

Chapter 2

Technologies for Improving the Nutritional Quality of Cereals



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2.1 Introduction

Plants are the major source of human diet with over 50,000 edible plants available worldwide. Among them, rice, maize, and wheat alone provide 60% of the world's food energy intake. Cereals are the most dominant staple foods (51%) of the world average diet, followed by animal-based foods (meat, fish, milk, and egg) (13.5%), fruits and vegetables, pulses and nuts (8.2%), and roots and tubers (5.3%) [1]. Grains and pulses have traditionally been considered “poor people’s foods”; however as their nutritional values continue to be revealed, whole foods and functional foods based on these are becoming increasingly popular.

Cereals and other grains not only provide substantial macronutrients, i.e., protein, lipids, and carbohydrate, but also many essential vitamins, minerals, and phytochemicals. Dietary fibers and phytochemical antioxidants, especially insoluble fibers and bound phenolics and their roles in human health, particularly intestinal health, have been an emerging area of research [2–4]. Cereals are consumed in prepared forms. Processing of cereals mainly include primary processing such as dehulling or debranning and milling followed by secondary treatments such as various cooking processes. Cereal grains are also consumed in sprout form or in fermented forms. These processes impart special characteristics to the physical and physiochemical qualities and alter nutritional and organoleptic properties of the original cereal grains.

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Impact of cereal processing technologies may be beneficial to human health as they can help remove toxins such as mycotoxins and anti-nutritive factors such as enzyme inhibitors and phytic acid and certain types of saponins, although it may also result in lowered nutritional quality as many nutrients may be lost during physical fractionation or heating. However, when used properly, many of the postprimary processing technologies can be used to improve the overall nutritional quality by minimizing the loss, enriching the nutrient content, and enhancing the digestibility and bioavailability of various nutrients, thus ultimately maximizing the health benefits. Current consumer perception on food nutritional quality is no longer limited to the conventional sense of nutritional value but has shifted to functional foods, i.e., foods that are demonstrated to have physiological benefits and/or reduce the risk of chronic disease beyond basic nutritional functions [5]. Many food bioactives, including phenolic compounds and carotenoids, play a vital role in reducing risk of chronic and degenerative diseases, especially those related to oxidative stress [4, 6, 7]. Processing method can significantly affect the retainment of composition of food bioactives and consequently the health beneficial effects such as antioxidant and anti-inflammatory activities [8]. This chapter is intended to give an overview of recent advances in cereal processing technologies that help improve nutritional quality of cereals. Conventional cooking by boiling, steaming, and roasting will not be covered in this review, and the focus will be on selected thermal (extrusion cooking, high pressure processing, microwave processing) and nonthermal processing technologies (milling, germination, fermentation, and enzymatic processing). Also mainly micronutrients and phytochemicals will be discussed.

2.2 Extrusion Cooking

All thermal processing technologies are theoretically deleterious when micronutrients are considered. Micronutrients other than the minerals go through chemical reactions thus are likely destroyed or degraded upon heating. Extrusion cooking is one of the most important and perhaps most widely used food processing technologies since the mid-1930s for a variety of foods, especially in the past two decades [9]. Although extrusion cooking have been used to produce foods with diverse textural properties, only in recent years, efforts have been made to improve the nutritional quality such as digestibility and nutrient bioavailability using this technology over conventional cooking methods [10, 11]. Effects of extrusion on food components and nutritional quality depend on different processing parameters including screw speed, die diameter, feed speed, and feed moisture content.

The overall effect on the nutritional quality and health outcome may also depend on the nutrients and bioactives in the feed, and research thus far have shown varied results. Extrusion may cause chemical and physicochemical changes of macronutrients like carbohydrates, protein, and lipids, thus affecting their digestibility and bioavailability. Extrusion changed starch components of barley and oats in solubility of dietary fiber and enhanced functional properties of cereal products [12–14]. The same may happen to micronutrients, e.g., vitamins, phytochemical antioxidants

such as phenolics, carotenoids, and other food bioactives [9, 15, 16]. The effect of extrusion cooking on the bioaccessibility and bioavailability is a dichotomous thermal process which causes bioactive compounds such as phenolics and vitamins to decompose, while the heat also leads to improved release of compounds as a result of disruption of the cell wall matrices and cleavage of certain covalent bonds [17].

Extrusion generally reduces total phenolic content (TPC) of cereals and grains; however, other than the parameters of the extrusion process, a major factor that affects the bioactive compounds of cereals is the type of grain and its cultivar. For example, Alexa et al. [18] found that the degree of reduction of TPC was much significant in dark red bean compared to that in navy bean. Similar result was found in a recent study on brown rice. Extrusion cooking was found to increase the free TPC, total flavonoid content (TFC), and antioxidant activities as measured by ferric reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC) assays, but not the bound phenolics and antioxidant activity [16]. However, closer examination of the profile of individual phenolic acids showed that although the seven phenolic acids (ferulic, vanillic, *p*-coumaric, chlorogenic, gallic, caffeic, and syringic acids) detected were affected differently, no significant effects were found in their composition. Vanillic acid in bound form was the only phenolic acid found to be increased significantly after extrusion cooling [16]. Other studies have shown different results. A recent study on the impact of extrusion on the phenolic profile and bioaccessibility of cereals (wheat, oat, and brown rice) showed that total free phenolic acids of brown rice and wheat were drastically decreased by 5.88% and 45.66%, respectively, whereas the total bound phenolic acids of all cereal grains were significantly increased by 6–9% [15]. The effect of extrusion also had different impact on the bioaccessibility of phenolics and antioxidant activity. Extrusion significantly decreased the bioaccessible phenolics of brown rice and oat by 31.09% and 30.95%, but it had minimal effect on those of wheat [15]. The differences observed may be due to the different matrix, especially protein structures of the cereals, as extrusion causes denaturation of grain proteins and alters or promotes tannin-protein interaction causing the formation of tannin-protein complexes which also affects the bioaccessibility and antioxidant activity [9]. Extrusion cooking of grit from different hulled barley led to a significant decrease in TPC and TFC which was dependent on both the feed moisture and extrusion temperature. However the antioxidant activity increased significantly upon extrusion, which may be caused from Maillard products, although the authors did not specifically pointed out [19].

Vitamins are even more severely affected during extrusion. Fat-soluble vitamins, such as vitamin A, including the provitamin A (e.g., β -carotene) and vitamin E, and the water-soluble vitamins such as vitamin C, B1, and folic acid have been most sensitive to extrusion cooking. Vitamins of the B group, such as B2, B6, B12, niacin, Ca-pantothenate, and biotin, are relatively stable during extrusion [20]. Oxidation occurred to the vitamins, phenolics, and carotenoids during extrusion cooking may be prevented or reduced by adding natural antioxidants such as ferulic acid and benzoin to the feed of cereal foods [21]. TPC, gamma-aminobutyric acid (GABA), and the antioxidant activity were significantly lower in extruded germinated brown rice (GBR) than those in un-extruded GBR [22].

2.3 High Pressure Processing

High pressure processing (HPP) or high hydrostatic pressure (HHP) processing is a nonthermal method that cooks food under very high pressure (5–1000 MPa) [23]. HPP inactivates certain microorganisms and enzymes and thus is mostly used as an alternative to pasteurization that leads to improved shelf life and increased microbial safety and quality of foods. The effect of HPP on the nutritional quality of cereal foods is also mainly on macronutrients, especially proteins as HPP has a limited effect on covalent bonds within foods or beverages. It has been found to affect the secondary structures which may help improve digestibility [24]. For this reason, the overwhelming majority of the literature on HPP and its effect on food nutritional quality was on perishable foods or their derivatives, and there was no reported studies on HHP and its effect on micronutrients in cereal grains before 2005 [23–25], and this situation has not changed since [26–29]. In terms of the impact of HPP treatment on food quality, more significant effect was found in color, flavor, texture, and sensory properties of fruit- and vegetable-based foods [30].

In a most recent review on using HPP to improve health and safety attributes of foods, Barba et al. [27] gave an overview of the latest findings and stated that HPP has emerged as a novel processing technology for food microbial safety and for foods with improved quality characteristics such as enhanced flavor and color. While a variety of foods including fruits, vegetables, dairy, and meat products have been studied and the effect of HPP on different micronutrients in those foods were discussed, none were related to cereals. In terms of micronutrients such as polyphenols, carotenoids, glucosinolates, and other phytonutrients, HPP is found to improve the extraction yield or recovery rate of these compounds from fruits and vegetables. Among the very limited studies on cereals, a recent study on rice showed that HPP improved grain shape, adhesiveness, cohesiveness, texture, and overall quality of rice, but its effect on nutritional quality was not studied. Moreover, despite the “encouraging potential to manipulate the functionality, extractability, allergenicity and bioavailability of micronutrients and components in a diverse variety of foods” of HPP, the authors concluded that more studies are needed to better understand the impacts of HPP on different bioactive compounds in food products with health benefits [31]. A study on HPP extract of buckwheat showed increased antioxidant activity, and the authors implied that the effect might be associated with the release of bound phenolic compounds, which was not verified [32].

2.4 Microwave Processing

Microwave processing is relatively mature thermal processing technology that is with high thermal efficiency, shorter processing time, reduced operational cost, and improved product quality [33]. It has many applications in both domestic and industrial food preparation. Microwave efficiently generates heat which is applied in drying, pasteurization, sterilization, thawing, tempering, and baking of fruits,

vegetables, meat, and fish products [34, 35]. Owing to the high temperature it generates, microwave heating has been found to not only alter the texture and color of foods but also change flavor and nutritional qualities of foods in a similar manner as conventional and other novel thermal processing technologies, although to a lesser extent because of significantly shorter time of exposure [34, 36]. Microwave cooking was more efficient than conventional boiling in starch release thus higher glycemic index [37], in terms of micronutrients, like other thermal processing techniques; microwave cooking is also a dichotomous process: on one hand, it helps the release of bioactive components by effectively disrupting the cell wall, and on the other hand, the heat also causes thermal decomposition of these compounds. In terms of food micronutrients, one of the main applications of microwave processing is the microwave-assistant extraction or its variations such as combination with ultrasonication, ohmic heating, electron irradiation, infrared heating, and vacuum processing [38]. Again, applications on cereals are less studied [34, 35]. Microwave cooking was more effective in preventing the loss of flavonoids of buckwheat groats than conventional cooking (boiling) [39]. Baba et al. studied the effect of microwave roasting on antioxidant and antiproliferative activities of barley flour and found although roasting reduced significantly the TPC, the bioactivities were dose-dependent and significant [40]. Microwave cooking of barley significantly reduced TPC and TFC and antioxidant activity, greater effects on nonenzymatic browning, polyphenol oxidase (PPO) activity, compared to sand roasting [41]. The effects of domestic processing with dry heat including microwave heat were examined against wet heat on sorghum and found microwave heating significantly increased TPC and individual phenolic compounds, total vitamin E content, and individual tocopherol and tocotrienol concentrations and antioxidant activity. Lutein and zeaxanthin content was slightly reduced by microwave cooking [42].

2.5 Milling

Milling and grinding is a processing technology that renders grains into finer primary fractions for secondary processing. Milling removes the endosperm (starch components) of the seeds from the pericarp, testa, and aleurone layers. There are two types of milling, wet milling and dry milling. Dry milling separates the kernel or grain into anatomical parts or fractions (endosperm, bran, and germ), whereas wet milling separates the grain constituents into different fractions, i.e., protein, starch, fiber, and oil [43]. Milling can significantly influence the nutritional quality of cereals as the nutrients are contained in different fractions. A large amount of bran is generated during milling of cereal grains, which in most cases is considered a processing by-product with low value. However, cereal bran has been found to contain most of the nutrients of the grain and is a great source of dietary fiber and micronutrients such as vitamins, minerals, and phytochemicals, especially various phenolic compounds [44, 45]. Retainment of these nutrients is therefore largely dependent on the milling conditions. The milling process imparts unique

characteristics and enhances organoleptic properties to the cereals; however it also changes the quantity and quality of nutrients and the physicochemical properties of the components, resulting in either improved or reduced nutritional quality. Optimizing milling conditions can therefore help in minimizing the loss of the nutrients and maximizing removal of antinutrients and toxins such as mycotoxins.

Milling is also a refining process which leads to reduced nutrients of cereals. Dietary fiber and micronutrients are significantly lower in refined wheat flour compared to the whole flour. Fractionation of the whole flour into different particle sizes also affects the content and digestibility, bioaccessibility, and bioavailability of both micro- and macronutrients [46]. Milling mechanically breaks down the cell wall of the cereal grains and thus improves the bioaccessibility for nutrients of the bran to the digestive enzymes, resulting in enhanced nutrient bioavailability the increased release of nutrients bound to the cell wall matrix [46, 47]. Extractable TPC and antioxidant activity were found to be increased when the insoluble dietary fiber of wheat bran was reduced to submicron size [48]. Grinding of wheat bran significantly increased TPC, TFC, and carotenoid content and antioxidant activity [49, 50]. Similar results were found in buckwheat hulls [51]. A recent study showed that both extractable and bound TPC, TFC, and antioxidant activity of superfine rice bran fiber fractions were significantly higher in finer powders [52].

2.6 Germination

Cereal grains and legume seeds are known to contain a plethora of phytochemicals that can act as antioxidant and anti-inflammatory agents when consumed. These bioactive compounds are considered as reasons for the many health benefits of cereal foods. Germination is a physiological process of plants that starts with water absorption of the seeds. The germination process involves the stimulation of the endogenous enzymatic activity and acceleration of a series of biochemical reactions. These events have been shown to induce hydrolysis of storage proteins and carbohydrates and to cause reduction in anti-nutritive compounds and augmentation of the levels of vitamins, phytochemicals, and GABA [53, 54]. Depending on the germination stage, the form of germinated grains or seeds for consumption may be sprouts or malts, which not only are significantly different in shape, textural, and sensory characteristics from the original seeds but also in nutritional value. Germinated seeds are traditionally consumed fresh but can also be in various dried forms. Cereal grains are among the richest sources of micronutrients in addition to protein, carbohydrates, and lipids. The biochemical and metabolic processes during germination change the composition and quantity of essential macronutrients, as well as those of vitamins and other micronutrients [55]. Antinutrient content is significantly reduced by germination, and in most cases, sprouts of cereal and pseudocereal seeds had increased crude protein content and total soluble sugars and reducing sugars and decreased total starch content compared to those of the grains. Lipid content is

generally decreased after germination [55]. In terms of micronutrients, conflicting results have been reported for vitamins; however in recent years, germination has been found to be a viable way to increase bioactives such as phenolics and GABA, which leads to enhanced nutritional quality [54, 56, 57]. Our recent study showed that TPC and antioxidant activity of amaranth sprouts were higher than that of the seeds, and the sprouts also had completely different phenolic acid, flavonoid, and betanin compositions [57]. Moongngarm and Saetung [53] found that some essential amino acids, especially leucine and lysine, and GABA were significantly increased in germinated brown and rough rice. Isoflavone and GABA contents were also significantly increased during soybean seed germination and sprouting ($P < 0.05$), and such increases also led to significantly elevated antioxidant activities. GABA is a neurotransmitter that has various beneficial functions, and germinated rice and soybean seed had a phenomenally >350-fold increase compared to ungerminated soybean [53, 54]. The effect of germination depends on the species of the cereal seeds. While decreased TPC was observed for millets and a few sorghum cultivars, other germinated cereal and pseudocereal seeds including buckwheat, amaranth, quinoa, and some sorghum showed significantly increased TPC [55]. GBR is one of the most studied cereal grain. Germination significantly improved the content of GABA, TPC, γ -oryzanol, and antioxidant activity in a time-dependent manner. Sun-drying did not significantly affect the composition of these compounds except GABA. Elevated concentrations of bioactives in GBR have been found to contribute to various health beneficial effects [58, 59]. GABA, TPC, and the antioxidant activity of GBR were also significantly lowered by extrusion cooking [22]. Alvarezjubete et al. [60] studied the polyphenolic composition and antioxidant activity of amaranth, quinoa, buckwheat, and wheat and found that TPC and antioxidant activity to be generally increased with sprouting, although the bread-making process destroys some of these bioactives. The vitamins C and E and β -carotene contents in germinated wheat also steadily increased with increasing germination time, so were the concentrations of phenolic compounds such as ferulic and vanillic acids [61]. The effect of germination on the TPC in malted and unmalted barley was found to be variable depending on the steeping and kilning processes [55].

2.7 Fermentation

Fermentation as a food processing technique dates back thousands of years. Many foods and beverages are fermentation products based on plants, e.g., beans, grain, vegetables, fruit, and tea, and animal-based raw materials (e.g., honey, dairy products, fish, and meat). Fermentation is an action by the microorganisms, i.e., yeast, fungi, and bacteria, that convert carbohydrates into alcohols and organic acids. The fermentation process creates unique texture, flavors and aromas for foods and beverages, and also enriched nutritional profiles. Fermentation is one of the most simple and economical ways of improving the nutritional value, sensory properties, and

functional qualities of cereals [62]. There are basically two types of fermentation process, submerged (SmF) and solid-state fermentation (SSF) [63, 64]. These processes have been reported to increase the release of phenolic compounds and antioxidant activities of cereals. The effects of fermentation on phenolic compounds depend on types of grains, microorganism species, and fermentation conditions particularly temperature, pH, and time [17]. TPC and antioxidant activity of SSF wheat by two filamentous fungi were significantly higher than unfermented grain [65]. Similar results were found recently by Sandhu et al. [66]. The increased phenolic compounds in SSF wheat were found to be mainly hydroxybenzoic acids and hydroxycinnamic acids [67], especially the latter which are mostly in bound form in unfermented wheat but released as a result of fermentation. Increased release of originally bound phenolics after fermentation increases the bioaccessibility and bioavailability of these antioxidants, as seen in wheat bran fermented with yeast and treatment of cell wall hydrolytic enzymes and in millets [68, 69]. SSF of rice also led to increased antioxidant and other bioactivities [70]. In recent years, bound phenolics have been a focus of many studies because of their antioxidant and anti-inflammatory effects and their role in gut health [3, 71, 72].

Liberation of phenolics in fermented cereal products may be from three main routes: (1) structural breakdown of cell wall after the microorganisms are colonized in cereal-based media, (2) hydrolysis of bound phenolics by enzymes produced by microorganisms during fermentation process, and (3) newly formed soluble phenolic compounds by the microorganisms [63].

2.8 Enzymatic Processing

Enzymes are proteinaceous compounds that act as catalysts in all living organisms. Enzymes from edible organisms (plants, animal tissues, microorganisms) have long been used in food processing. The abovementioned fermentation processes are in fact actions by the enzymes by the microorganisms (bacteria, yeasts, and fungi). Although consumers are rarely using enzymes directly in day-to-day food preparation, enzymes are used in large-scale industrial production of foods and food ingredients. Commercial enzymes used in modern-day food industry are mainly isolated from microorganisms instead of plants or animals due to several advantages such as easy, cost-effective, and consistent production [73]. Enzymes are used for ingredient production, texture modification, and other applications such as production of high-fructose corn syrup, beverage clarification, brewing, baking, production of low-lactose milk, and meat tenderization [74]. Enzymes are also used for enhanced thermal and operational stability, improved specific activity, modification of pH-activity profiles, and increased product specificity [75]. The most important enzymes used in food processing include α -amylase, glucoamylase, protease, lactase, lipase, phospholipase, esterase, cellulase, xylanase, pectinase, glucose oxidase, laccase,

catalase, peroxidase, α -acetolactate dehydrogenase, asparaginase, debittering enzymes, narininase, lysozyme, β -glucosidase, papain, and pepsin [73, 76].

For cereal processing, α -amylase, glucoamylase, and protease are used in baking, brewing, starch liquefaction and bread and cake making, and quality improvement. The quality of sourdough rye and wheat breads was significantly improved in texture and bread volume and in the release of phenolics and other bioactives in the presence of α -amylase, xylanase, and lipase [77]. Enzymes are used widely in the baking industry. Amylases are generally used for converting starch into sugar and dextrins, oxidases for bleaching the dough, hemicellulases for improved gluten strength, but proteases for reduced gluten elasticity. The collective action of these enzymes leads to improvement in maintenance of bread volume, crumb softness, crust crispiness, browning, and freshness [76]. Xylanases in particular can help in the redistribution of water and leave the dough softer and easier to knead, resulting in improved dough characteristics such as better dough flexibility, machinability, stability, and loaf volume and in greater bread quality such as delayed crumb formation and finer and more uniform crumbs [78]. Many of these enzymes are used instead of yeast in the brewery industry to make alcoholic beverages. α -Amylase and β -glucosidase and protease are added to unmalted barley to convert complex carbohydrates to simple sugars to reduce cost and aid the malting process and to induce fast maturation and aid filtration.

An emerging area of use of enzymes especially the carbohydrases is the so-called enzymatic polishing of grains. This is a novel processing technology that uses enzymes to modulate the grain properties such as the taste, texture, and shelf life, with minimum negative effects on nutritional value. Enzyme polishing can also liberate cell-bound nutrients such as phenolics and fibers from bran without removing the germ and bran layer. Enzymatic polishing clearly has advantages in preserving loss of nutrients compared to mechanical milling; however it still requires further research effort in scale-up and in lowering the cost [79].

To summarize, cereal grains are a major source of human food rich in macronutrients and various micronutrients. Modern society and the cereal food industry have created various processing technologies that have been applied to cereal processing. These technologies have helped in developing diverse types of cereal foods; however, because of the refining process, many nutrients are lost or reduced. Such loss or reduction in nutritional quality during primary and secondary processing of cereals can be minimized, and as discussed in the present chapter, through optimizing the different novel processing technologies, nutrients can be retained and in many cases can even be increased. This chapter focused more on the micronutrients, especially phytochemicals, e.g., phenolics, carotenoids, and other compounds that are known to contribute to the health beneficial effects of cereals. Cereal bran contains the majority of dietary fiber and phenolic content, and thermal processing technologies may give dichotomous results in that the heat increases the degradation of bioactives but also breaks the cell wall so more compounds are released. Many technologies help increase the bioaccessibility and bioavailability of bioactives. While increased processing inevitably leads to more loss of bioactive components,

continued research effort on technologies for the enhancement of bioactive compounds and dietary fiber contents will ultimately lead to improved bioaccessibility, bioavailability, and health effects of cereal and cereal-based foods.

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