Chapter 6

Changes in Nutritional Properties and Bioactive Compounds in Cereals During Extrusion Cooking

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.68753

Abstract

Maintaining and improving the nutritional quality of foods during processing are the main market and industry concerns. Thus, research should focus on novel and sustainable ways for selecting the appropriate processing method that either increases or does not affect the nutrient content of foods. Thermal processing techniques such as extrusion cooking are widely used for producing breakfast cereals, snack foods, pasta, pet food, etc. Extrusion cooking is a continuous process that uses a combination of high-temperature, high-pressure, and high shear conditions in a short period of time, which results in molecular transformation and chemical reactions within the extruded products. Extrusion cooking brings on many biochemical changes such as denaturation of proteins, gelatinization of starch, lipid modifications, inactivation of microorganisms and enzymes, formation of volatile flavor components, and increase in soluble dietary fiber. Furthermore, extrusion cooking has the potential to improve the nutritional quality of the products by improving starch and protein digestibility and increasing the retention of bioactive compounds with antioxidant properties. Also, this highly efficient technology minimizes water pollution and energy consumption. This review aims to discuss the current information regarding changes in nutritional properties and bioactive compounds in cereals processed by extrusion cooking.

Keywords: extrusion cooking, cereals, nutritional properties, bioactive compounds, food processing

1. Introduction

Improving health through nutrition has been a very demanding and challenging field of study and would continue to be in the future. Maintaining and increasing the nutritional quality of food during processing are a potentially important area for research [1].

Food-processing operations are primarily focused on inactivating disease-causing microorganism (pathogens) and enzymes and on reducing moisture content to concentrate the processed foods. However, it is important to keep in mind that several changes in foodstuffs including appearance, composition, and nutritional and sensorial properties (color, texture, and flavor) can occur during processing. Interestingly, recent research has now established that food-processing operations have positive effects that improve the quality and health benefits of food [2].

Extrusion cooking is one of the most important food-processing alternatives. This process has been used since the mid-1930s for the production of breakfast cereals, ready-to-eat snack foods, and other textured foods. Furthermore, at this moment, extrusion process has become the major processing technology for food and feed industries, and it is rapidly evolving from an art into science and technology [3].

Extrusion cooking is preferred over other food-processing methods because it is a high-temperature short-time (HTST) process, which preserves important nutrients, denatures antinutritional components of foods (trypsin inhibitors, tannins, and phytates), disinfects the final product, and maintains normal colors and flavors of the food [4, 5].

Consumers have developed a growing understanding of how the composition of food products can impact on the nutritional quality of foods. Likewise, bioactive compounds or phytochemicals in food and food products play a relevant role in human health, providing protection against many chronic and degenerative diseases [6].

2. General and nutritional aspects of cereals

2.1. General aspects of cereals

Cultivation of cereal grains was the first agricultural attempt of the early man, and we still enjoy them today depending on the region we live and what grows there well [7]. Botanically, cereals are classified as grasses and belong to the monocot family Poaceae, also known as Gramineae. Within each cereal species, numerous varieties produced by breeding exist in order to optimize agronomical, technological, and nutritional properties [8]. The major cereals consumed in the world include wheat, corn, rice, oats, rye, barley, buckwheat, sorghum, and millet as minor grains. Wheat, corn, and rice take up the greatest part of the land cultivated by cereals and produce the largest quantities of cereals grains [8].

Cereals are composed of (1) endosperm (the main part of the grain, mainly starch), (2) germ (the smallest part of the grain; it contains vitamin E, folate, thiamine, phosphorus, and magnesium),

and (3) bran (the outer layer of the grain that contains fiber omega-3 fatty acids, vitamins, dietary minerals, and phytochemicals). Whole grains are important components of the human diet as shown by inclusion in the Food Guide Pyramid and US Dietary Guidelines [2, 7, 9]. However, cereal grains have poor protein quality due to their low content of the essential amino acids lysine and tryptophan, which are referred to as the main limiting amino acids in cereals [10].

In their natural form (as in whole grain), cereals are a rich source of vitamins, minerals, carbohydrates, fats, protein, and phytochemicals. However, when refined by the removal of the bran and germ, the remaining endosperm is mostly composed of carbohydrates and lacks the majority of the other nutrients [7].

Epidemiological studies have shown that a habitual intake of whole-grain cereal products is inversely associated with the risk for developing various types of chronic diseases such as obesity, cardiovascular disease, Type II diabetes, and some types of cancer [2, 11]. It has been suggested that these health benefits are not attributed only to a single component, but to the combined effects of several of them: dietary fiber, phenolic acids and flavonoid compounds, and other bioactive components present in cereal grains [11, 12].

Phenolic compounds exist in free and bound form in cereals. Bound phenolic compounds are referred to as phenolic compounds and are covalently bound with the cell wall components [13]. Phenolic acids are the most common phenolic compounds in cereals. They have a strong antioxidant activity and may modulate cellular oxidative status and protect biologically important molecules from oxidative damage such as DNA, proteins, and membrane lipids [14].

Cereal products are a complex multicomponent system that might contain mixtures of protein, vitamin, minerals, oils, polysaccharides, and bioactive compounds or phytochemicals. Hence, there is a reason for the increasing demand of new processed foods from whole cereals; they are convenient and nutritious to satisfy the demands of health-conscious consumers.

2.2. Nutritional and bioactive compounds in cereals

Cereal grains are grown in greater quantities and provide more food energy worldwide than any other types of crops. They are therefore staple food crops [7]. About 50% of the calories consumed by the world population originate from three cereals: rice (23%), wheat (17%), and maize (10%) [15, 16]. These are grown for their highly nutritious edible seeds, which are often referred to as grains.

Besides the main energy source, they supply a variety of nutrients and other food components such as bioactive compounds or phytochemicals [13]. Cereals are an important source of calories for humans, both by the direct intake and as the main feed for livestock [13]. Dietitians suggest to include whole-grain products in the diet, which provide large quantities of macronutrients (carbohydrates, proteins, and lipids), vitamins (particularly of the B group and vitamin E), and micronutrients, such as selenium, zinc, copper, and magnesium [17, 18]. Besides, cereals contain phytochemicals like phenols, phytoestrogens, and fermentable carbohydrates such as dietary fiber and resistant starch or oligosaccharides, which have been recently associated with cholesterol lowering, cardiovascular disease protection, and cancer-risk decrease [18, 19].

The chemical or nutritional composition of cereal grains is mainly characterized by the high content of carbohydrates. The carbohydrates for the human diet are classified in bioavailable and not bioavailable (or fiber). The bioavailable fraction, mainly starch, is deposited in the endosperm (comprising 65–75% of their total weight). The non-bioavailable fiber located in the bran (2–13%) is constituted by polymers such as arabinoxylans (1.5–8%), β-glucans (0.5–7%), sugars (≈3%), cellulose (≈ 2.5%), and glucofructans (≈ 1%). The other nutritional or chemical compounds are the proteins, which are the second most important compounds of cereals (comprising range of 7–11%). Lipids are located mainly in the germ fraction (average of 2–4%); a small fraction of them are in the aleurone layer and to the lesser extent in the endosperm. Cereal lipids have a similar fatty acid composition in which linoleic acid contents reaches 39–69%, while oleic acid and palmitic acid make up to 11–36 and 18–28%, respectively. Minerals in cereals are the minor constituents (1–3%). Nevertheless, the high content of vitamin B is of nutritional relevance [7, 8, 20]. Depending on the structure of each grain and the amount of their chemical constituents, there exist significant differences among cereals and even among species and varieties within each cereal.

More than 25,000 bioactive food constituents are present in the diet, and cereals are not the exception. The majority of food phytochemicals are also antioxidants, and many of these compounds play a role in modifying processes involved in the development of various diseases. It has been reported that these phytochemicals can also work in vivo as individual compounds, exerting their antioxidant property by neutralizing reactive oxygen or reactive nitrogen compounds and contributing to antioxidant defense of the body, thus promoting longevity, cell maintenance, and DNA repair [21, 22].

The most important groups of bioactive compounds in grains include phenolic compounds (phenolics acids, alkylresorcinols, and flavonoids), carotenoids, vitamin E, dietary fiber, and β-glucan [14, 24]. Phenolic compounds are secondary metabolites of plants and are part of the defense system against the sun's ultraviolet light as well as pathogens. These compounds play an important role in combating oxidative stress in the human body by maintaining a balance between oxidants and antioxidants [23, 24]. The antioxidant properties of cereal grains are mainly attributed to phenolic compounds [25]. Hence, the presence of phenolic compounds in cereals and their distribution can protect against cancer, cardiovascular diseases, diabetes, hypertension, asthma, and even infection if consumed in abundance in cereals [14, 22, 26].

Phenolic compounds (mainly phenolic acids) are concentrated in the bran fraction of cereal grains and exist in free, soluble conjugated, and insoluble bound forms [27]. Ferulic acid is the most abundant phenolic acid in cereal grains, followed by *p*-coumaric, sinapic, and caffeic acids [28]. In wheat and maize, ferulic acid represents up to 90% of the total phenolic acids and <95% in bound form [27, 29]. However, in other cereals such as finger millet (*Eleusine coracana*), phenolic acids represent 71% of the free-form phenolics, being protocatechuic acid the most abundant of them [30].

Cereals and other food items have to be processed before consumption to improve digestion and facilitate metabolism in humans [2]. Various processing technologies have been developed to enable the release and/or to increase the accessibility of nutritional and phytochemical components in cereal grains. Among these, the most common technique in food processing

is to apply mechanical treatment resulting in reduction of particle size, breakdown of cereal matrices, or degradation of fiber polymers. Likewise, thermal processing techniques such as steaming, autoclaving (pressured steam heating), drum drying, roasting, and microwave heating [11] are often utilized. Among the thermal treatments, the high-temperature short-time extrusion cooking technology has proven to have limitless applications in processing of cereal-based product.

3. Changes in extrusion cooking of cereals

Nowadays several breakfast cereal products are produced by flaking, oven and gun puffing, baking, shredding, and direct expansion. Extrusion cooking technology is becoming popular over other common processing methods due to its automated control, high capacity, continuous operation, high productivity, versatility, adaptability, energy efficiency, and low cost. Moreover, it also enables design and development of new food product, high product quality, unique product shapes and characteristics, energy saving, and no effluent generation [31, 32]. Extrusion cooking of breakfast cereals is a much easier and cheaper processing method than the conventional ones, and many components may be incorporated in the recipe [18].

There are three major types of extruders being used in the food industry: piston extruders, roller-type extruders, and screw extruders. Screw extruders are the most common extruders used these days and can be categorized as single- and twin-screw extruders [33]. In the single-screw extrusion cooking process, the extruder can be divided into three regions: conveying, swelling, and melting/degradation, in terms of the transition of cereal starch. Both the conveying and swelling regions are located in the cooling zone, where the flow pattern behaves as a plug flow reactor. The melting of starch granules and degradation of starch molecules occur simultaneously in the third region. The flow pattern is changed from plug flow reactor to continuous stirred tank reactor; thus, more mixing and longer residence time occurred in the heating zone. However, with twin-screw extruders, it is common to employ a section of spirally flighted screw elements behind the die head zone to provide a steady pumping action and to generate high die pressure [33].

Extrusion cooking of foods has been practiced for over 50 years. The food extruder, which was initially limited to mixing and forming macaroni and ready-to-eat cereal pellets, is now considered a high-temperature short-time bioreactor that transforms raw ingredients into modified intermediate and finished products [33]. Besides, several food products are developed by extrusion, i.e., pasta, breakfast cereals, bread crumbs, biscuits, crackers, croutons, baby foods, snack foods, confectionery items, chewing gum, texturized vegetable protein, pet foods, dried soups, dry beverage mixes, and instant flours to make tortillas [33–35].

During extrusion cooking, its simultaneous actions of temperature, pressure, and shear, along with their intensities and interactions vary enormously depending on feed ingredients, extruder configuration, and the desired characteristics of the final product [25]. This process consists in using high temperature and short time in which moistened, expansive, and carbohydrate or protein food materials are plasticized and cooked in a tube.

The combination of moisture, pressure, temperature, and mechanical shear results in molecular transformations and chemical reactions that allow obtaining expanded products and porous structure [1, 36, 37]. The expansion is the result of both the elastic swelling and bubble growth effects. The characteristics of the products obtained by extrusion cooking depend on the moisture content, extrusion temperature [38], residence time, pressure, and shear [33, 39].

The extrusion cooking process is preferable to other food-processing techniques in terms of its high productivity and significant nutrient retention due to the high temperatures and short times that are required [4]. Likewise, this technology has several applications including increasing numbers of ready-to-eat cereals, salty and sweet snacks, coextruded snacks, indirect expanded products, croutons for soups and salads, an expanding array of dry pet food and fish foods, textured meat-like materials from defatted high-protein flours, nutritious precooked food mixtures for infant feeding, and instant flour to make tortillas [32, 40, 41]. Moreover, extrusion has been used in the development of expanded cereals that include the addition of other ingredients (i.e., fruits and vegetables) in order to increase the health benefits [42].

Interest has grown in the physicochemical, functional, and nutritionally relevant effects of extrusion processing. Prevention or reduction of nutrient destruction, together with improvements in starch or protein digestibility, is clearly of importance in most extrusion applications [1]. Another advantage of extrusion cooking is the destruction of antinutritional factors, especially trypsin inhibitors, hemagglutinis, tannins, and phytates, all of which inhibit protein digestibility [1, 43]. Several extrusion-processing conditions are accounted for the quality of finished products. The control of feed rate, screw speed, barrel temperature, and barrel pressure, together with the abovementioned critical parameters, will determine the crispness, hardness, and various other characteristics that will influence the success of the final product [44].

3.1. Effect of extrusion process parameters on physical and chemical properties of extruded products

Cereal thermal processes such as baking, roasting, and extrusion cause a number of physical and chemical changes due to starch gelatinization, protein denaturation, component interactions, and browning reactions. These changes result in improved organoleptic properties, increased nutrient availability, and inactivation of heat-labile toxic compounds and enzyme inhibitors [25].

Food products obtained by extrusion technology are composed mainly of cereals, pulses, and/or vegetable proteins. The major role of these ingredients is to give structure, texture, mouth feel, and many other characteristics desired for specific finished products [33].

Functional properties of extruded foods play an important role in their acceptability including water absorption, water solubility, oil absorption indexes, expansion index, bulk density, and viscosity of the dough [33]. Several changes in the matrix food have been reported using the extrusion process, which are the result of the combination of moisture content of the starting materials, pressure-temperature, and screw speed, which are responsible of physical and chemical transformations in the final product and therefore affect product quality [42].

Extrusion cooking technology brings numerous chemical changes, such as gelatinization or starch, denaturation of protein, lipid modification, as well as inactivation of enzymes and microorganisms [45]. Denaturation of grain proteins during extrusion cooking allows the opening of loose structures for tannin-protein interactions causing the formation of tannin-protein complexes and retention of antioxidant activity. These complexes are broken down in the human gastrointestinal tract to release bound tannins and act as free radical scavengers [46]. Another important chemical effect occurring during extrusion is the browning or the formation of Maillard reaction products (MRP), which contributes to the antioxidant properties of the final product [47].

However, several investigators have reported that during extrusion, there is the loss of bioactive compounds with antioxidant properties (i.e., phenolics, tocopherols, carotenoids, anthocyanins, flavonoids, tannin, and other bioactive compounds) [48, 49]. Thermal degradation of phenolic compounds may be due to complex formation with Maillard reaction by-products and high moisture content promoting phenolic polymerization [50] affecting their extractability and antioxidant activity [51]. In contrast, earlier research on cereal products has shown that thermal processing might contribute in releasing bound phenolic acids by breaking down cellular constituents and cell walls [52]. For instance, transformation in more easily extractable forms of phenolic compounds has been reported in single-screw extruders with low moisture contents (<15/100 g), high shear stress, and high temperatures [53]. All of these chemical changes are associated with structural changes that occur in the materials subjected to extrusion increasing the release of the bioactive compounds in the cell wall matrix [54], thus making these materials more easily extractable [55]. All these physical changes are related to high shearing force in combination with high temperature and pressure that can efficiently disintegrate the rigid cell walls of the matrix food.

3.2. Effects of extrusion cooking process on nutritional properties of cereals

Nutritional properties in cereals are provided by two main groups of nutrients: macronutrients comprising of lipids, proteins, and carbohydrates, and micronutrients that include vitamins and minerals. Many researchers have reported both the positive and negative effects of the extrusion process on the nutritional quality of food and feed mixtures. These results are dependent on the different extruder conditions (temperature, feed moisture, screw speed, and screw configuration) and raw material characteristics (composition, particle size) [1].

As discussed above, extrusion cooking has been studied extensively to produce a wide variety of foods [33–35]. Interestingly, as a multistep, multifunction thermal/mechanical process, extrusion could have beneficial or detrimental changes on bioavailability and content of nutrients of cereal products [25]. On the one hand, extrusion (1) induces starch gelatinization improving its digestibility, (2) promotes the destruction of antinutritional factors (undesirable enzymes, trypsin inhibitors, and hemagglutinins), (3) increases the content of soluble fiber, (4) improves protein digestibility, and (5) reduces lipid peroxidation [1]. On the other hand, extrusion can also negatively affect the bioavailability of certain nutrients [56]. The heat-labile vitamins and some amino acids are lost, and the Maillard reaction that occurs during the process can reduce

the nutritional value of the proteins [1]. In this section, we will discuss the various effects of extrusion cooking on the nutritional properties of cereals.

3.2.1. Macronutrients

3.2.1.1. Lipids

While lipids can act as lubricants during extrusion, the amount of lipid content can affect the properties of the extrudates. Hence, the presence of lipids in less than 3% does not affect extrusion, but in quantities above 5% can reduce expansion rate, and above 10% they reduce slip within the extruder barrel, making extrusion difficult [57].

Extruded foods, particularly expanded products, are susceptible to lipid oxidation, one of the main causes of food deterioration [58]. Although there is not much research focused on the nutritional changes in lipids after extrusion, it has been reported that extrusion cooking can minimize lipid oxidation, thus increasing the nutritional and sensory quality and shelf life of foods [1]. Among the factors involved in the delay of oxidation in extruded foods are (1) denaturation of lipase and other enzymes that may contribute to oxidation [58]; (2) formation of lipid-amylose complexes, thereby reducing both starch and lipid availability and increasing oxidative stability and shelf life of extruded products [59]; (3) release of endogenous antioxidants in grains during extrusion that may provide protection against peroxidation [60]; and (4) creation of Maillard reaction products with antioxidant activity. In this regard, Sproston et al. [61] recently showed that a Maillard reaction product (MRP) derived from D-glucose and L-cysteine possesses antioxidant properties and that such product could be useful in inhibiting lipid oxidation in complex emulsions.

Polyunsaturated fatty acids (PUFA) ω-3 and ω-6 are essential for humans, and because of their greater number of instaurations, they are particularly sensitive to oxidation [62]. Thus, food-processing alternatives that result in minimal loss and the lower degree of oxidation of these components are desirable. Suzuki et al. [63] demonstrated that PUFA ω-3 and ω-6 in salmon muscle were retained after extrusion and its pretreatment, suggesting that foods rich in PUFA can be processed through extrusion without significant losses. In contrast, Ramos Diaz et al. [64] studied the effect of extrusion on corn-base snacks containing different combinations of amaranth and quinoa. They reported that extrusion substantially reduced the content of fatty acids (palmitic, oleic, linoleic, and linolenic acids) and α-, β-, and γ-tocopherols compared to flour blends. The authors attributed the considerable reduction in the content of fatty acids and tocopherols during extrusion to the formation of amylose-lipid complexes [59, 65]. It is also important to note that in the above-discussed studies, the ingredients used were different; hence, the available amylose for lipid binding and the formation of complexes was also different [59].

3.2.1.2. Proteins and amino acids

Cereals (maize, sorghum, rice, barley) and pulses (beans, peas, chickpeas, lentils, and other dry edible seeds) have traditionally been the dominant dietary plant protein source [66]. Protein nutritional value depends on the content of essential amino acids and the digestibility and utilization

of the protein [67]. Several factors can affect protein digestibility of cereals, among them are the grain structure and composition, the presence of disulfide bonds, surface functional groups, and protein hydrophobicity and conformation [68]. Also, processing such as pressure, temperature, fermentation, freeze/thaw cycles, and shear can also modify protein digestibility [69].

Several reports have shown that extrusion can improve protein digestibility by denaturing proteins and exposing of enzyme-susceptible sites. This phenomenon is attributed to the effects of high shear on protein structure and conformation that occur during extrusion, leading to the manufacture of products with highly digestible proteins [70]. Vaz and Arêas [70] showed that the increase in protein solubility observed in extruded meat-based formulations was associated with protein degradation and denaturation during the process. Similarly, enzymes and enzyme inhibitors generally lose activity during extrusion unless they are stable to heat and shear. Reductions in protease inhibitors can contribute to better plant protein utilization [57].

In addition, extrusion has been proposed as a viable alternative to influence allergenic properties of food proteins. The potential reduction in antigenicity is due to degradation of protein structures that ultimately results in the reduction of IgE- and IgG-binding capacity during thermal processing of foodstuffs [71].

3.2.1.2.1. Maillard reaction and advanced glycation end products

As it has been discussed, extrusion process under high pressure causes major chemical changes, thermal degradation, dehydration, depolarization, and recombination of fragments, all of which can promote glycoxidation [69, 72]. The concentration of advanced glycation end products (AGE) in foods, which are formed by Maillard reaction, has been demonstrated as a risk factor associated with the etiology of age-related diseases in humans, such as atherosclerosis, nephropathy, retinopathy, osteoarthritis, neurodegenerative diseases, and diabetes mellitus [73]. In addition, AGE by binding to their receptors (RAGE), which are found in a wide variety of cells, can lead to oxidative stress, vasoconstriction, and inflammatory responses. The AGE can covalently cross-link tissue proteins and, thereby, modify structural and functional properties of the proteins [74, 75]. During extrusion, the Maillard reaction is sometimes induced to contribute to desired flavor and color and to enhance palatability [76]. However, excessive Maillard browning can result in losses of lysine, destruction of vitamins, and reduction of bioavailability of trace elements [77]. Retention of lysine in the breakfast cereals is considered most important since it is the limiting amino acid among most of cereal snacks [10]. Thus, the Maillard reaction can result in unfavorable consequences such as a decreased protein quality due to the loss of bioavailable essential amino acids and, as mentioned before, the production of AGE. Future studies should focus on the optimization of processing conditions in a way that the desired beneficial effects are promoted, and the undesired effects are minimized.

3.2.1.3. Carbohydrates, starch, and fiber

One of the more widely researched aspects of extrusion on the nutritional content of products is the way extrusion technology can affect carbohydrate digestibility. Starch is usually

the major food constituent in extruded foods such as breakfast cereals, snacks, and weaning foods. Humans do not readily digest raw starch [78]. However, the digestibility of starch may be improved by the extrusion process due to its partial gelatinization and fragmentation attributed to the effect of shear and temperature. The depolymerization of the starch allows it to be more readily available to digestive enzymes. Moreover, during extrusion the physical breakdown of starch molecules takes place, resulting in smaller and more digestible fragments [79]. The extrusion process can increase the available digestible carbohydrate in cereals by up to threefold compared to raw (unextruded) cereals [80]. In the literature, there are several examples illustrating that extrusion improves starch digestibility.

Borejszo and Khan [81] found that sucrose, raffinose, and stachyose decreased significantly in extruded pinto bean starch fractions. While Alonso et al. [82] reported that compared to raw peas, starch and stachyose were lower in extruded peas [57]. Similarly, Mahasukhonthachat et al. [83] reported that the rate of starch digestion of sorghum increased by tenfold after extrusion when compared with non-extrudates, while Haralampu [84] reported that 22% of the resistant starch was lost (i.e., increase in more digestible starch), possibly due to high shear.

High starch digestibility is desirable in the food industry for the manufacture of specialized nutritional foods such as infant and weaning foods or to target particular consumer needs (elderly requiring rapidly digestible forms of starch, people participating in athletic activities, and those looking to reduce the content of indigestible oligosaccharides that cause flatulence in foodstuffs). However, these products tend to induce a higher glycemic response than their unprocessed raw ingredients. High blood levels of postprandial glucose and insulin have been implicated in the development of insulin insensitivity and chronic metabolic diseases such as Type II diabetes and cardiovascular disease [85]. By altering not only the digestibility of starch but also the conformation of starch, extrusion offers the ability to reduce the high glycemic index of some foods by converting starch to digestion-resistant starch. Hence, the formation of resistant starch by extrusion may have value to promote reduced calories in food products [86]. In this respect, an interesting observation is that extrusion can also increase the amount of resistant starch and soluble dietary fiber present in extrudates.

Different researchers have reported an increase in enzyme-resistant starch content in wheat, maize [87], and barley (2–3%) after extrusion [88]. In regard with the fiber content, Jing et al. [89] optimized extrusion process parameters (temperature 115°C, feed moisture 31%, and screw speed, 180 rpm) to obtain the highest values of soluble dietary fiber in soybean residues. Under these conditions, the soluble dietary fiber content residue increased by 10.6% and had higher water retention, oil retention, and swelling capacities than unextruded residues. Similar results were found by Chen et al. [90] using optimal conditions (170°C and an extrusion screw speed of 150 rpm/min) for blasting extrusion in soybean residue. These researchers found that the content of soluble dietary fiber from soybean residues increased by more than tenfold and showed improved water solubility, water retention capacity, and swelling capacity compared to unprocessed soybean. Furthermore, they tested the physiological effects of their high dietary fiber product and observed that it was able to significantly reduce total cholesterol, low-density lipoprotein cholesterol, and triglyceride levels in vivo.

The increase in soluble dietary fiber in extruded products could be explained by the formation of additional components by transglucosidation, whereby 1,4 carbon-oxygen bonds are cleaved, and new anhydroglucose linkages are formed, and the resulting novel bonds would be resistant to digestion by enzymes [91]. Another possibility is to increase insoluble dietary fiber with the formation of retrograded amylose, insoluble at room temperature [91, 92]. This could also be attributed to the formation of covalent interactions between macronutrients leading to components that are insoluble and not hydrolyzed by digestive enzymes [92, 93]. These indigestible glucans may be Maillard reaction products likely resulting from chemical reactions between starch and proteins present within the dietary fiber-containing matrix [93].

3.2.2. Micronutrients

3.2.2.1. Vitamins

In general, vitamins differ greatly in chemical structure and composition. Their stability during thermal process is also variable. The extent of degradation depends on various parameters during food processing and storage, e.g., moisture, temperature, light, oxygen, time, and pH [72]. Extrusion cooking has a significant effect on the stability of hydrosoluble vitamins. For instance, higher barrel temperature and low feed moisture induce ascorbic acid degradation during extrusion [6]. On the other hand, using short barrel (90 mm) extruders result in higher retention rate of the vitamin B group (44–62%) than long barrel extruders (20%). The retention of vitamins is generally not related with their initial level in foods and varies with cereal type. In corn, pyridoxine (vitamin B6) showed stability to extrusion cooking compared to oats and corn/pea ingredients [94]. In another study of fortified corn extrudates, the effect of temperature during the extrusion process on thiamine (B1) and riboflavin (B2) content was explained [95]. The authors found no significant differences between riboflavin content in traditional extrudates produced at feed moistures of 80 and 110°C barrel temperature. Interestingly, riboflavin content of extruded products at 20% feed moisture was higher than the one produced at 25% feed moisture at 130°C.

Extrusion cooking also affects the stability of fat-soluble vitamins such as vitamins A and E [96], which are natural antioxidants in cereal grains. The levels of vitamin E decreased (63%) in extruded buckwheat. Likewise, in other extruded cereals (oat, barley, wheat, rye, and buckwheat), a significant decrease (63–94%) in tocopherols and tocotrienols was observed [55, 97]. Isomers of vitamin E such as α-tocopherol and α-tocotrienol are the least resistant to temperature compared to other isomers [97].

3.2.2.2. Minerals

Minerals are considered stable during heat treatment. However, smaller molecules may be affected by either the extrusion process itself or changes in larger molecules, which in turn can affect other compounds present in the food [98]. To date, few studies have reported mineral stability during extrusion cooking of cereal grains. Interestingly, extrusion cooking can improve the absorption of minerals by reducing other factors that inhibit their absorption [99]. Phytates may form insoluble complexes with minerals decreasing their bioavailability in the

gastrointestinal tract. However, extrusion may hydrolyze the complex phytate minerals to release phosphate molecules [1].

In a study, a range of 13–35% reduction in phytate content from a wheat bran-starch-gluten extruded mix was reported in Ref. [100]. Polyphenols may also inhibit mineral absorption. The presence of tannins can form insoluble complexes with divalent ions in the gastrointestinal tract, inhibiting their bioavailability. Interestingly, extruded foods could also exhibit an increase in mineral absorption, which may be attributed to the destruction of polyphenols during the extrusion cooking [1, 99]. Similarly, absorption of minerals could be impaired by fiber (components such as cellulose, lignin, and hemicelluloses). However, the high temperature during the extrusion could reorganize the fiber components modifying their chelating properties [82].

3.3. Effects of extrusion cooking process on bioactive compounds of cereals

3.3.1. Phenolic compounds (phenolic acids and anthocyanins)

Aside from their nutritional contribution, cereals contain bioactive compounds with potential health benefits. These biologically active phytochemicals are found to be natural antioxidants and could be beneficial in reducing the risk of many diseases [1]. Food processing results in the destruction or change of natural bioactive compounds, which may affect the antioxidant properties of foods [2, 101]. According to the literature, food processing can alter antioxidant activity positively and negatively. In this regard, extrusion cooking can have either effect on the phenolic content in cereal grains.

On the one hand, extrusion causes decomposition of heat-labile phenolic compounds and polymerization of some others [102], resulting in the decrease of the extractable phenolic content. On the other hand, extrusion disrupts cell wall matrices and breaks covalent bonds in high-molecular-weight polyphenol complexes [53], improving the phenolic accessibility. The net effect of extrusion on total phenolic content depends on which of these phenomena are predominant [11]. Furthermore, antioxidant activity is correlated with the presence of bioactive compounds such as phenolics, carotenoids, flavonoids, and anthocyanins in foods [103].

Recently, several studies have reported the effect of extrusion and extrusion conditions on the phytochemical content and antioxidant activity of cereal grains. Important losses or increases of bioactive compounds are reported due to the thermal effects and chemical changes that occur during extrusion [42]. For instance, the release of phenolic compounds is highly dependent on moisture content, time, and temperature [25, 104].

In a study on dark buck wheat flour, no change in antioxidant capacity after its extrusion at 170°C was reported in Ref. [105]. Another study showed a significant reduction in both antioxidant capacity (60–68%) and total phenolics (46–60%) in barley extrudates compared with unprocessed barley flour [102]. Zielinski et al. [97] found significant changes in selected cereals (wheat, barley, rye, and oat) during extrusion cooking at different temperatures (120, 160, 200°C). The authors found significant increases in phenolic acids (mainly ferulic acid), while sinapic and caffeic acids were not detected in the extruded grains. Other authors are

using an optimized technique to obtain extruded products (cereals or mixture cereal/legume) with high nutritional quality and high antioxidant value. A ready-to-eat expanded snack with high nutritional and antioxidant value was developed from a mixture (70/30) of whole amaranthine, transgenic maize, and black beans by optimizing the extrusion process [106]. Using optimal conditions for extrusion, these authors found an increase in total phenolic content (74%) and antioxidant activity evaluated as ORAC (18%) and ABTS (20%) in the extruded snack with respect to the unprocessed whole-grain mixture. In general, the increase in phenolics during the extrusion process could be due to the destruction of cell walls, the consequent release of phenolic compounds, and the Maillard reaction products quantified as phenolic compounds [106]. In another study, a significant decrease of total polyphenols and antioxidant activity was observed in a bean/corn mixture during extrusion. However, this decrease was attributed to the process conditions [107]. In a different work, extruded sorghum did not cause the loss of condensed tannins but made them difficult to extract [108]. In general, a reduction of the phenolic content caused by the thermal process resulted from the polymerization of these compounds and consequently less extractability [51]. Several researchers have shown either the retention or increase of bioactive compounds during the extrusion cooking in cereals such as wheat, barley, rye, and oat-based products [97, 109].

Phenolic compounds during extrusion may undergo decarboxylation due to high barrel temperatures. Also, high moisture content may promote polymerization of phenols and tannins reducing their extractability and antioxidant activity [110]. While the increase in phenolic acids in extruded products is generally due to the release from the cell wall matrix, most bioactive compounds are temperature sensitive, and barrel temperature plays a significant role in the stability of their antioxidant properties [6]. In a study with pigmented (white, yellow, blue, and red) Mexican maize processed by extrusion cooking, the flours obtained were used to make tortillas. These tortillas showed high retention of total phenolic content (76–93%), total ferulic acid (58–97%), and antioxidant activity evaluated as ORAC assay (93–75%) compared to tortillas made with the traditional process [29]. These results clearly indicate that extrusion cooking is an alternative to obtain products with higher levels of phytochemicals and antioxidant activity. Similarly, Aguayo-Rojas et al. [32] found higher retention in total phenolic content (76–87%) and antioxidant activity (ORAC, 87–90%), in tortillas from pigmented Mexican maize elaborated from extruded flours.

During extrusion cooking, a significant decrease (<50%) in total anthocyanins in blue Mexican maize has been reported. This decrement is mainly attributed to the flavonoids' sensitivity to high temperatures [29, 32, 111]. However, there is also an increase in biologically important monomers and dimers due to the disruption of the cell wall food matrix [112].

3.3.2. Other bioactive compounds

Carotenoids and isoflavones are also affected by extrusion cooking. In a report using a corn/soy blend, the extrusion barrel temperature and the moisture content showed an increase in the acetyl derivatives of genistein and daidzein and a decrease in malonyl analogues indicating thermal decarboxylation [113]. In a study with eight genotypes of creole Mexican maize (yellow and red) processed into extruded flours and tortillas, the total carotenoid content

showed a retention range of 69–79% with respect to raw maize. Likewise, the concentration of the individual carotenoid compounds (Lutein, Zeaxanthin, β-cryptoxanthin, and β-carotene) decreased with the extrusion process. Interestingly, lutein, the major carotenoid in maize, showed an average retention of 60–71% with respect to raw maize. The significant loss on levels and profiles of carotenoids and lipophilic antioxidant activity during the elaboration or tortillas could be attributed mainly to the effect of thermal process, which induce carotenoid degradation and reactions such as isomerization and oxidation [114]. In light of the above, it is prudent to conclude that the effect of extrusion on bioactive compounds is not only dependent of the grain variety, but it is also important to select the appropriate processing conditions.

4. Future perspectives and conclusions

The consumption of whole grains is considered to have significant health benefits in prevention from chronic diseases such as cardiovascular disease, diabetes, and cancer. Cereal grains undergo physical and chemical changes during processing, so careful considerations should be taken to minimize or prevent any unfavorable changes in nutritional properties and the content of bioactive compounds. Most of the bioactive and phenolic compounds are mainly concentrated in the outer layer of cereal grains, and thus consuming whole-grain products is considered the best solution to increase the health benefits of cereal products. Extruders can be used to cook, form, mix, texturize, and shape food products under conditions that favor quality retention, high productivity, and low cost. In this regard, extrusion cooking is an ideal method for manufacturing a number of cereal products and to produce whole-grain products maintaining all the anatomic parts of the grain.

Despite the importance of selecting the appropriate food-processing conditions to improve the nutritional characteristics and increase the amount of biocomponents of the final product; research in this area is still limited. Thus, novel studies focusing on the optimization of thermal and nonthermal operations during extrusion have a vast potential for the food industry. Processing operations optimized for food safety may be combined with phytochemical studies to analyze both the nutritional and safety aspects. Finally, extrusion cooking has a potential for becoming the most important food-processing technology in the future, which can potentially be exploited.

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