(4), 505–512.
- Anderson, G. H., Liu, Y., Smith, C. E., Liu, T. T., Nunez, M. F., Mollard, R. C., & Luhovyy, B. L. (2014). The acute effect of commercially available pulse powders on postprandial glycaemic response in healthy young men. *British Journal of Nutrition*, 112(12), 1966–1973.
- Anton, A. A., Gary Fulcher, R., & Arntfield, S. D. (2009). Physical and nutritional impact of fortification of corn starch-based extruded snacks with common bean (*Phaseolus vulgaris* L.) flour: Effects of bean addition and extrusion cooking. *Food Chemistry*, 113(4), 989–996.
- Arntfield, S. D., Scanlon, M. G., Malcolmson, L. J., Watts, B., Ryland, D., & Savoie, V. (1997). Effect of tempering and end moisture content on the quality of micronized lentils. *Food Research International*, 30(5), 371–380.
- Azarnia, S., Boye, J. I., Warkentin, T., Malcolmson, L., Sabik, H., & Bellido, A. S. (2011). Volatile flavour profile changes in selected field pea cultivars as affected by crop year and processing. *Food Chemistry*, 124(1), 326–335.
- Ballesteros, D., & Walters, C. (2011). Detailed characterization of mechanical properties and molecular mobility within dry seed glasses: Relevance to the physiology of dry biological systems. *Plant Journal*, 68(4), 607–619.
- Batista, K. A., Prudêncio, S. H., & Fernandes, K. F. (2010a). Changes in the biochemical and functional properties of the extruded hard-to-cook cowpea (*Vigna unguiculata* L. Walp.). *International Journal of Food Science & Technology*, 45(4), 794–799.
- Batista, K. A., Prudêncio, S. H., & Fernandes, K. F. (2010b). Changes in the functional properties and antinutritional factors of extruded hard-to-cook common beans (*Phaseolus vulgaris* L.). *Journal of Food Science*, 75(3), 286–290.
- Bellido, G., Arntfield, S. D., Cenkowski, S., & Scanlon, M. (2006). Effects of micronization pretreatments on the physicochemical properties of navy and black beans (*Phaseolus vulgaris* L.). *LWT - Food Science and Technology*, 39(7), 779–787.
- Bennink, M. R. (2002). Consumption of black beans and navy beans (*Phaseolus vulgaris*) reduced azoxymethane-induced colon cancer in rats. *Nutrition and Cancer*, 44(1), 60–65.
- Berg, T., Singh, J., Hardacre, A., & Boland, M. J. (2012). The role of cotyledon cell structure during *in vitro* digestion of starch in navy beans. *Carbohydrate Polymers*, 87(2), 1678–1688.
- Bewley, J. D. (1986). Membrane changes in seeds as related to germination and the perturbations resulting from deterioration in storage. *Physiology of Seed deterioration*, 27–45. <https://doi.org/10.2135/essaspecpub11.c2>
- Bhattarai, R. R., Dhital, S., Wu, P., Chen, X. D., & Gidley, M. J. (2017). Digestion of isolated legume cells in a stomach-duodenum model: Three mechanisms limit starch and protein hydrolysis. *Food and Function*, 8(7), 2573–2582.
- Bizot, H., Le Bail, P., Leroux, B., Davy, J., Roger, P., & Buleon, A. (1997). Calorimetric evaluation of the glass transition in hydrated, linear and branched polyhydroglucose compounds. *Carbohydrate Polymers*, 32(1), 33–50.
- Boonyai, P., Bhandari, B., & Howes, T. (2006). Applications of thermal mechanical compression tests in food powder analysis. *International Journal of Food Properties*, 9(1), 127–134.
- Bouasla, A., Wójtowicz, A., & Zidoune, M. N. (2017). Gluten-free precooked rice pasta enriched with legumes flours: Physical properties, texture, sensory attributes and microstructure. *LWT - Food Science and Technology*, 75, 569–577.
- Brummer, Y., Kaviani, M., & Tosh, S. M. (2015). Structural and functional characteristics of dietary fibre in beans, lentils, peas and chickpeas. *Food Research International*, 67, 117–125.
- Buettner, A., & Schieberle, P. (2000). Influence of mastication on the concentrations of aroma volatiles—Some aspects of flavour release and flavour perception. *Food Chemistry*, 71(3), 347–354.
- Buitimea-Cantúa, N. E., Gutiérrez-Urbe, J. A., & Serna-Saldívar, S. O. (2018). Phenolic-protein interactions: Effects on food properties and health benefits. *Journal of Medicinal Food*, 21(2), 188–198.
- Buitink, J., Claessens, M. M. A. E., Hemminga, M. A., & Hoekstra, F. A. (1998). Influence of water content and temperature on molecular mobility and intracellular glasses in seeds and pollen. *Plant Physiology*, 118(2), 531–541.
- Buttery, R. G., Seifert, R. M., & Ling, L. C. (1975). Characterization of some volatile constituents of dry red beans. *Journal of Agricultural and Food Chemistry*, 23(3), 516–519.
- Caffall, K. H., & Mohnen, D. (2009). The structure, function, and biosynthesis of plant cell wall pectic polysaccharides. *Carbohydrate Research*, 344(14), 1879–1900.
- Carbonaro, M., Maselli, P., & Nucara, A. (2015). Structural aspects of legume proteins and nutraceutical properties. *Food Research International*, 76(P1), 19–30.
- Chávez-Mendoza, C., & Sánchez, E. (2017). Bioactive compounds from Mexican varieties of the common bean (*Phaseolus vulgaris*): Implications for health. *Molecules*, 22(8), 1360. <https://doi.org/10.3390/molecules22081360>.
- Chávez-Murillo, C. E., Veyna-Torres, J. I., Cavazos-Tamez, L. M., de la Rosa-Millán, J., & Serna-Saldívar, S. O. (2018). Physicochemical characteristics, ATR-FTIR molecular interactions and *in vitro* starch and protein digestion of thermally-treated whole pulse flours. *Food Research International*, 105, 371–383.
- Chen, P. X., Tang, Y., Marcone, M. F., Pauls, P. K., Zhang, B., Liu, R., & Tsao, R. (2015). Characterization of free, conjugated and bound phenolics and lipophilic antioxidants in regular- and non-darkening cranberry beans (*Phaseolus vulgaris* L.). *Food Chemistry*, 185, 298–308.
- Chigwedere, C. M., Humerez Flores, J. N., Panozzo, A., Van Loey, A. M., & Hendrickx, M. E. (2019). Instability of common beans during storage causes hardening: The role of glass transition phenomena. *Food Research International*. <https://doi.org/10.1016/j.foodres.2018.12.006>
- Chigwedere, C. M., Nkonkola, C. M., Rai, S., Kyomugasho, C., Kermani, Z. J., Pallares, P., ... Hendrickx, M. E. (2019). Cotyledon protein molecular interconversions explain pectin solubilization during cooking of common beans (*Phaseolus vulgaris*). *Food Research International*, 116, 462–470.
- Chigwedere, C. M., Olaoye, T. F., Kyomugasho, C., Kermani, Z. J., Pallares, A. P., Van Loey, A. M., ... Hendrickx, M. E. (2018). Mechanistic insight into softening of Canadian wonder common beans (*Phaseolus vulgaris*) during cooking. *Food Research International*, 106, 522–531.
- Chigwedere, C. M., Tadele, W. W., Yi, J., Wibowo, S., Kebede, B. T., Van Loey, A. M., ... Hendrickx, M. E. (2019). Insight into the evolution of flavor compounds during cooking of common beans utilizing a headspace untargeted fingerprinting approach. *Food Chemistry*, 275, 224–238.
- Christensen, L. P., Edelenbos, M., & Kreutzmann, S. (2007). Fruits and vegetables of moderate climate. In R. G. Berger (Ed.), *Flavours and fragrances chemistry, bioprocessing and sustainability* (pp. 135–181). Berlin: Springer.
- Chung, H. J., Liu, Q., Hoover, R., Warkentin, T. D., & Vandenberg, B. (2008). *In vitro* starch digestibility, expected glycemic index, and thermal and pasting properties of flours from pea, lentil and chickpea cultivars. *Food Chemistry*, 111(2), 316–321.
- Clark, S., & Duncan, A. M. (2017). The role of pulses in satiety, food intake and body weight management. *Journal of Functional Foods*, 38, 612–623.
- Coda, R., Varis, J., Verni, M., Rizzello, C. G., & Katina, K. (2017). Improvement of the protein quality of wheat bread through faba bean sourdough addition. *LWT - Food Science and Technology*, 82, 296–302.
- Cremer, D. R., & Eichner, K. (2000). The reaction kinetics for the formation of Strecker aldehydes in low moisture model systems and in plant powders. *Food Chemistry*, 71(1), 37–43.
- Cremer, D. R., Vollenbroeker, M., & Eichner, K. (2000). Investigation of the formation of Strecker aldehydes from the reaction of Amadori rearrangement products with alpha-amino acids in low moisture model systems. *European Food Research and Technology*, 211, 400–403.

- Cuvelier, K., Storsley, J., Mollard, R., Thandapilly, S. J., & Ames, N. (2017). A review of the impact of whole pulses on glycemic response. *Cereal Foods World*, 62(2), 53–58.
- De J Berrios, J., Swanson, B. G., & Cheong, W. A. (1998). Structural characteristics of stored black beans (*Phaseolus Vulgaris L.*). *Scanning*, 20, 410–417.
- De J Berrios, J., Swanson, B. G., & Cheong, W. A. (1999). Physico-chemical characterization of stored black beans (*Phaseolus vulgaris L.*). *Food Research International*, 32(10), 669–676.
- de León, L. F., Elías, L. G., & Bressani, R. (1992). Effect of salt solutions on the cooking time, nutritional and sensory characteristics of common beans (*Phaseolus vulgaris*). *Food Research International*, 25(2), 131–136.
- Del Rosario, R., De Lumen, B. O., Habu, T., Flath, R. A., Mon, T. R., & Teranishi, R. (1984). Comparison of headspace of volatiles from winged beans and soybeans. *Journal of Agricultural and Food Chemistry*, 32(5), 1011–1015.
- del Valle, J. M., Cottrell, T. J., Jackman, R. L., & Stanley, D. W. (1992). Hard-to-cook defect in black beans: The contribution of proteins to salt soaking effects. *Food Research International*, 25(6), 429–436.
- del Valle, J. M., & Stanley, D. W. (1995). Reversible and irreversible components of bean hardening. *Food Research International*, 28(5), 455–463.
- Devi, R., Chaudhary, C., Jain, V., Saxena, A. K., & Shilpa, C. (2018). Effect of soaking on anti-nutritional factors in the sun-dried seeds of hybrid pigeon pea to enhance their nutrients bioavailability. *Journal of Pharmacognosy and Phytochemistry*, 7(2), 675–680.
- Dhital, S., Bhattarai, R., Gorham, J., & Gidley, M. (2016). Intactness of cell wall structure controls the *in-vitro* digestion of starch in legumes. *Food Function*, 7(3), 1367–1379.
- Díaz-Sánchez, E. K., Guajardo-Flores, D., Serna Guerrero, D., Gutierrez-Urbe, J. A., & Jacobo-Velázquez, D. A. (2018). The application of chemical elicitors improves the flavonoid. *Revista Mexicana de Ingeniería Química*, 17(1), 123–130.
- Dixit, K. A., Kumar, V., Rani, A., Manjaya, J. G., & Bhatnagar, D. (2011). Effect of gamma irradiation on lipoxigenases, trypsin inhibitor, raffinose family oligosaccharides and nutritional factors of different seed coat colored soybean (*Glycine max L.*). *Radiation Physics and Chemistry*, 80(4), 597–603.
- dos Santos Siqueira, B., Vianello, R. P., Fernandes, K. F., & Bassinello, P. Z., (2013). Hardness of carioca beans (*Phaseolus vulgaris L.*) as affected by cooking methods. *LWT - Food Science and Technology*, 54(1), 13–17.
- Duke, S. H., & Kakefuda, G. (1981). Role of the testa in preventing cellular rupture during imbibition of legume seeds. *Plant Physiology*, 67(3), 449–456.
- Edwards, C. H., Warren, F. J., Campbell, G. M., Gaisford, S., Royall, P. G., Butterworth, P. J., & Ellis, P. R. (2015). A study of starch gelatinisation behaviour in hydrothermally-processed plant food tissues and implications for *in vitro* digestibility. *Food and Function*, 6(12), 3634–3641.
- ElMaki, H. B., AbdelRahaman, S. M., Idris, W. H., Hassan, A. B., Babiker, E. E., & El Tinay, A. H. (2007). Content of antinutritional factors and HCl-extractability of minerals from white bean (*Phaseolus vulgaris*) cultivars: Influence of soaking and/or cooking. *Food Chemistry*, 100(1), 362–368.
- El-Tabey Shehata, A. M. (1992). Hard-to-cook phenomenon in legumes. *Food Reviews International*, 8(2), 191–221.
- Espinosa-Andrews, H., & Rodríguez-Rodríguez, R. (2018). Water state diagram and thermal properties of fructans powders. *Journal of Thermal Analysis and Calorimetry*, 132(1), 197–204.
- Estévez, M., Ventanas, S., & Heiononen, M. (2011). Formation of Strecker aldehydes between protein carbonyls— α -amino adipic and γ -glutamic semialdehydes—and leucine and isoleucine. *Food Chemistry*, 128(4), 1051–1057.
- FAOSTAT. (2018). Retrieved from <http://www.fao.org/faostat/en/compare>
- Fennema, O. R. (1996). Water and ice. In O. R. Fennema (Ed.), *Food chemistry* (pp 11–88). New York: Marcel Dekker Inc.
- Finley, J. W., Hurst, W. J., & Lee, C. Y. (2018). *Principles of food chemistry* (4th ed.). Switzerland: Springer.
- Forney, A. K., Halseth, D. E., & Kelly, W. C. (1990). Quality of canned 'ruddy' kidney beans as influenced by planting date, harvest time, and length of storage before canning. *Journal of the American Society for Horticultural Science*, 115(6), 1051–1054.
- Foschia, M., Horstmann, S. W., Arendt, E. K., & Zannini, E. (2017). Legumes as functional ingredients in gluten-free bakery and pasta products. *Annual Review of Food Science and Technology*, 8(1), 75–96.
- García, E., Lajolo, F. M., & Swanson, B. G. (1993). A comparative study of normal and hard-to-cook Brazilian common bean (*Phaseolus vulgaris*): Ultrastructural and histochemical aspects. *Food Structure*, 12(2), 147–154.
- García-Vela, L. A., del Valle, J. M., & Stanley, D. W. (1991). Hard-to-cook defect in black beans: The effect of soaking in various aqueous salt solutions. *Canadian Institute of Food Science and Technology Journal*, 24(1–2), 60–67.
- Ghafoor, M., Misra, N. N., Mahadevan, K., & Tiwari, B. K. (2014). Ultrasound assisted hydration of navy beans (*Phaseolus vulgaris*). *Ultrasonics Sonochemistry*, 21(1), 409–414.
- Ghasemlou, M., Gharibzadeh, S. M. T., & Emam-Djomeh, Z. (2013). Relating consumer preferences to textural attributes of cooked beans: Development of an industrial protocol and microstructural observations. *LWT - Food Science and Technology*, 50(1), 88–98.
- Ghribi, A. M., Gafsi, I. M., Sila, A., Blecker, C., Danthine, S., Attia, H., Bougatef, A., & Besbes, S. (2015). Effects of enzymatic hydrolysis on conformational and functional properties of chickpea protein isolate. *Food Chemistry*, 187, 322–330.
- Giménez, M. A., González, R. J., Wagner, J., Torres, R., Lobo, M. O., & Samman, N. C. (2013). Effect of extrusion conditions on physicochemical and sensorial properties of corn-broad beans (*Vicia faba*) spaghetti type pasta. *Food Chemistry*, 136(2), 538–545.
- Giuberti, G., Gallo, A., Cerioli, C., Fortunati, P., & Masoero, F. (2015). Cooking quality and starch digestibility of gluten free pasta using new bean flour. *Food Chemistry*, 175, 43–49.
- Glahn, R. P., Tako, E., Cichy, K., & Wiesinger, J. (2016). The cotyledon cell wall and intracellular matrix are factors that limit iron bioavailability of the common bean (*Phaseolus vulgaris*). *Food and Function*, 7(7), 3193–3200.
- Goubet, I., Le Quere, J. L., & Voilley, A. J. (1998). Retention of aroma compounds by carbohydrates: Influence of their physicochemical characteristics and of their physical state: A review. *Journal of Agricultural and Food Chemistry*, 46(5), 1981–1990.
- Guichard, E. (2002). Interactions between flavor compounds and food ingredients and their influence on flavor perception. *Food Reviews International*, 18(1), 49–70.
- Hentges, D. L., Weaver, C. M., & Nielsen, S. S. (1991). Changes of selected physical and chemical components in the development of the hard-to-cook bean defect. *Journal of Food Science*, 56(2), 436–442.
- Hincks, M. J., McCannel, A., & Stanley, D. W. (1987). Hard-to-cook defect in black beans. Soaking and cooking processes. *Journal of Agricultural and Food Chemistry*, 35(4), 576–583.
- Hincks, M. J., & Stanley, D. W. (1986). Multiple mechanisms of bean hardening. *Journal of Food Technology*, 21(6), 731–750.
- Hincks, M. J., & Stanley, D. W. (1987). Lignification: Evidence for a role in hard-to-cook beans. *Journal Food Biochemistry*, 11(1), 41–58.
- Hohlberg, A. I., & Stanley, D. W. (1987). Hard-to-cook defect in black beans. Protein and starch considerations. *Journal of Agricultural and Food Chemistry*, 35(4), 571–576.
- Hsu, K. H., Kim, C. J., & Wilson, L. A. (1983). Factors affecting water uptake of soybeans during soaking. *Cereal Chemistry*, 60(3), 208–211.
- Hughes, J. S., & Swanson, B. G. (1985). Microstructural changes in maturing seeds of the common bean (*Phaseolus vulgaris L.*). *Food Structure*, 4(2), 2.
- Hu, X. W., Wang, Y. R., Wu, Y. P., & Baskin, C. C. (2009). Role of the lens in controlling water uptake in seeds of two fabaceae (papilionoideae) species treated with sulphuric acid and hot water. *Seed Science Research*, 19(2), 73–80.
- Ibarz, A., González, C., & Barbosa-Cánovas, G. V. (2004). Kinetic models for water adsorption and cooking time in chickpea soaked and treated by high pressure. *Journal of Food Engineering*, 63(4), 467–472.
- Jackson, M. G., & Varriano-Marston, E. (1981). Hard-to-cook phenomenon in beans: Effects of accelerated storage on water absorption and cooking time. *Journal of Food Science*, 46, 799–803.
- Jaeger, H., Janositz, A., & Knorr, D. (2010). The Maillard reaction and its control during food processing. The potential of emerging technologies. *Pathologie-Biologie*, 58(3), 207–213.
- Jamdar, S. N., Deshpande, R., & Marathe, S. A. (2017). Effect of processing conditions and *in vitro* protein digestion on bioactive potentials of commonly consumed legumes. *Food Bioscience*, 20, 1–11.
- Jing, C., Wen, Z., Zou, P., Yuan, Y., Jing, W., Li, Y., & Zhang, C. (2018). Consumption of black legumes *Glycine soja* and *Glycine max* lowers serum lipids and alters the gut microbiome profile in mice fed a high-fat diet. *Journal of Agricultural and Food Chemistry*, 66(28), 7367–7375.
- Jombo, T. Z., Minnaar, A., & Taylor, J. R. N. (2018). Effects of gamma-irradiation on cotyledon cell separation and pectin solubilisation in hard-to-cook cowpeas. *Journal of the Science of Food and Agriculture*, 98(5), 1725–1733.

- Jones, P. M. B., & Boulter, D. (1983). The cause of reduced cooking rate in *Phaseolus vulgaris* following adverse storage conditions. *Journal of Food Science*, 48(2), 623–626.
- Jood, S., Bishnoi, S., & Sehgal, S. (1998). Antinutritional factors of moongbean. *Journal of Food Biochemistry*, 22, 245–257.
- Joshi, M., Adhikari, B., Panozzo, J., & Aldred, P. (2010). Water uptake and its impact on the texture of lentils (*Lens culinaris*). *Journal of Food Engineering*, 100(1), 61–69.
- Joshi, M., Aldred, P., McKnight, S., Panozzo, J. F., Kasapis, S., Adhikari, R., & Adhikari, B. (2013). Physicochemical and functional characteristics of lentil starch. *Carbohydrate Polymers*, 92(2), 1484–1496.
- Jousse, F., Jongen, T., Agterof, W., Russell, S., & Braat, P. (2002). Simplified kinetic scheme of flavor formation by the Maillard reaction. *Journal of Food Science*, 67(7), 2534–2542.
- Kapso, K. G., Njintang, Y. N., Komnek, A. E., Hounhouigan, J., Scher, J., & Mbofung, C. M. F. (2008). Physical properties and rehydration kinetics of two varieties of cowpea (*Vigna unguiculata*) and bambara groundnuts (*Voandzeia subterranea*) seeds. *Journal of Food Engineering*, 86(1), 91–99.
- Kardum, N., & Glibetic, M. (2018). Polyphenols and their interactions with other dietary compounds: Implications for human health. *Advances in Food and Nutrition Research*, 84, 103–144.
- Kaspchak, E., Mafra, L. I., & Mafra, M. R. (2018). Effect of heating and ionic strength on the interaction of bovine serum albumin and the antinutrients tannic and phytic acids, and its influence on *in vitro* protein digestibility. *Food Chemistry*, 252, 1–8.
- Kikuchi, K., Koizumi, M., Ishida, N., & Kano, H. (2006). Water uptake by dry beans observed by micro-magnetic resonance imaging. *Annals of Botany*, 98(3), 545–553.
- Kilmer, O. L., Seib, P. A., & Hosney, R. C. (1994). Effects of minerals and apparent phytase activity in the development of the hard-to-cook state of beans. *Cereal Chemistry*, 71(5), 476–482.
- Kinyanjui, P. K., Njoroge, D. M., Makokha, A. O., Christiaens, S., Ndaka, D. S., & Hendrickx, M. (2015). Hydration properties and texture fingerprints of easy- and hard-to-cook bean varieties. *Food Science & Nutrition*, 3(1), 39–47.
- Koizumi, M., Kikuchi, K., Isobe, S., Ishida, N., Naito, S., & Kano, H. (2008). Role of seed coat in imbibing soybean seeds observed by micro-magnetic resonance imaging. *Annals of Botany*, 102(3), 343–352.
- Kon, S. (1979). Effect of soaking temperature on cooking and nutritional quality of beans. *Journal of Food Science*, 44(5), 1329–1335.
- Kon, S., Brown, A. H., Ohannesson, J. G., & Booth, A. N. (1973). Split peeled beans: Preparation and some properties. *Journal of Food Science*, 38, 496–498.
- Korte, R. (1972). Heat resistance of phytohemagglutinins in weaning food mixtures containing beans (*Phaseolus vulgaris*). *Ecology of Food and Nutrition*, 1(4), 303–307.
- Laleg, K., Cassan, D., Barron, C., Prabhasankar, P., & Micard, V. (2016). Structural, culinary, nutritional and anti-nutritional properties of high protein, gluten free, 100% legume pasta. *PLoS One*, 11(9), 1–19.
- Le Meste, M., Champion, D., Roudaut, G., Blond, G., & Simato, D. (2002). Glass transition and food technology: A critical appraisal. *Journal of Food Science*, 67(7), 2444–2458.
- Lee, H., Ha, M. J., Shahbaz, H. M., Kim, J. U., Jang, H., & Park, J. (2018). High hydrostatic pressure treatment for manufacturing of red bean powder: A comparison with the thermal treatment. *Journal of Food Engineering*, 238, 141–147.
- Leopold, A. C., Sun, W. Q., & Bernal-Lugo, I. (1994). The glassy state in seeds: Analysis and function. *Seed Science Research*, 4(03), 267–274.
- Leprince, O., & Walters-Vertucci, C. (1995). A calorimetric study of the glass transition behaviors in axes of bean seeds with relevance to storage stability. *Plant Physiology*, 109(4), 1471–1481.
- Liu, K., & Bourne, M. C. (1995). Cellular, biological, and physicochemical basis for the hard-to-cook defect in legume seeds. *Critical Reviews in Food Science and Nutrition*, 35(4), 263–298.
- Liu, K., Hung, Y. C., & Phillips, R. D. (1993). Mechanisms of hard-to-cook defect in cowpeas: Verification via microstructure examination. *Food Structure*, 12(1), 51–58.
- Liu, K., McWatters, K. H., & Phillips, R. D. (1992). Protein insolubilization and thermal destabilization during storage as related to hard-to-cook defect in cowpea. *Journal of Agricultural and Food Chemistry*, 40(12), 2403–2407.
- Liu, K., Phillips, D. R., & McWatters, K. H. (1993). Induced hard-to-cook state in cowpeas by freeze-thawing and calcium chloride soaking. *AGRIS*, 70(2), 193–195.
- Liu, K., Phillips, R. D., Hung, Y., Shewfelt, R. L., & McWatters, K. H. (1992). Hard-to-cook defect in cowpeas: Storage-induced development. *Journal of Food Science*, 57(5), 1155–1160.
- López-Martínez, L. X., Leyva-López, N., Gutiérrez-Grijalva, E. P., & Heredia, J. B. (2017). Effect of cooking and germination on bioactive compounds in pulses and their health benefits. *Journal of Functional Foods*, 38, 624–634.
- Lovegren, N. V., Fisher, G. S., Legendre, M. G., & Schuller, W. H., 1979. Volatile constituents of dried legumes. *Journal of Agricultural and Food Chemistry*, 27(4), 851–853.
- Luna-Vital, D. A., Mojica, L., González de Mejía, E., Mendoza, S., & Loarca-Piña, G. (2015). Biological potential of protein hydrolysates and peptides from common bean (*Phaseolus vulgaris* L.): A review. *Food Research International*, 76(P1), 39–50.
- Ma, F., Cholewa, E., Mohamed, T., Peterson, C. A., & Gijzen, M. (2004). Cracks in the palisade cuticle of soybean seed coats correlate with their permeability to water. *Annals of Botany*, 94(2), 213–228.
- Ma, M., Wang, Y., Wang, M., Jane, J., & Du, S. (2017). Physicochemical properties and *in vitro* digestibility of legume starches. *Food Hydrocolloids*, 63, 249–255.
- Ma, Z., Boye, J. I., Azarnia, S., & Simpson, B. K. (2016). Volatile flavor profile of Saskatchewan grown pulses as affected by different thermal processing treatments. *International Journal of Food Properties*, 19(10), 2251–2271.
- Machado, C. M., Ferruzzi, M. G., & Nielsen, S. S. (2008). Impact of the hard-to-cook phenomenon on phenolic antioxidants in dry beans (*Phaseolus vulgaris*). *Journal of Agricultural and Food Chemistry*, 56(9), 3102–3110.
- Malcolmson, L., Frohlich, P., Boux, G., Bellido, A.-S., Boye, J., & Warkentin, T. D. (2014). Aroma and flavour properties of Saskatchewan grown field peas (*Pisum sativum* L.). *Canadian Journal of Plant Science*, 94(8), 1419–1426.
- Marteau, C., Ruyffelaere, F., Aubry, J. M., Penverne, C., Favier, D., & Nardello-Rataj, V. (2013). Oxidative degradation of fragrant aldehydes. Autoxidation by molecular oxygen. *Tetrahedron*, 69(10), 2268–2275.
- Martin-Cabrejas, M. A., Esteban, R. M., Perez, P., Maina, G., & Waldron, K. W. (1997). Changes in physicochemical properties of dry beans (*Phaseolus vulgaris* L.) during long-term storage. *Journal of Agricultural and Food Chemistry*, 45(8), 3223–3227.
- Martin-Cabrejas, M. A., Jaime, L., Karanja, C., Downie, A. J., Parker, M. L., Lopez-Andreu, F. J., Maina, G., Esteban, R. M., Smith, A. C., & Waldron, K. W. (1999). Modifications to physicochemical and nutritional properties of hard-to-cook beans (*Phaseolus vulgaris* L.) by extrusion cooking. *Journal of Agricultural and Food Chemistry*, 47(3), 1174–1182.
- McCollum, J. P. (1952). Factors affecting cotyledonal cracking during the germination of beans (*Phaseolus vulgaris*). *Plant Physiology*, 28(2), 267–274.
- McDonald, M. B., Vertucci, C. W., & Roos, E. E. (1988). Seed coat regulation of soybean seed imbibition. *Crop Science*, 28(6), 987–992.
- Mendoza, F. A., Kelly, J. D., & Cichy, K. A. (2017). Automated prediction of sensory scores for color and appearance in canned black beans (*Phaseolus vulgaris* L.) using machine vision. *International Journal of Food Properties*, 20(1), 83–99.
- Mikac, U., Sepe, A., & Serša, I. (2015). MR microscopy for noninvasive detection of water distribution during soaking and cooking in the common bean. *Magnetic Resonance Imaging*, 33(3), 336–345.
- Minka, S. R., Mbofung, C. M., Gandon, C., & Bruneteau, M. (1999). The effect of cooking with kanwa alkaline salt on the chemical composition of black beans (*Phaseolus vulgaris*). *Food Chemistry*, 64(2), 145–148.
- Mishra, P. K., Tripathi, J., Gupta, S., & Variyar, P. S. (2017). Effect of cooking on aroma profile of red kidney beans (*Phaseolus vulgaris*) and correlation with sensory quality. *Food Chemistry*, 215, 401–409.
- Mkanda, A. V., Minnaar, A., & de Kock, H. L. (2007). Relating consumer preferences to sensory and physicochemical properties of dry beans (*Phaseolus vulgaris*). *Journal of the Science of Food and Agriculture*, 87(15), 2868–2879.
- Molina, M. R., Baten, M. A., Gomez-Brenes, R. A., King, K. W., & Bressani, R. (1976). Heat treatment: A process to control the development of the hard-to-cook phenomenon in black beans (*Phaseolus vulgaris*). *Journal of Food Science*, 41(3), 661–666.
- Murthy, U. M. N., Kumar, P. P., & Sun, W. Q. (2003). Mechanisms of seed ageing under different storage conditions for *Vigna radiata* (L.) Wilczek: Lipid peroxidation, sugar hydrolysis, Maillard reactions and their relationship to glass state transition. *Journal of Experimental Botany*, 54(384), 1057–1067.
- Murthy, U. M., & Sun, W. Q. (2000). Protein modification by Amadori and Maillard reactions during seed storage: Roles of sugar hydrolysis and lipid peroxidation. *Journal of Experimental Botany*, 51(348), 1221–1228.

- Naviglio, D., Formato, A., Pucillo, G. P., & Gallo, M. (2013). A cyclically pressurised soaking process for the hydration and aromatisation of cannellini beans. *Journal of Food Engineering*, 116(3), 765–774.
- Ndungu, K. E., Emmambux, M. N., & Minnaar, A. (2012). Micronisation and hot air roasting of cowpeas as pretreatments to control the development of hard-to-cook phenomenon. *Journal of the Science of Food and Agriculture*, 92(6), 1194–1200.
- Nielsen, J. M. (1999). East African Magadi (*trona*): Fluoride concentration and mineralogical composition. *Journal of African Earth Sciences*, 29(2), 423–428.
- Njoroge, D. M., Kinyanjui, P. K., Chigwedere, C. M., Christiaens, S., Makokha, A. O., Sila, D. N., & Hendrickx, M. E. (2016). Mechanistic insight into common bean pectic polysaccharide changes during storage, soaking and thermal treatment in relation to the hard-to-cook defect. *Food Research International*, 81, 39–49.
- Njoroge, D. M., Kinyanjui, P. K., Christiaens, S., Shpigelman, A., Makokha, A. O., Sila, D. N., & Hendrickx, M. E. (2015). Effect of storage conditions on pectic polysaccharides in common beans (*Phaseolus vulgaris*) in relation to the hard-to-cook defect. *Food Research International*, 76, 105–113.
- Nosworthy, M. G., Franczyk, A. J., Medina, G., Neufeld, J., Appah, P., Utioh, A., Frohlich, P., & House, J. D. (2018). Effect of processing on the *in vitro* and *in vivo* protein quality of yellow and green split peas (*Pisum sativum*). *Journal of Agricultural and Food Chemistry*, 65(35), 7790–7796.
- Nozzolillo, C., & Bezada, M. D. (1984). Browning of lentil seeds, concomitant loss of viability, and the possible role of soluble tannins in both phenomena. *Canadian Journal of Plant Science*, 64(4), 815–824.
- Nyakuni, G. A., Kikafunda, J. K., Muyonga, J. H., Kyamuhangire, W. M., Nakimbugwe, D., & Ugen, M. (2008). Chemical and nutritional changes associated with the development of the hard-to-cook defect in common beans. *International Journal of Food Sciences and Nutrition*, 59(7–8), 652–659.
- Oatway, L., Vasanthan, T., & Helm, J. H. (2001). Phytic acid. *Food Reviews International*, 17(4), 419–431.
- Offer, C. E., & Patrick, J. W. (1984). Cellular structures, plasma membrane surface areas and plasmodesmatal frequencies of seed coats of *Phaseolus vulgaris* L. in relation to photosynthate transfer. *Functional Plant Biology*, 11(2), 79–99.
- Oliveira, A. L., Colnaghi, B. G., Silva, E. Z. Da, Gouvêa, I. R., Vieira, R. L., & Augusto, P. E. D. (2013). Modelling the effect of temperature on the hydration kinetic of adzuki beans (*Vigna angularis*). *Journal of Food Engineering*, 118(4), 417–420.
- Oomah, B. D., Liang, L. S. Y., & Balasubramanian, P. (2007). Volatile compounds of dry beans (*Phaseolus vulgaris* L.). *Plant Foods for Human Nutrition*, 62(4), 177–183.
- Padhi, E. M. T., & Ramdath, D. D. (2017). A review of the relationship between pulse consumption and reduction of cardiovascular disease risk factors. *Journal of Functional Foods*, 38, 635–643.
- Pallares, Pallares, A., Rousseau, S., Chigwedere, C. M., Kyomugasho, C., Hendrickx, M., & Grauwet, T. (2018). Temperature–pressure–time combinations for the generation of common bean microstructures with different starch susceptibilities to hydrolysis. *Food Research International*, 106, 105–115.
- Pan, Z., Atungulu, G. G., Wei, L., & Haff, R. (2010). Development of impact acoustic detection and density separations methods for production of high quality processed beans. *Journal of Food Engineering*, 97(3), 292–300.
- Paredes-López, O., Carabez-Trejo, A., Palma-Tirado, L., & Reyes-Moreno, C. (1991). Influence of hardening procedure and soaking solution on cooking quality of common beans. *Plant Foods for Human Nutrition*, 41(2), 155–164.
- Paredes-Lopez, O., Reyes-Moreno, C., Montes-Rivera, R., & Carabez-Trejo, A. (1989). Hard-to-cook phenomenon in common beans: Influence of growing location and hardening procedures. *International Journal of Food Science and Technology*, 24(5), 535–542.
- Parrish, D. J., & Leopold, A. C. (1977). Transient changes during soybean imbibition. *Plant Physiology*, 59(6), 1111–1115.
- Parrish, D. J., & Leopold, A. C. (1978). On the mechanism of aging in soybean seeds. *Plant Physiology*, 61(3), 365–368.
- Pauling, L., Corey, R. B., & Branson, H. R. (1951). The structure of proteins: Two hydrogen-bonded helical configurations of the polypeptide chain. *Proceedings of the National Academy of Sciences*, 37(4), 205–211.
- Pedrosa, M. M., Cuadrado, C., Burbano, C., Muzquiz, M., Cabellos, B., Olmedilla-Alonso, B., & Asensio-Vegas, C. (2015). Effects of industrial canning on the proximate composition, bioactive compounds contents and nutritional profile of two Spanish common dry beans (*Phaseolus vulgaris* L.). *Food Chemistry*, 166, 68–75.
- Piergiovanni, A. R. (2011). Kinetic of water adsorption in common bean: Considerations on the suitability of Peleg's model for describing bean hydration. *Journal of Food Processing and Preservation*, 35(4), 447–452.
- Pirhayati, M., Soltanizadeh, N., & Kadivar, M. (2011). Chemical and microstructural evaluation of “hard-to-cook” phenomenon in legumes (pinto bean and small-type lentil). *International Journal of Food Science and Technology*, 46(9), 1884–1890.
- Plhak, L. C., Caldwell, K. B., & Stanley, D. W. (1989). Comparison of methods used to characterize water imbibition in hard-to-cook beans. *Journal of Food Science*, 54(2), 326–329.
- Plhak, L. C., Stanley, D. W., Hohlberg, A. I., & Aguilera, J. M. (1987). Hard-to-cook defect in black beans—Effect of pretreatment and storage condition on extractable phenols and peroxidase activity. *Canadian Institute of Food Science and Technology*, 20(5), 378–382.
- Pokorný, J., & Korczak, J. (2001). Preparation of natural antioxidants. *Antioxidants in Food*, 311–330. <https://doi.org/10.1533/9781855736160.4311>.
- Ramdath, D., Renwick, S., & Duncan, A. M. (2016). The role of pulses in the dietary management of diabetes. *Canadian Journal of Diabetes*, 40(4), 355–363.
- Rehman, Z., Salariya, A. M., & Zafar, S. I. (2001). Effect of processing on available carbohydrate content and starch digestibility of kidney beans (*Phaseolus vulgaris* L.). *Food Chemistry*, 73(3), 351–355.
- Reyes-Moreno, C., Okamura-Esparza, J., Armienta-Rodelo, E., Gomez-Garza, R. M., & Milan-Carrillo, J. (2000). Hard-to-cook phenomenon in chickpeas (*Cicer arietinum* L.): Effect of accelerated storage on quality. *Plant Foods for Human Nutrition*, 55(3), 229–241.
- Reyes-Moreno, C., Paredes-López, O., & Gonzalez, E. (1993). Hard-to-cook phenomenon in common beans—A review. *Critical Reviews in Food Science and Nutrition*, 33(3), 227–286.
- Richardson, J. C., & Stanley, D. W. (1991). Relationship of loss of membrane functionality and hard-to-cook defect in aged beans. *Journal of Food Science*, 56(2), 590–591.
- Rivera, J. A., Hohlberg, A. I., Aguilera, J. M., Plhak, L. C., & Stanley, D. W. (1989). Hard-to-cook defect in black beans—peroxidase characterization and effect of heat pretreatment and storage conditions on enzyme inactivation. *Canadian Institute of Food Science and Technology Journal*, 22(3), 270–275.
- Rodhouse, J. C., Haugh, C. A., Roberts, D., & Gilbert, R. J. (1990). Red kidney bean poisoning in the UK: An analysis of 50 suspected incidents between 1976 and 1989. *Epidemiology & Infection*, 105(3), 485–491.
- Roos, Y. H. (2010). Glass transition temperature and its relevance in food processing. *Annual Review of Food Science and Technology*, 1, 469–496.
- Rosa-Sibakov, N., Heiniö, R. L., Cassan, D., Holopainen-Mantila, U., Micard, V., Lantto, R., & Sozer, N. (2016). Effect of bioprocessing and fractionation on the structural, textural and sensory properties of gluten-free faba bean pasta. *LWT - Food Science and Technology*, 67, 27–36.
- Ross, K. A., Arntfield, S. D., Beta, T., Cenkowski, S., Fulcher, R. G., Arntfield, S. D., & Cenkowski, S. (2008). Understanding and modifying water uptake of seed coats through characterizing the glass transition. *International Journal of Food Properties*, 11(3), 544–560.
- Ross, K. A., Arntfield, S. D., & Cenkowski, S. (2013). A polymer science approach to physico-chemical characterization and processing of pulse seeds. *Polymer Science*. <https://doi.org/10.5772/46145>.
- Ross, K. A., Zhang, L., & Arntfield, S. D. (2010). Understanding water uptake from the induced changes occurred during processing: Chemistry of pinto and navy bean seed coats. *International Journal of Food Properties*, 13(3), 631–647.
- Rovalino-Córdova, A. M., Fogliano, V., & Capuano, E. (2018). A closer look to cell structural barriers affecting starch digestibility in beans. *Carbohydrate Polymers*, 181, 994–1002.
- Ruini, L. F., Ciati, R., Pratesi, C. A., Marino, M., Principato, L., & Vannuzzi, E. (2015). Working toward healthy and sustainable diets: The “Double Pyramid Model” developed by the Barilla Center for Food and Nutrition to raise awareness about the environmental and nutritional impact of foods. *Frontiers in Nutrition*, 2, 9. <https://doi.org/10.3389/fnut.2015.00009>
- Sablani, S. S., Kasapis, S., & Rahman, M. S. (2007). Evaluating water activity and glass transition concepts for food stability. *Journal of Food Engineering*, 78(1), 266–271.
- Salas, J. J., García-González, D. L., & Aparicio, R. (2006). Volatile compound biosynthesis by green leaves from an *Arabidopsis thaliana* hydroperoxidase lyase knockout mutant. *Journal of Agricultural and Food Chemistry*, 54(21), 8199–8205.

- Schoeninger, V., Coelho, S. R. M., Christ, D., & Sampaio, S. C. (2014). Processing parameter optimization for obtaining dry beans with reduced cooking time. *LWT - Food Science and Technology*, *56*(1), 49–57.
- Sefa-Dedeh, S., & Stanley, D. W. (1979). The relationship of microstructure of cowpeas to water absorption and dehulling properties. *Cereal Chemistry*, *56*(4), 379–386.
- Shao, S., Meyer, C. J., Ma, F., Peterson, C. A. & Bernards, M. A. (2007). The outermost cuticle of soybean seeds: Chemical composition and function during imbibition. *Journal of Experimental Botany*, *58*(5), 1071–1082.
- Sheldrick, G. M., Goddard, R. and Kruger, C. (1985). *Crystallographic computing 3: data collection, structure determination, proteins and databases*. Oxford: Oxford University Press.
- Shi, L., Arntfield, S. D., & Nickerson, M. (2018). Changes in levels of phytic acid, lectins and oxalates during soaking and cooking of Canadian pulses. *Food Research International*, *107*, 660–668.
- Siddiq, M., & Uebersax, M. A. (2012). *Dry beans and pulses production, processing and nutrition* (Vol. 1). Hoboken, NJ: John Wiley and Sons.
- Simon, E. W. (1974). Phospholipids and plant membrane permeability. *New Phytologist*, *73*(3), 377–420.
- Simons, C. W., & Hall, C. (2018). Consumer acceptability of gluten-free cookies containing raw cooked and germinated pinto bean flours. *Food Science and Nutrition*, *6*(1), 77–84.
- Siva, N., Thavarajah, P., & Thavarajah, D. (2018). The impact of processing and cooking on prebiotic carbohydrates in lentil. *Journal of Food Composition and Analysis*, *70*, 72–77.
- Smykal, P., Vernoud, V., Blair, M. W., Soukup, A., & Thompson, R. D. (2014). The role of the testa during development and in establishment of dormancy of the legume seed. *Frontiers in Plant Science*, *5*, 1–19.
- Srisuma, N., Hammerschmidt, R., Uebersax, M. A., Ruengsakulrach, S., Bennink, M. R., & Hosfield, G. L. (1989). Storage induced changes of phenolic acids and the development of hard-to-cook in dry beans (*Phaseolus vulgaris*, var *Seafarer*). *Journal of Food Science*, *54*(2), 311–314.
- Stanley, D. W. (1992). A possible role for condensed tannins in bean hardening. *Food Research International*, *25*(3), 187–192.
- Stevenson, R. J., & Chen, X. D. (1996). A study of volatile “trapping” in spray dried whey protein concentrate by “crushing” and/or vacuuming, and detection by solid-phase microextraction gas chromatography mass spectrometry. *Food Research International*, *29*(5–6), 495–504.
- Sun, W. (1997). Glassy state and seed storage stability: The WLF kinetics of seed viability loss at $T > T_g$ and the plasticization effect of water on storage stability. *Annals of Botany*, *79*(3), 291–297.
- Sun, W. Q., & Leopold, A. C. (1993). The glassy state and accelerated aging of soybeans. *Physiologia Plantarum*, *89*(4), 767–774.
- Taiwo, K. A., & Akanbi, O. C. (1997). The effects of soaking and cooking time on the cooking properties of two cowpea varieties. *Journal of Food Engineering*, *33*(97), 337–346.
- Tang, J., Sokhansanj, S., & Sosulski, F. (1994). Moisture absorption characteristics of Laird lentils and hardshell seeds. *Cereal Chemistry*, *71*(5), 423–427.
- Thomas, R., de Man, J. M., & de Man, L. (1989). Soymilk and tofu properties as influenced by soybean storage conditions. *Journal of the American Oil Chemists Society*, *66*(6), 777–782.
- Torres, J., Rutherford, S. M., Muñoz, L. S., Peters, M., & Montoya, C. A. (2016). The impact of heating and soaking on the *in vitro* enzymatic hydrolysis of protein varies in different species of tropical legumes. *Food Chemistry*, *194*, 377–382.
- van Ruth, S. M. (2001). Methods for gas chromatography-olfactometry: A review. *Biomolecular Engineering*, *17*(4–5), 121–128.
- van Ruth, S. M., Dings, L., Aprea, E., & Otake, S. (2005). Comparison of volatile flavour profiles of kidney beans and soybeans by GC-MS and PTR-MS. *Food Science and Technology*, *11*, 63–70.
- van Ruth, S. M., Dings, L., Buhr, K., & Posthumus, M. A. (2004). *In vitro* and *in vivo* volatile flavour analysis of red kidney beans by proton transfer reaction-mass spectrometry. *Food Research International*, *37*(8), 785–791.
- Vance, C. P., Kirk, T. K., & Sherwood, R. T. (1980). Lignification as a mechanism of disease resistance. *Annual Review of Phytopathology*, *18*(1), 259–288.
- Varriano-Marston, E., & Jackson, G. M. (1981). Hard-to-cook phenomenon in beans: Structural changes during storage and imbibition. *Journal of Food Science*, *46*(5), 1379–1385.
- Varriano-Marston, E., & Omana, E. (1979). Effects of sodium salt solutions on the chemical composition and morphology of black beans (*Phaseolus vulgaris*). *Journal of Food Science*, *44*(2), 531–536.
- Vertucci, C. W., & Farrant, J. M. (1995). Acquisition and loss of desiccation tolerance. In J. Kigel & G. Galili (Eds.), *Seed development and germination* (pp. 237–271). New York, NY: Marcel Dekker Inc.
- Vindiola, O. L., Seib, P. A., & Hosney, R. C. (1986). Accelerated development of the hard-to-cook state in beans. *Cereal Foods World*, *31*, 538–552.
- Voragen, A. G. J., Coenen, G.-J., Verhoef, R. P., & Schols, H. A. (2009). Pectin, a versatile polysaccharide present in plant cell walls. *Structural Chemistry*, *20*(2), 263–275.
- Walters, C. (1998). Understanding the mechanisms and kinetics of seed aging. *Seed Science Research*, *8*(2), 223–244.
- Walters, C. (2004). Temperature dependency of molecular mobility in preserved seeds. *Biophysical Journal*, *86*(2), 1253–1258.
- Walters, C., Hill, L. M., & Wheeler, L. J. (2005). Dying while dry: Kinetics and mechanisms of deterioration in desiccated organisms. *Integrative and Comparative Biology*, *45*(5), 751–758.
- Williams, R. J. (1994). Methods for determination of glass transitions in seeds. *Annals of Botany*, *74*(5), 525–530.
- Worku, A., & Sahu, O. (2017). Significance of fermentation process on biochemical properties of *Phaseolus vulgaris* (red beans). *Biotechnology Reports*, *16*(August), 5–11.
- Wu, S., Feng, S., & Kojima, M. (2015). Effects of different storage on qualities of adzuki and red kidney beans. *Journal of Food Research*, *4*(3), 103–117.
- Yaylayan, V. A. (2003). Recent Advances in the chemistry of strecker degradation and amadori rearrangement: Implications to aroma and color formation. *Food Science and Technology Research*, *9*(1), 1–6.
- Yi, J., Njoroge, D. M., Sila, D. N., Kinyanjui, P. K., Christiaens, S., Bi, J., & Hendrickx, M. E. (2016). Detailed analysis of seed coat and cotyledon reveals molecular understanding of the hard-to-cook defect of common beans (*Phaseolus vulgaris* L.). *Food Chemistry*, *210*, 481–490.
- Yin, X., Ma, Z., Hu, X., Li, X., & Boye, J. I. (2018). Molecular rearrangement of Laird lentil (*Lens culinaris Medikus*) starch during different processing treatments of the seeds. *Food Hydrocolloids*, *79*, 399–408.
- Zamora, R., Gallardo, E., & Hidalgo, F. J. (2007). Strecker degradation of phenylalanine initiated by 2,4-decadienal or methyl 13-oxooctadeca-9,11-dienoate in model systems. *Journal of Agricultural and Food Chemistry*, *55*(4), 1308–1314.
- Zamora, R., Gallardo, E., & Hidalgo, F. J. (2008). Model studies on the degradation of phenylalanine initiated by lipid hydroperoxides and their secondary and tertiary oxidation products. *Journal of Agricultural and Food Chemistry*, *56*(17), 7970–7975.
- Zanella-Díaz, E., Mújica-Paz, H., Soto-Caballero, M. C., Welti-Chanes, J., & Valdez-Fragoso, A. (2014). Quick hydration of tepary (*Phaseolus acutifolius* A. Gray) and pinto beans (*Phaseolus vulgaris* L.) driven by pressure gradients. *LWT - Food Science and Technology*, *59*(2), 800–805.
- Zhang, L., & McCarthy, M. J. (2013). NMR study of hydration of navy bean during cooking. *LWT - Food Science and Technology*, *53*(2), 402–408.
- Zhao, B., & Chang, K. C. (2008). Evaluation of effects of soaking and precooking conditions on the quality of precooked dehydrated pea, lentil and chickpea products. *Journal of Food Processing and Preservation*, *32*(3), 517–532.