We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

5,000
Open access books available

125,000
International authors and editors

140M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter 5

The Extrusion Cooking Process for the Development of Functional Foods

Martha G. Ruiz-Gutiérrez, Miguel Á. Sánchez-Madrigal and Armando Quintero-Ramos

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.68741

Abstract

The extrusion cooking technology is applied to the development of instant functional foods. It has advantages of low cost, sustainability, and versatility for production of a wide variety of food products. For formulation of functional foods, bioactive compounds are added to base mixtures, the main sources being fruits, vegetables, cereals, oleaginous plants, legumes, and industrial food by-product such as pomace. These sources provide phenolic compounds such as anthocyanins, flavonoids, and procyanidins besides betalains, carotenoids, vitamins, amino acids, and complex polysaccharides such as dietary fiber sources. During the extrusion cooking process, ingredients are mixed, conditioned, and transformed to a melt fluid, thus causing degradation or a release of functional compounds because of structural and chemical changes caused by the effects of some process variables such as temperature, moisture content, screw speed, and inherent factors such as geometrical configuration of the extruder. Retention of bioactive compounds to obtain extruded functional foods is an important topic. The description of degradation by means of mathematical models has been used to determine the impact of process variables on stability and concentrations of certain compounds in final extruded products. These models have been successfully applied, showing a good fit and adequately describing the variability of these compounds in extrusion cooking systems under specific conditions.

Keywords: extrusion, functional food, bioactive compound, stability, functional properties
1. Introduction

Currently, consumers demand nutritious food that provides health benefits. This situation has led to transformation of the food processing industry to ensure provision of healthy foods to consumers recognized as “functional foods.” Functional foods were first introduced in Japan in the 1980s. Over the years, several authors and institutions have defined this term differently, but the most common or simple definition is “a food or processed food that contains ingredients that have added positive health benefits beyond the basic nutritional function.” These ingredients or components are related to disease prevention and improvement of quality of life. A wide range of bioactive compounds have beneficial effects on human health, including probiotics and prebiotics, dietary fiber, vitamins, minerals, proteins, as well as secondary plant metabolites, which include phenolic acids, flavonoids, alkaloids, terpenoids, and glucosinolates. Besides, natural colorants such as betalains (betacyanins and betaxanthins) as well as carotenoids and anthocyanins are of interest owing to their pigmenting potential and antioxidant properties. These components are interesting because many of them possess antioxidant activity and have been shown to have anti-inflammatory, antibacterial, antiviral, and cancer-protective activities. These bioactive compounds are contained in a great variety of foods; Table 1 shows some sources of these components.

Stability of bioactive compounds such as betacyanins, betaxanthins, and anthocyanins, which are used as natural pigments, is affected by certain external factors such as temperature, pH, and concentration as well as the presence of oxygen, enzymes, water activity, light, and metals. Temperature is one of the main factors that affect most of these bioactive compounds. As for betalains, it is reported that their degradation increases with the increasing temperature and heating time [2, 14]. Those authors reported pigment degradation (betalains) in encapsulated red cactus pear powder as a function of temperature (80, 100, 120, and 140°C) during an extrusion process. Betalain content (betacyanins and betaxanthins) was affected by

| Sources               | Bioactive compounds                                                                 | Reference          |
|-----------------------|------------------------------------------------------------------------------------|--------------------|
| Fruits                | Apple, grape, cherry, peach, mangos, blueberry, cranberry, raspberry, bilberry, cactus pear | Polyphenols, anthocyanins, carotenoids, flavonoids, betalains (betacyanins, betaxanthins) [1–6] |
| Vegetables            | Carrot, tomato, onion, cauliflower, broccoli                                      | Carotenoids, lycopene, polyphenols, glucosinolates, vitamins [7, 8] |
| Grains                | Pigmented corn, oat, barley, wheat, amaranth, bean, rice                          | Anthocyanins, polyphenols, flavonoids, soluble fiber, ε-lysine [1, 9–12] |
| Oleaginous by-products| Defatted soybean paste, pumpkin, and defatted sunflower pasta                     | Proteins, polyphenols, carotenoids [13] |

Table 1. Food sources of bioactive compounds.
temperature, indicating that more than a half of these components were lost during the extrusion cooking process because of chemical changes such as isomerization, decarboxylation, and cleavage [15]. It has also been reported that betacyanin degradation in a betanin solution follows first-order reaction kinetics [14, 16]. In addition, the extrusion process results in losses in total polyphenol content and in antioxidant activity owing to temperature effects, indicating that high temperatures, >80°C, may decompose or alter their molecular structure, for example, may cause decarboxylation of free phenolic acids or formation of insoluble complexes with food components like proteins [17, 18]. The degradation of polyphenols and natural pigments during the extrusion process has been linked to the decrease in antioxidant activity of these components because of their structural changes, specifically because of their ability to donate hydrogen atoms from hydroxyl groups to free radicals [19]. The loss of other natural pigments such as anthocyanins and carotenoids under the influence of heat during the extrusion process has also been reported [9, 20, 21]. The relations among total polyphenolic content, antioxidant activity, and degradation of anthocyanins caused by high temperature after the extrusion cooking process in varieties of blue maize flour were also reported by Sánchez-Madrigal et al. [9].

As already described above, pH is another factor that affects bioactive compounds such as natural colorants. Although betalains alter their charge because of a pH change, they are not as susceptible as anthocyanins. This is because in the aqueous phase, anthocyanins exist as a mixture of four molecular species, and the concentration of these forms varies depending on pH. Table 2 shows the different forms and colors that anthocyanins acquire at different pH levels.

In acidic media (at low pH values), anthocyanins are more stable than in alkaline solutions, where they become more susceptible to degradation, as verified in a study by Sánchez-Madrigal et al. [9], who evaluated the effects of two types of calcium salts—calcium hydroxide, Ca(OH)2, and calcium lactate, C6H10O6Ca—at different pH levels and concentrations, during an extrusion and nixtamalization process. The main results revealed that both salts resulted in changes in anthocyanins and therefore in their color. Anthocyanin concentration decreased as Ca(OH)2 concentration increased but increased as the C6H10O6Ca concentration increased. This phenomenon can be attributed to the pH changes caused by each calcium salt, affecting the stability of anthocyanins in flour, which are more stable in acidic media than in alkaline media [22, 23]. Besides, it was observed that flour color is closely related to the

| pH   | Molecular species          | Color          |
|------|---------------------------|----------------|
| 1–3  | Flavylium cation          | Red            |
| 4–5  | Carbinol or pseudo base   | Colorless      |
| 7–8  | Quinoidal base            | Blue-violet    |
| >5 (ring opening) | Chalcone | Colorless or light yellow |

Brouillard [22]; He and Giusti [23].

Table 2. Molecular species of anthocyanins at different pH levels.
structural changes in anthocyanins because of prevailing pH in the cooking medium, resulting in different colors and hues at different pH levels [22–24]. Similar anthocyanin changes were reported in another study [25] during production of tortilla chips with extruded and nixtamalized flours.

Although during the extrusion cooking process a loss of bioactive compounds prevails, it is also reported that under certain process conditions, phenolic compounds are transformed into more easily extractable forms associated with structural changes occurring in the materials subjected to extrusion, thus increasing the release of bioactive compounds present in the cell wall matrix [26, 27]. In a study by Leyva-Corral et al. [1], during production of an instant extruded cereal with apple pomace, it was found that amounts of certain individual phenolic compounds increased under certain extrusion conditions (temperature and moisture content). For example, p-coumaric acid content increased as the temperature increased at all the moisture levels tested, decreasing at temperatures higher than 144°C. For ferulic acid, they found that an increase in moisture content at any temperature studied increased this compound’s concentration in the extrudates, reaching the highest value at 195°C. Meanwhile, rutin and phloridzin contents increased until 140°C at intermediate moisture levels (26–29%) and then decreased at higher temperatures.

Knowing the factors affecting the different components that form a food matrix, such as composition, intrinsic characteristics (pH and ionic strength, among others) combined with some extrusion process variables may help a technologist to influence the characteristics or final properties of the desired product. In addition, the presence, incorporation, and stability of bioactive compounds for the development of functional extruded products are topics that must be studied to meet consumer demands.

2. Importance of extrusion processes in product development

The processing methods designed to produce functional foods are diverse and technologically different because they depend on the type of product to be developed. Consequently, there are different kinds of functional food products such as beverages and semisolid or solid foods. These can be obtained by processing methods such as thermal processes, drying technology, freezing processes, and minimal processing technologies. Each one has advantages and technological limitations (in terms of the development of food products), which have an impact on the cost and consumer preferences. An alternative in food processing is the extrusion cooking process because of its low cost, sustainability, and versatility for production of a wide variety of food products such as expanded cereals, pasta, and instant meals [28]. This is a technology based on thermal processes of high-temperature-short time (HT-ST). Extrusion cooking can be defined as a continuous process in which materials, such as proteins and starches, are plasticized to form a fluid melt in a chamber or barrel as a result of high temperature, pressure, and shear stress, causing the material to be conveyed and forced to flow through a die of specific shape [29]. An extruder is composed of basic elements such as a barrel, single or twin screw, heating and cooling jackets, die, pressure recorder, raw material feeder, and controllers of screw speed and feed.
rate. Because extrusion cooking produces different types of food, extruders have become more specialized for food applications [30]. The extruders can be classified into two types: single screw and twin screw. A single-screw extruder was the first equipment used for food development for a direct cooking and forming application. It is mechanically simpler, less expensive, and easier to maintain but has some drawbacks in terms of operation, such as poor mixing and the necessity of premixing of ingredients and feeding conditioning before the process. Twin-screw extruders are classified according to the direction of rotation of the screws, in the same direction (corotating) or in the opposite directions (counterrotating), and the degree of intermeshing. Corotating twin-screw extruders are the most common in the food and snack industry for their efficiency, good control of residence time distribution, self-cleaning mechanism, and processing uniformity [31, 32]. These extruders are considerably more versatile than single-screw extruders and show more stable operation, with a wide range of applications and stability of product quality. The control of extrusion process operations—along with knowledge about the effects of variables of operation, such as temperature, screw speed, and feed moisture content—is necessary to obtain products with various desired physicochemical characteristics. Additionally, other inherent factors of extrusion equipment, such as the screw profile, size and shape of the die, and length and diameter of the barrel, are important geometrical characteristics that should be consistent with the characteristics of the desired food product.

During processing of materials, raw materials are conditioned (cleaning, classification, grinding, and conditioning to required moisture levels) and mixed with various ingredients such as bioactive compounds to produce diverse types of products of different shapes. Raw materials are fed into the extrusion equipment, where they are mixed and subjected to heating and friction. The solid phase is transformed into fluid melt at high temperature and pressure and forced to flow through the die. Due to the pressure change between barrel chamber and atmospheric pressure, instant vaporization occurs, and we get an expanded product with porous structure (Figure 1), which will depend on operating conditions and composition of the mix, among other factors. At the same time as structural changes occur in the solid matrix, e.g., starch gelatinization, protein denaturation and solubilization, and formation of complexes between amylose and lipids, there are reactions of degradation of antioxidants (such as vitamins, polyphenols, anthocyanins, and pigments), which are influenced by the type and intensity of the thermal and mechanical energy applied and are related to the process variables and screw and barrel geometric configurations.

2.1. Effects of extruder variables on product properties

Although the extrusion process is basically a simple technological operation, its control is complicated owing to the effects exerted by some variables of the process. The processing conditions are determined by independent and dependent variables of the system. The independent variables are those that can be controlled, such as feed composition, moisture content, rate of feed, screw speed, and barrel temperature. The dependent variables are those that assume a certain value that depends on the magnitude of an independent variable. These include the properties of extrudates, such as viscosity, which is affected by the composition, moisture content, temperature, and shear rate associated with the screw speed. The flow rate
is associated with configuration of the screw barrel, screw speed, viscosity, and pressure drops in the system; other properties that can be included here are pressure exerted on the system, power, specific energy, residence time, and product characteristics (texture, gelatinization, color, water absorption index, expansion index, density, and chemical composition, among others). Small changes in these variables can affect the quality and characteristics of the final product. The most influential variables in extrusion processes are temperature, screw speed, and system pressure. In addition, moisture content of the mixtures influences properties such as viscosity of the melt fluid, residence time of the material in the extruder, and shear stress applied to the food, thereby affecting the physical characteristics of extrudates or energy consumption. Figure 2a shows the effects of extrusion temperature and moisture content on a process designed to obtain an instant extruded cereal with the addition of apple pomace. It was found that specific mechanical energy input is affected by the moisture content of the mixtures, where higher values of specific energy are obtained at moisture content of 28%, and a further increase causes a decrease in energy input. This phenomenon can be attributed to the gelatinization mechanism, which is minimized at high

Figure 1. Expansion of cornstarch due to extrusion.
moisture content, causing sliding of the material during the process. The expansion index (Figure 2b) is affected by the moisture content of the mixtures and extrusion temperature. Increases in feed moisture content increase expansion of the extrudates at low temperatures. Nonetheless, an increase in temperature reduces the expansion even at high moisture content. Evidently, properties such as expansion are dependent on the abovementioned factors, which correlate with the degree of gelatinization and composition of the mixtures [33]. Besides, the behavior of the expansion index could be correlated with fiber content of apple pomace, as reported in other studies, where it was found that fiber addition minimizes the expansion of cereals [8, 10].

Another study [34] has shown the effect exerted by the feed rate, resulting in a high expansion index, with a low water solubility index (WSI) and high hardness of extrudates. The increase in feed moisture content results in products with high density, low expansion, high water absorption index (WAI), lower WSI, and high hardness. The increase in barrel temperature increased expansion of the extrudates but reduced density with an increase in the WSI. These results show the effects of operating conditions during extrusion of cereals (feed rate, feed moisture content, screw speed, and barrel temperature) on physicochemical characteristics of the extruded products, e.g., on expansion, density, WAI, and WSI. These studies show versatility of the extrusion process for obtaining quality products with a suitable nutritional balance and functional characteristics that can be presented in various ways.

2.2. The extrusion cooking process for the development of functional foods

Some of the food extrusion applications are instant extruded products such as breakfast cereals, snack foods, baby food, instant soups, instant flour, and others. Figure 3 shows a process diagram for the development of functional extruded products. Extruder machines are integrated into a production line of the extrudates.
The extrusion cooking process involves temperatures >100°C, where the food is mixed, transported, heated, and forced through one or more restricted openings (dies) at the discharge end of the barrel, expanding when emerging from the die. Subsequently, this extrudate is dried, sweetener coated, and packed, or directly packed. In the cold extrusion process, the processing temperature is low [35], and the product is mixed and formed without noticeable cooking, which typically causes degradation of some components. For this purpose, besides low temperatures, the screw and barrel configuration for low friction (a deep-flighted screw and smooth barrel) and low screw speeds are used. Some of the extruded products are described in Table 3. Among these are expanded cereals with different forms and appearances, extruded fruit products, extruded products based on proteins, and confectionery products. Each one can be reformulated for the production of functional extruded products via incorporation of soluble fiber, antioxidants (polyphenols, anthocyanins, or vitamins), or low-calorie sweeteners with the addition of calcium and microelements, proteins, and natural colorants, among others.
3. Stability of functional components during the extrusion cooking process

Lately, the research in this field is focused on the development of functional foods because of the industry tendencies and consumer demands. A wide range of these kinds of products are obtained through an extrusion cooking process as described above. Nonetheless, during this process, chemical changes occur, affecting the presence and concentration of bioactive compounds in the extruded final product. For this reason, extruder equipment is considered a reactor of high-stress mechanical and thermal conditions that can accelerate chemical reactions among the components present in some ingredients, causing changes in their structures such as breaking of physical bonds, leading to the loss of functional compounds. The stability of bioactive or functional compounds in extruded products is reported as a loss or increase after extrusion cooking. Table 4 shows the stability of some bioactive compounds used in the extrusion cooking process.

The losses of bioactive compounds are mainly due to the effects of temperature and mechanical stress changing the structure of compounds. A well-studied change is degradation of anthocyanins during this process. These could be converted to chalcones and small molecules without previous hydrolysis of the glycosidic bonds to form the corresponding aglycons [43, 44]. Anthocyanins that are more affected by high temperature are cyanidin 3-arabinoside and peonidin 3-arabinoside, in contrast to cyanidin 3-galactoside, cyanidin 3-glucoside, peonidin 3-galactoside, and peonidin 3-glucoside [6]. Other authors have reported degradation of cyanidin 3-glucoside into protocatechuic acid [11]. Regarding the reduction in the amounts of other polyphenols, the main change caused by the thermal process during extrusion is decarboxylation of free phenolic acids, which promotes polymerization of phenolics and tannins, thereby leading to reduced extractability and antioxidant activity [45].

Table 3. Food products obtained by an extrusion process.

| Characteristics       | Products                                      |
|-----------------------|----------------------------------------------|
| Extruded cereal products | Ready-to-eat cereals  
Expanded snack foods  
Precooked flour  
Pasta products  
Pellets for snacks  
Bases for instant soups  |
| Extruded fruit products | Fruit leather  
Fruit bars  |
| Extruded protein products | Snacks (protein bars)  
Textured vegetable protein products  
Restructured seafood  
Semimoiest and expanded pet foods  
Processed cheeses  |
| Confectionery products | Chocolate  
Fruit gum  
Chewing gum  |

Heldman and Hartel [36]; Riaz [37].

91
| Source                  | Bioactive compounds | Process conditions                                                                 | Loss (%)   | Reference |
|------------------------|---------------------|-------------------------------------------------------------------------------------|------------|-----------|
| Thiamin                | Thiamin             | Moisture content: 11, 13, and 14%                                                   | 67–100%    | [38]      |
|                        |                     | Temperature: 140–200°C                                                               |            |           |
|                        |                     | Screw speed: 65, 73, and 81 rpm                                                     |            |           |
|                        |                     | Residence time: 85–131 s                                                            |            |           |
|                        |                     | Thiamin content: 9, 37, and 93 mg/kg                                               |            |           |
| Blueberry concentrate  | Anthocyanins        | Temperature: until 138°C                                                            | 90%        | [3]       |
|                        |                     | Screw speed: 300 rpm                                                                |            |           |
| Grape juice            | Anthocyanins        | Temperature: until 138°C                                                            | 74%        | [3]       |
|                        |                     | Screw speed: 300 rpm                                                                |            |           |
| Yellow maize grits     | L-Lysine            | Moisture content: 13, 15, and 17%                                                   | 51–89%     | [39]      |
|                        |                     | Temperature: 150, 165, and 180°C                                                    |            |           |
|                        |                     | Screw speed: 65, 73, and 81 rpm                                                     |            |           |
|                        |                     | Residence time: 89–101 s                                                            |            |           |
| Fruit powders (berries)| Anthocyanins        | Temperature: 163°C                                                                  | 65%        | [4]       |
|                        |                     | Residence time: 3.5 min                                                             |            |           |
| L-Acid ascorbic        | L-Acid ascorbic     | Temperature: 75–150°C                                                               | 56.4–79.2% | [40]      |
|                        |                     | Screw speed: 100 and 300 rpm                                                        |            |           |
|                        |                     | Residence time: 31.58–48.81 s                                                       |            |           |
| Navy beans             | Phenolic compounds  | Moisture content: 10%                                                               | 10%        | [10]      |
|                        |                     | Temperature: 22%                                                                   |            |           |
|                        |                     | Screw speed: 160°C                                                                 |            |           |
|                        |                     | Bean content: 15, 30, and 45%                                                       |            |           |
| Small red beans        | Phenolic compounds  | Moisture content: 22%                                                              | 70%        | [10]      |
|                        |                     | Temperature: 160°C                                                                 |            |           |
|                        |                     | Screw speed: 150 rpm                                                               |            |           |
|                        |                     | Bean content: 15, 30, and 45                                                        |            |           |
| Blueberry pomace       | Anthocyanins        | Moisture content: 45%                                                              | 33–42%     | [5]       |
|                        |                     | Temperature: 160, 180, and 200°C                                                   |            |           |
|                        |                     | Screw speed: 150 and 200 rpm                                                       |            |           |
| Source               | Biactive compounds | Process conditions                                                                 | Loss (%)       | Reference |
|---------------------|--------------------|-------------------------------------------------------------------------------------|----------------|-----------|
| Kiwicha             | Polyphenols        | Temperature: 180°C  
Screw speed: 254.5 rpm  
Residence time: 10–13 s | 64.4–80.3%     | [41]      |
| Dried cranberry pomace | Procyanidins  
DP4 and DP9 | Moisture content: 30%  
Temperature: 150, 170, and 190°C  
Screw speed: 150 and 200 rpm  
Pomace content: 30, 40, and 50% | DP4: 23–28%  
DP9: 68–77% | [6]       |
| Bilberry extract    | Anthocyanins       | Moisture content: 22%  
Temperature: 100, 130, and 160°C  
Residence time: ≤ 60 s | 90%            | [42]      |
| Chokeberry          | Anthocyanins       | Temperature: 100–140°C  
Screw speed: 300–500 L/min  
Chokeberry content: 1.2 kg/38.8 kg starch | 35–100%        | [43]      |
| Blue maize          | Anthocyanins       | Moisture content: 30%  
Temperature: 80°C  
Extruder speed: 30 Hz | 41–53%         | [9]       |
| Blue maize          | Total polyphenols  | Moisture content: 30%  
Temperature: 80°C  
Extruder speed: 30 Hz | 12.5–38.3%     | [9]       |
| Pumpkin             | α-Carotene         | Moisture content: 15%  
Temperature: 150–170°C  
Pumpkin content: 4, 6, and 8% | 100%           | [21]      |
| Pumpkin             | L-Acid ascorbic    | Moisture content: 15%  
Temperature: 150–170°C  
Pumpkin content: 4, 6, and 8% | HT: 49–76%    
LT: 13–40% | [21]      |
| Black rice          | Bond polyphenols   | Moisture content: 12–17%  
Temperature: 60, 100, and 120°C  
Screw speed: 200 rpm | 15%            | [11]      |
## Bioactive compounds losses

| Source | Bioactive compounds | Process conditions | Loss (%) | Reference |
|--------|--------------------|--------------------|----------|-----------|
| Red cactus pear encapsulated powder | Betacyanins | Moisture content: 0.22 kg/kg; Temperature: 80, 100, 120, and 140°C; Screw speed: 225, 275, and 325 rpm; Residence time: 36.62–60.13 s; Powder content: 2.5% (w/w) | 33–51% | [2] |
| Red cactus pear encapsulated powder | Betaxanthins | Moisture content: 0.22 kg/kg; Temperature: 80, 100, 120, and 140°C; Screw speed: 225, 275, and 325 rpm; Residence time: 36.62–60.13 s; Powder content: 2.5% (w/w) | 55–77% | [2] |
| Red cactus pear encapsulated powder | Polyphenols | Moisture content: 0.22 kg/kg; Temperature: 80, 100, 120, and 140°C; Screw speed: 225, 275, and 325 rpm; Residence time: 36.62–60.13 s; Powder content: 2.5% (w/w) | 36–47% | [2] |
| Oat/apple pomace | Polyphenols | Moisture content: 21–30%; Temperature: 104–175°C; Screw speed: 150 and 200 rpm; Oat/apple pomace content: 40/14% | 2.9–20.1% | [1] |

## Bioactive compound increases

| Source | Bioactive compounds | Process conditions | Increase (%) | Reference |
|--------|--------------------|--------------------|--------------|-----------|
| Bean/corn | Total polyphenols | Moisture content: 16.3%; Temperature: 50–190°C; Screw speed: 90 rpm | 23% | [12] |
| Bean/corn | Flavonoids | Moisture content: 16.3%; Temperature: 50–190°C; Screw speed: 90 rpm | 36% | [12] |
On the other hand, Table 4 shows an increase in the concentration of some bioactive compounds mainly flavonols and procyanidins. The flavonols upregulated after the extrusion process are myricetin, quercetin, and their various glucosides. This change may be explained as follows: many flavonols may get bound to the cell wall components, especially after damage to cells [46]. Another explanation of the increased flavonol content is enhanced extraction of compounds because of disruption of the solid matrix upon extrusion [6]. Similar findings for other polyphenols such as caffeic acid and p-coumaric acid at some specific temperatures and moisture conditions have been reported [1]. Another change observed in polyphenols is the increased amounts of free polyphenols because extrusion leads to higher extraction efficiency and decreased amounts of bound polyphenols; researchers have also observed an increase in the amounts of procyanidins of low molecular weight (DP1 and DP2) as a result of decreased concentrations of procyanidins with DP ≥ 4 [6].

The antioxidant activity of extruded products is related to the amount of bioactive compounds and their losses caused by the extrusion cooking process. The general tendency is that the extrusion cooking process leads to losses of bioactive compounds and a decrease in the antioxidant activity as a consequence. Nonetheless, in some cases, antioxidant capacity is increased due to the structural changes in compounds. Table 5 shows studies where antioxidant activity was determined before and after extrusion cooking, reporting a loss or increase under different process conditions and with different sources of bioactive compounds.

Some researchers have studied the changes in individual polyphenols using black rice [11] and apple pomace [1] as sources of bioactive compounds subjected to the extrusion cooking process. The stability of individual polyphenols is shown in Table 6.

### Table 4. Stability of bioactive compounds used in the extrusion cooking process.

| Source            | Bioactive compounds                           | Process conditions                                      | Loss (%) | Reference |
|-------------------|-----------------------------------------------|--------------------------------------------------------|----------|-----------|
| Blueberry pomace  | Monomers biologically important              | Moisture content: 45%                                  | 18%      | [5]       |
|                   |                                               | Temperature: 160, 180, and 200°C                        |          |           |
|                   |                                               | Screw speed: 150 and 200 rpm                           |          |           |
| Dried cranberry pomace | Flavonols (FL)  | Moisture content: 30%                                  |          |           |
|                   | Procyanidins DP1 and DP2                      | Temperature: 150, 170, and 190°C                      |          |           |
|                   |                                               | Screw speed: 150 and 200 rpm                           |          |           |
|                   |                                               | Pomace content: 30, 40, and 50%                        |          |           |
|                   |                                               | FL:30–34%                                              |          |           |
|                   |                                               | DP1: 61–157%                                           |          |           |
|                   |                                               | DP2: 49–164%                                           |          |           |
| Black rice        | Total polyphenols (TP) and free polyphenols (FP) | Moisture content: 12–17%                              |          |           |
|                   |                                               | Temperature: 60, 100, and 120°C                        |          |           |
|                   |                                               | Screw speed: 200 rpm                                   |          |           |
|                   |                                               | TP: 12.6%                                              |          |           |
|                   |                                               | FP: 17%                                                |          |           |

Table 5. Stability of bioactive compounds used in the extrusion cooking process.
3.1. Modeling of degradation of bioactive compounds

Kinetic models of zero- and first-order reactions can predict the stability of these functional compounds. Thermomechanical degradation of functional components during an extrusion cooking process has been mostly fitted to first-order models, such as the one in Eq. (1):

### Table 5. Losses and increases of antioxidant activity under the influence of the extrusion cooking process.

| Source | Bioactive compound | Extrusion cooking conditions | Antioxidant activity change (%) | Reference |
|--------|--------------------|------------------------------|---------------------------------|-----------|
| Navy   | Total polyphenols  | Moisture content: 22%        | Losses: 22%                     | [10]      |
|        |                    | Temperature: 160°C           |                                 |           |
|        |                    | Screw speed: 150 rpm         |                                 |           |
|        |                    | Beans content: 15, 30, and 45%|                                 |           |
| Small red beans | Total polyphenols | Moisture content: 22%        | Losses: 65%                     | [10]      |
|        |                    | Temperature: 160°C           |                                 |           |
|        |                    | Screw speed: 150 rpm         |                                 |           |
|        |                    | Beans content: 15, 30, and 45%|                                 |           |
| Bean/corn | Polyphenols    | Moisture content: 20%        | Increase: 27%                   | [12]      |
|        | Flavonoids       | Temperature: 180°C           |                                 |           |
|        |                    |                                |                                 |           |
| Kiwicha | Polyphenols      | Temperature: 180°C           | Losses: 29–58%                  | [41]      |
|        |                    | Screw speed: 254.5 rpm        |                                 |           |
|        |                    | Residence time: 10–13 s       |                                 |           |
| Blue maize | Anthocyanins   | Moisture content: 30/100 g    | Losses: 12.8–34.9%              | [9]       |
|        |                    | Temperature: 80°C             |                                 |           |
|        |                    | Extruder speed: 30 Hz         |                                 |           |
| Red cactus pear | Betalains   | Moisture content: 0.22 kg/kg  | Losses: 35–47%                  | [2]       |
| encapsulated powder |                | Temperature: 80, 100, 120, and 140°C |                                 |           |
|        |                    | Screw speed: 225, 275, and 325 rpm |                                 |           |
|        |                    | Residence time: 36.62–60.13 s |                                 |           |
|        |                    | Powder content: 2.5% (w/w)    |                                 |           |
| Pumpkin | Lutein, zeaxanthin, and α-carotene | Moisture content: 15% | Increase | [21] |
|        |                    | Temperature: 150–170°C        |                                 |           |
|        |                    | Pumpkin content: 4, 6, and 8% |                                 |           |
where $C_0$ represents the initial concentration of a component, $C_t$ is the concentration of the component at time $t$, $k$ denotes the reaction rate constant, and $t$ is the residence time in the extruder. Furthermore, dependence of the constant reaction rate on the extrusion cooking temperature can be described by the Arrhenius equation, as shown in Eq. (2):

$$k = A_0 \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (2)$$

where $A_0$ is the pre-exponential, $E_a$ is activation energy of the reaction, $R$ is the universal gas constant, and $T$ is absolute temperature.

Eq. (1) has been used to describe a decrease in the amounts of thiamin [38], amino acids [39], anthocyanins [42], and betalains [2], and Eq. (2) has been used to calculate activation energy during an extrusion cooking process. Table 7 shows reported values of the degradation rate constant and activation energy. Studies have shown that thiamin degradation is dependent on extrusion temperature, feed moisture, and screw speed, but the degradation of thiamin is most dependent on extrusion temperature [38].

As for losses of amino acids—lysine, arginine, and cysteine—the results have shown that the reaction rate constants are strongly dependent on temperature, lysine being the amino acid that is more sensitive to temperature than the others are, although shear stress additionally affects the amino acid loss [39]. In natural pigments such as betacyanins (red-purple pigments) and betaxanthins (yellow-orange pigments), $k$ values tend to decrease as
temperature increased. An increase in temperature causes the material to flow faster in the extruder, and consequently, the pigments have shorter exposure to high temperature and shear stress during the extrusion. Furthermore, the rate constants for the degradation of betacyanins are higher than those obtained for betaxanthins. Nonetheless, activation energy for the degradation of betaxanthins was found to be greater than that for degradation of betacyanins, indicating that betaxanthins are more sensitive to a temperature increase during the extrusion cooking process [2]. For anthocyanins [42], both $k$ values and activation energy are affected by temperature, but mechanical stressors and moisture of the material also have to be considered as parameters influencing anthocyanin degradation in an extrusion cooking process.

### Author details

Martha G. Ruiz-Gutiérrez, Miguel Á. Sánchez-Madrigal and Armando Quintero-Ramos*

*Address all correspondence to: aquinter@uach.mx

Faculty of Chemical Sciences, Autonomous University of Chihuahua, Nuevo Campus Universitario Circuito Universitario s/n, Chihuahua, Chihuahua, México

### References

[1] Leyva-Corral J, Quintero-Ramos A, Camacho-Dávila A, Zazueta-Morales JJ, Aguilar-Palazuelos E, Ruiz-Gutiérrez MG, Meléndez-Pizarro CO, Ruiz-Anchondo TJ. Polyphenolic compound stability and antioxidant capacity of apple pomace in an extruded cereal. LWT - Food Science and Technology. 2016;65:228-236. DOI:10.1016/j.lwt.2015.07.073
[2] Ruiz-Gutiérrez MG, Amaya-Guerra CA, Quintero-Ramos A, Pérez-Carrillo E, Ruiz-Anchondo TJ, Báez-González JC, Meléndez-Pizarro CO. Effect of extrusion cooking on bioactive compounds in encapsulated red cactus pear powder. Molecules. 2015;20:8875-8892. DOI: 10.3390/molecules20058875

[3] Camire ME, Chaovanalikit A, Dougherty MP, Briggs JL. Blueberry and grape anthocyanins as breakfast cereal colorants. Journal of Food Science. 2002;67:438-441. DOI: 10.1111/j.1365-2621.2002.tb11425.x

[4] Camire M, Dougherty M, Briggs J. Functionality of fruit powders in extruded corn breakfast cereals. Food Chemistry. 2007;101:765-770. DOI: 10.1016/j.foodchem.2006.02.031

[5] Khanal RC, Howard LR, Brownmiller CR, Prior RL. Influence of extrusion processing on procyanidin composition and total anthocyanin contents of blueberry pomace. Journal of Food Science. 2009;74:52-58. DOI: 10.1111/j.1750-3841.2009.01063.x

[6] White BL, Howard LR, Prior RL. Polyphenolic composition and antioxidant capacity of extruded cranberry pomace. Journal of Agriculture Food Chemistry. 2010;58:4037-4042. DOI: 10.1021/jf902838b

[7] Puupponen-Pimia R, Hakkinen ST, Aarni M, Suortti T, Lampi AM, Eurola M, Piironen V, Nuutila AM, Oksman-Caldentey KM. Blanching and long-term freezing affect various bioactive compounds of vegetables in different ways. Journal of the Science of Food and Agriculture. 2003;83:1389-1402. DOI: 10.1002/jsfa.1589

[8] Altan A, McCarthy KL, Maskan M. Evaluation of snack foods from barley-tomato pomace blends by extrusion processing. Journal of Food Engineering. 2008;84:231-242. DOI: 10.1016/j.jfoodeng.2007.05.014

[9] Sánchez-Madrigal MÁ, Quintero-Ramos A, Martínez-Bustos F, Meléndez-Pizarro CO, Ruiz-Gutiérrez MG, Camacho-Dávila A, Torres-Chávez PI, Ramírez-Wong B. Effect of different calcium sources on the bioactive compounds stability of extruded and nixtamalized blue maize flours. Journal of Food Science and Technology. 2015;52:2701-2710. DOI: 10.1007/s13197-014-1307-9

[10] Anton A, Fulcher RG, Arntfield SD. 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. 2009;113:989-996. DOI: 10.1016/j.foodchem.2008.08.050

[11] Ti H, Zhang R, Zhang M, Wei Z, Chi J, Deng Y, Zhang, Y. Effect of extrusion on phytochemical profiles in milled fractions of black rice. Food Chemistry. 2015;178:186-194. DOI: 10.1016/j.foodchem.2015.01.087

[12] Delgado-Licón E, Martínez-Ayala AL, Rocha-Guzman NE, Gallegos-Infante JA, Atienzo-Lazos M, Drzewiecki J, Martínez-Sánchez CE, Gorinstein S. Influence of extrusion on the bioactive compounds and the antioxidant capacity of the bean/corn mixtures. International Journal of Food Sciences and Nutrition. 2009;60:522-532. DOI: 10.1080/0963748080197666
[13] Sharma, SK, Bansal, S, Mangal, M, Dixit, AK, Gupta, RK, Mangal AK. Utilization of food processing by-products as dietary, functional, and novel fiber: A review. Critical Reviews in Food Science and Nutrition. 2016;56:1647-1661. DOI: 10.1080/10408398.2013.794327

[14] Saguy I, Kopelman IJ, Mizrahi S. Thermal kinetic degradation of betanin and betalamic acid. Journal of Agricultural and Food Chemistry. 1978;26:360-362. DOI: 10.1021/ja60216a052

[15] Huang AS, von Elbe JH. Kinetics of the degradation and regeneration of betanine. Journal of Food Science. 1985;50:1115-1120. DOI: 10.1111/j.1365-2621.1985.tb13024.x

[16] Herbach KM, Stintzing FC, Carle R. Thermal degradation of betacyanins in juices from purple pitaya [Hylocereus polyrhizus (Weber) Britton & Rose] monitored by high-performance liquid chromatography-tandem mass spectrometric analyses. European Food Research and Technology. 2004;219:377-385. DOI: 10.1007/s00217-004-0948-8

[17] Dlamini NR, Taylor JRN, Rooney LW. The effect of sorghum type and processing on the antioxidant properties of African sorghum-based foods. Food Chemistry. 2007;105:1412-1419. DOI: 10.1016/j.foodchem.2007.05.017

[18] Altan A, McCarthy KL, Maskan M. Effect of extrusion process on antioxidant activity, total phenolics and β-glucan content of extrudates developed from barley-fruit and vegetable by-products. International Journal of Food Science and Technology. 2009;44:1263-1271. DOI: 10.1111/j.1365-2621.2009.01956.x

[19] Devi PB, Vijayabharathi R, Sathyabama S, Malleshi NG, Priyadarisini VB. Health benefits of finger millet (Eleusine coracana L.) polyphenols and dietary fiber: A review. Journal of Food Science and Technology. 2014;51:1021-1040. DOI: 10.1007/s13197-011-0584-9

[20] Escalante-Aburto A, Ramírez-Wong B, Torres-Chávez P, López-Cervantes J, Figueroa-Cárdenas JD, Barrón-Hoyos, JM, Morales-Rosas I, Ponce-García N, Gutiérrez-Dorado R. Obtaining ready-to-eat blue corn expanded snacks with anthocyanins using an extrusion process and response surface methodology. Molecules. 2014;19:21066-21084. DOI: 10.3390/molecules191221066

[21] Obradović V, Babić J, Šubarić D, Jozinović A, Ačkar D, Klarčić I. Influence of dried Hokkaido pumpkin and ascorbic acid addition on chemical properties and colour of corn extrudates. Food Chemistry. 2015;183:136-143. DOI: 10.1016/j.foodchem.2015.03.045

[22] Brouillard R. Chemical structure of anthocyanins. In: Markakis P, editor. Anthocyanins as Food Colors. New York: Academic Press Inc; 1982. pp. 1-40

[23] He J, Giusti MM. Anthocyanins: Natural colorants with health-promoting properties. Annual Review of Food Science and Technology. 2010;1:163-187. DOI: 10.1146/annurev.food.080708.100754

[24] Tsuda T. Dietary anthocyanin-rich plants: Biochemical basis and recent progress in health benefits studies. Molecular Nutrition and Food Research. 2012;56:159-170. DOI: 10.1002/mnfr.201100526
[25] Sánchez-Madrigal MÁ, Quintero-Ramos A, Martínez-Bustos F, Meléndez-Pizarro CO, Ruiz-Gutiérrez MG. Effect of different calcium sources on the antioxidant stability of tortilla chips from extruded and nixtamalized blue corn (Zea mays L.) flours. Food Science and Technology. 2014;34:143-149. DOI: 10.1590/S0101-20612014000100021

[26] Zielinski H, Michalska A, Piskula MK, Kozlowska H. Antioxidants in thermally treated buckwheat groats. Molecular Nutrition & Food Research. 2006;50:824-832. DOI: 10.1002/mnfr.200500258

[27] Reyes LF, Villarreal JE, Cisneros-Zevallos L. The increase in antioxidant capacity after wounding depends on the type of fruit or vegetable tissue. Food Chemistry. 2007;101:1254-1262. DOI: 10.1016/j.foodchem.2006.03.032

[28] Rossen JL, Miller RC. Food extrusion. Food Technology. 1973;27:46-53

[29] Harper JM, Clark JP. Food extrusion. C R C Critical Reviews in Food Science and Nutrition. 1979;112:155-215. DOI: 10.1080/10408397909527262

[30] Camire, ME. Extrusion cooking. In: Henry CJK, Chapman C, editors. The Nutrition Handbook for Food Processors. 1st ed. Boca Raton FL: Woodhead Publishing Ltd; 2002. pp. 314-330

[31] Schuler EW. Twin-screw extrusion cooking system for food processing. Cereal Food World. 1986;31:413-416

[32] Muthukumarappan K, Karunanithy Ch. Extrusion process design. In: Ahmed J, Rahman MS, editors. Handbook of Food Process Design. Oxford, UK: Wiley-Blackwell; 2012. pp. 710-742. DOI: 10.1002/9781444398274.ch25

[33] Chinnaswamy R, Hanna MA. Physicochemical and macromolecular properties of starch-cellulose fiber extrudates. Food Structure. 1991;10:229-239

[34] Ding Q, Ainsworth P, Tucker G, Marson H. The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice-based expanded snacks. Journal of Food Engineering. 2005;66. pp. 283-289

[35] Guy RCE, Horne AW. Extrusion and co-extrusion of cereals. In: Blanshard JMV, Mitchell JR, editors. Food Structure–Its Creation and Evaluation. 1st ed. London: Butterworth; 1988. pp. 331-350. ch18

[36] Heldman DR, Hartel RW. Principles of Food Processing. New York: Chapman and Hall; 1997. pp. 253-283

[37] Riaz MN. Selecting the right extruder. In: Guy R, editor. Extrusion Cooking-Technologies and Applications. 1st ed. Cambridge: Woodhead Publishing; 2001. pp. 29-50

[38] Ilo S, Berghofer E. Kinetics of thermomechanical destruction of thiamin during extrusion cooking. Journal of Food Science. 1998;63:312-316. DOI:10.1111/j.1365-2621.1998.tb15732.x
[39] Ilo S, Berghofer E. Kinetics of lysine and other amino acids loss during extrusion cooking of maize grits. Journal of Food Science. 2003;68:496-502. DOI: 10.1111/j.1365-2621.2003.tb05701.x

[40] Plunkett A, Ainsworth P. The influence of barrel temperature and screw speed on the retention of L-ascorbic acid in an extruded rice based snack product. Journal of Food Engineering. 2007;78:1127-1133. DOI: 10.1016/j.foodeng.2005.12.023

[41] Repo-Carrasco-Valencia R, Pena J, Kallio H, Salminen S. Dietary fiber and other functional components in two varieties of crude and extruded kiwicha (Amaranthus caudatus). Journal of Cereal Science. 2009;49:219-224. DOI: 10.1016/j.jcs.2008.10.003

[42] Hirth M, Leiter A, Beck SM, Schuchmann HP. Effect of extrusion cooking process parameters on the retention of bilberry anthocyanins in starch based food. Journal of Food Engineering. 2014a;125:139-146. DOI: 10.1016/j.foodeng.2013.10.034

[43] Hirth M, Preiß R, Mayer-Miebach E, Schuchmann HP. Influence of HTST extrusion cooking process parameters on the stability of anthocyanins, procyanidins and hydroxycinnamic acids as the main bioactive chokeberry polyphenols. LWT - Food Science and Technology. 2014b;62:511-516. DOI: 10.1016/j.lwt.2014.08.032

[44] Jackman RL, Yada RY, Tung MA, Speers RA. Anthocyanins as food colorants: A Review. Journal of Food Biochemistry. 1987;11:201-247. DOI: 10.1111/j.1745-4514.1987.tb00123.x

[45] Brennan C, Brennan M, Derbyshire E, Tiwari BK. Effects of extrusion on the polyphenols, vitamins and antioxidant activity of foods. Trends Food Science and Technology. 2011;22:570-575. DOI: 10.1016/j.tifs.2011.05.007

[46] Hutzler P, Fischbach R, Heller W, Jungblut T, Reuber S, Schmitz R, Veit M, Weissenbock G, Schnitzler J. Tissue localization of phenolic compounds in plants by confocal laser scanning microscopy. Journal of Experimental Botany. 1998;49:953-965. DOI: 10.1093/jxb/49.323.953