

Effect of pH on Color and Texture of Food Products

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Abstract Color and texture are important quality characteristics and major factors affecting sensory perception and consumer acceptance of foods. pH has an important effect on pigments (e.g., chlorophyll, carotenoids, anthocyanins, etc.) responsible for fruit color, vegetables and meat color. Also pH has a great impact on water-holding capacity and tenderness of muscle foods that are improved at acidic conditions below the typical pH of post-mortem. Moreover, during processing of food, the pH value affects many phenomena and processes such as protein properties as denaturizing, gelification, enzymatic activities, growth and mortality of microorganisms, germinating or inactivation of bacterial spores and chemical reactions such as the Maillard reaction. Thus, knowledge of pH effects and its control during processing is necessary to produce safe, high-quality and value-added products. The goal of this paper is to identify the effect of pH on color and texture of food products to show the importance of control this parameter.

Keywords pH · Vegetables · Meat · Fish · Color · Texture

Introduction

From 1980s to the present day, the food industry is driven by consumers' desire for high-quality, minimally processed, additive-free, shelf stable, convenient and safe food products [151]. Hence, a challenge to food processors is to prevent or at least minimize the color and texture degradation to produce high-quality products. In this sense, pH control is very important to prevent color and texture loss. pH, a measurement of the activity of hydronium ions (H_3O^+) in a substance, is a dominant factor that determines the proceeding chemical reaction and hence the quality of the product, particularly in food and biochemical processes [22, 32, 33, 37, 60]. pH was originally defined by Sørensen [133] in 1909 in terms of the concentration of hydrogen ions (in modern nomenclature) as $\text{pH} = -\lg(\text{cH}/\text{c}^\circ)$ where cH is the hydrogen ion concentration in mol dm^{-3} , and $\text{c}^\circ = 1 \text{ mol dm}^{-3}$ is the standard amount concentration.

Conventionally, pH is measured electrochemically using a pH-sensitive glass electrode and a reference electrode. There are, however, numerous alternative methods and devices for pH measurement based on electrochemical and non-electrochemical principles. While the practical use of the available methods and devices is mostly limited to atmospheric pressure pH measurement, there have been some attempts at high pressure pH measurement of water and buffer solutions. Samaranayake and Sastry [119] and Min et al. [89] have recently reviewed these investigations. Since food systems exhibit inherently complex chemistry and are often opaque, none of the methods based on reaction volume, electrical conductivity and spectrophotometry is applicable for high pressure pH measurement of foods. Furthermore, the use of glass electrode assemblies is typically limited to lower pressures ($\leq 150 \text{ MPa}$) due to the fragile nature of glass [25].

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Accurate measurement and reporting of pH data have been a long-standing problem due to the effects of temperature and pressure. An increase in the temperature of any solutions will cause a decrease in its viscosity and an increase in the mobility of its ions in solution. An increase in temperature may also lead to an increase in the number of ions in solution due to the dissociation of molecules (this is particularly true for weak acids and bases). As pH is a measure of the hydrogen ion concentration, a change in the temperature of a solution will be reflected by a subsequent change in pH [7, 169]. pH reaction is difficult to be described with appropriate mathematical models, as it normally comes with inherent nonlinear dynamics with system uncertainty [6, 11].

During processing of food, the pH value affects many phenomena and processes, for example, protein properties as denaturing, gelification, enzymatic activities, the growth and mortality of microorganisms, the germinating or inactivation of bacterial spores and chemical reactions such as the Maillard reaction [136].

Color, flavor and texture are important quality characteristics and major factors affecting sensory perception and consumer acceptance of foods. The pH of most food products varies between 3.5 and 7.0. pH has an important effect on pigments (e.g., chlorophyll, carotenoids, anthocyanins, etc.) responsible for the color of fruits, vegetables and meat. Thus, knowledge of pH is necessary to produce safe, high-quality and value-added products.

Foods are subjected to cooking or processing to increase their edibility and palatability. Processing also aims to prolong the shelf life while the original sensory and nutritional properties are maintained as high as possible within the constraints put forward by microbial safety. To achieve the balance between food quality and safety, there is a need to optimize conventional processing techniques currently applied in food industries and to develop novel processing techniques [99].

The goal of this paper is to identify the effect of pH on color and texture of food products to show the importance of control this parameter in food processing.

The Influence of pH on Color

Color is one of the first quality attributes a customer can detect in food products. It is also the most important attribute used by the customer to evaluate the quality of a product (meat, fish, vegetables and fruits) and its possible taste without touching the commodity [142].

Moreover, fruits and vegetables are good sources of natural antioxidants for the human diet, containing many different antioxidant components which provide protection against harmful free radicals and have been strongly

associated with reduced risk of chronic diseases. These antioxidants include carotenoids, vitamins, flavonoids, other phenolic compounds, dietary glutathione and endogenous metabolites [82]. It is common that many vegetables are cooked by boiling and microwave process before use or industrial process (blanching, canning, sterilization or freezing). These cooking processes or industrial processes would certainly bring about a number of changes in physical characteristics and chemical composition of vegetables [138] affecting the content, composition, antioxidant activity and bioavailability of antioxidants.

In addition, operations such as cutting and slicing may induce a rapid enzymatic depletion of several naturally occurring antioxidants as a result of cellular disruption which allows contacts of substrates and enzymes. Generally, the antioxidant concentrations and activities in processed vegetables were lower than those of the corresponding raw samples. This was caused by their degradation, but also by absorption of water during boiling, which diluted the compounds and decreased their content per weight unit [107].

pH has an important effect on pigments (e.g., chlorophyll, carotenoids, anthocyanins, myoglobin, etc.) responsible for the color of fruits, vegetables and meats. The color compounds of processed fruits and vegetables can change during processing due to the presence of microorganism and the inactivation or not of enzymes, which can result in undesired chemical reactions (both enzymatic and non-enzymatic) in the food matrix.

Chlorophylls

Chlorophylls, the pigments responsible for the characteristic green color of fruits and vegetables, are highly susceptible to degradation during processing, resulting in color changes in food [125].

It is well known that the excessive heating of food products causes considerable losses in the organoleptic quality of food. Blanching inactivates chlorophyllase and enzymes responsible for senescence and rapid loss of green color. However, chlorophyll degradation is initiated by damaged tissue during blanching and other processing steps [58, 142]. There is general agreement that the main cause of green vegetable discoloration during processing is the conversion of chlorophylls to pheophytins by the influence of pH. The green color of vegetables turns to an olive green when heated or placed in acidic conditions [50, 52]. During this reaction, hydrogen ions can transform the chlorophylls to their corresponding pheophytins by substitution of the magnesium ion in the porphyrin ring [90]. The conversion of chlorophyll to pheophytin and pheophorbide results in a change from bright green to dull olive green or olive yellow, which is ultimately perceived by the consumer as a loss of quality [53, 151].

Since chlorophyll stability is known to be affected by pH and color is one of the most important quality attributes of vegetable products, numerous studies have been conducted to investigate the color changes or degradation of chlorophylls during heating [28, 63, 126] through the application of pH control [9, 54], high-temperature short-time processing [123, 137, 148] or a combination of high-temperature short-time processing with pH adjustments [18, 54, 72], and it is reported that the chlorophyll degradation follows a first-order reaction kinetic model [23, 57, 134, 149]. Alkalizing agents in blanch and brine solutions, such as sodium bicarbonate, hexametaphosphate, disodium glutamate, sodium hydroxide, zinc and magnesium hydroxide, have been used to raise the pH of green vegetables and, therefore, retain chlorophyll after processing [9, 49, 80, 84]. Considering that the green color is one of the major sensory characteristics in determining the final quality of thermally processed green vegetables, it is important to prevent or at least minimize chlorophyll degradation during thermal processing in the food industry.

Koca et al. [72] studied the kinetic parameters for chlorophyll *a*, chlorophyll *b* and visual green color degradation as a function of pH in buffered solutions at pH 5.5, 6.5 and 7.5, in blanched green peas at 70, 80, 90 and 100 °C, by high-performance liquid chromatography and tristimulus colorimetry. They concluded that the rate constants of green color loss and chlorophyll degradation decreased with increasing pH, indicating that the green color was retained at higher pH conditions. It was found that chlorophyll *a* degraded faster than chlorophyll *b* at all pH values for each temperature applied. The results revealed that chlorophyll *a* was more susceptible to thermal degradation than chlorophyll *b* in acidic conditions.

At room temperature, chlorophylls *a* and *b* exhibit extreme stability but at temperatures higher than 50 °C treatment affects their stability for example, a significant reduction in the chlorophyll content of broccoli juice (the average ratio of chlorophyll *a* versus chlorophyll *b* used in the study was 2.9:1) was observed for treatments that combined high pressure with temperatures exceeding 50 °C [19, 151]. The temperature dependency of the degradation rate constant of chlorophyll *a* is higher than that of chlorophyll *b*. Van Loey et al. [151] in their study with broccoli juice concluded that chlorophyll *a* is less thermostable as compared to chlorophyll *b*, and hence chlorophyll *a*, which is the major chlorophyll compound in green plants, degrades more quickly.

Ryan-Stoneham and Tong [117] studied the degradation kinetics of chlorophyll in peas as a function of pH. The objective of their investigation was to determine the kinetic parameters of chlorophyll degradation as a function of pH in the constant pH kinetic reactor at pH of 5.5, 6.2, 6.8 and 7.5 and develop a mathematical model that related the rate

constant of chlorophyll as a function of temperature and pH. They concluded that the pH of vegetables during thermal processing is not constant. The magnitude of pH changes is dependent upon the type of vegetable, the initial pH and the time–temperature history of the vegetable of interest (whether high-temperature short-time or low-temperature long-time). The prediction of chlorophyll concentration would be more accurate by treating pH as a variable and by knowing the chlorophyll degradation kinetics as a function of pH. A simpler approach can be applied to improve the accuracy of the prediction assuming the pH of the vegetable remained constant at an average pH value (between the initial and final pH values) and the rate constant at that average pH is known for a specified processing condition and product.

Tijkens et al. [142] modelled the effect of pH on the color degradation of blanched broccoli with five different acids. The fundamental pathways were simplified for the blanched product under study, and attention was solely devoted to the behavior of coloring compounds, expressed as observed color in blanched produce. This simplified model is based on the degradation of chlorophyll and, therefore, the green color, as a function of time and pH. They concluded that color of blanched and thawed broccoli strongly depends on the pH of the surrounding environment. The more acidic, the faster the discoloration. The hydrophobicity of the acids, used to impose a certain pH, had a marked effect on the rate of discoloration: the more hydrophobic, the faster the rate of color change. pH boundaries at the transition between environment and product cannot be neglected. A separate process at neutral and higher pH values gradually takes over the acidic extraction of magnesium ions from the chlorophyll. This latter process is, at least in the pH region studied here, independent of pH.

Anthocyanins

Anthocyanins are water-soluble vacuolar flavonoid pigments; they are widely distributed in nature, among flowers, fruits and vegetable, and are responsible for their bright colors such as green, red and blue [73, 87]. Significant properties of anthocyanin extracts are color density and color hue. These can be affected by pH, SO₂, heat, light, metals, copigmentation and ‘thin film’ effects and others [86]. With increasing pH values anthocyanin color becomes paler, however, if the product being colored contains components capable of acting as copigments, color may be retained and also light stabilized to a certain extent [10].

Anthocyanins become paler on heating, because the equilibrium between the four anthocyanin species shifts toward the colorless carbinol base and chalcone forms [15].

Total anthocyanin color is developed only in strongly acidic solutions. In isolation, anthocyanins have little color above pH 3.5, but in natural media, they become much more colored by copigmentation with other (plant) components, which may themselves be colorless. Based on observations of some relatively simple anthocyanins in vitro, the following scheme, related to pH changes, is generally accepted [17]: at a pH of approximately 3 or lower, the orange, red or purple flavylium cation predominates. As the pH is raised, kinetic and thermodynamic competition occurs between the hydration reaction on position 2 of the flavylium cation and the proton transfer reactions related to its acidic hydroxyl groups. While the first reaction gives colorless carbinol pseudo-bases, which can undergo ring opening to yellow retro-chalcones, the latter reactions give rise to more violet quinonoidal bases. Further deprotonation of the quinonoidal bases can take place at pH between 6 and 7 with the formation of more bluish resonance-stabilized quinonoid anions. At the pH values typical for fresh and processed fruits and vegetables, each anthocyanin will thus most probably be represented by a mixture of equilibrium forms.

Kouniaki et al. [75] studied the stability of two anthocyanins and ascorbic acid present in fruit juices made from blackcurrants at high-pressure processing. Products containing anthocyanins are susceptible to color changes during processing and storage. These changes are due to anthocyanin degradation and brown pigment formation. This has been studied by Kouniaki et al., and results have related anthocyanin stability to the levels of ascorbic acid and phenolic compounds found in fruits. They demonstrated that ascorbic acid apart from being an antioxidant also tends to accelerate the degradation of anthocyanins. The rapid loss of ascorbic acid appeared to contribute to the lower rate of anthocyanin loss (e.g., fridge temperature), whereas the low rate of ascorbic acid loss appeared to result in high anthocyanin losses (e.g., room temperature and 30 °C).

Reyes and Cisneros-Zevallos [113] investigated the thermal stability of aqueous anthocyanins from grape, purple carrot, and purple and red-fleshed sweet potato at pH 3. The results from their investigations showed higher stability by storing extracts at low pH and temperature conditions. The stability of aqueous anthocyanin extracts to pH (≤ 3) followed first-order kinetics. Commercial purple carrot extracts showed the highest stability followed by red-flesh potato extracts, whereas purple-flesh potato and commercial grape were the least stable extracts.

Fan et al. [41] studied the color stability of anthocyanins extracted from fermented purple sweet potato culture at pH 2–7. These studies were limited simple aqueous solution models that mainly contain water. Five major anthocyanins were detected by high-performance liquid chromatography (HPLC). Results shown that purple sweet potato

anthocyanins are more stable under the acid conditions (pH 2.0–4.0) than the subacid conditions (pH 5.0–6.0).

Walkowiak-Tomczak and Czapski [158] investigated the effect of pH (3.0, 4.0 and 5.0), time (0, 15 and 30 days) and temperature of storage (10, 20 and 30 °C), oxygen availability and ascorbic acid (0, 100 and 200 mg/100 g) on anthocyanin stability and color parameters in red cabbage colorant preparations. Red cabbage is a rich source of phenolic compounds, with the anthocyanins being the most abundant class [26, 35, 87, 165, 166]. Walkowiak-Tomczak and Czapski [158] found that during the storage of solutions of red cabbage preparations at 20 mg anthocyanins/100 ml, the content of anthocyanins dropped with increases in pH, ascorbic acid concentration, as storage time and temperature. Moreover, colorant losses were higher in samples stored under aerobic conditions than under relatively anaerobic ones. Anthocyanin losses, considerable at times, were not reflected in a sensory evaluation of a 10-point scale, as all the samples received high scores of color intensity and only the tone changed. Changes in color parameters were, in many cases, also dependent on pH.

Li et al. [83] studied the identification and thermal stability of purple-fleshed sweet potato anthocyanins in aqueous solutions with various pH values and fruit juices. This study aims to identify the constituents of purple-fleshed sweet potato anthocyanins (PSPAs) and investigates the effect of pH value (2–6) on the thermal stability of PSPAs in aqueous solutions at 80, 90 and 100 °C. They concluded that a higher stability of PSPAs was achieved at pH 3 and 4. Apple juice and pear juice colored with PSPAs showed the highest stability during heating at 80–100 °C.

Jing et al. [65] have investigated in radish juice (*Raphanus sativus L.*) (anthocyanin-rich system) thermal and pH stability of anthocyanins and glucosinolates at pH 2.5 or 5.8 for 2 h thermal treatment at 90 or 100 °C. They concluded that thermal treatments at pH 5.8 resulted in more anthocyanin degradation but less glucosinolate degradation than that attainable at pH 2.5. Thermal loss of anthocyanins and glucosinolates were sensitive to different pH environments. Radish juices treated at 100 °C for 2 h had an additional 22.7 or 15.85 % loss in anthocyanins at pH 2.5 and 5.8, respectively, comparing with counterparts treated at 90 °C. However, treatments at 100 °C only caused an additional 10.18 or 11.63 % loss in glucosinolates at pH 2.5 and 5.8, respectively, comparing with counterparts treated at 90 °C. Kirca et al. [71] studied the stability of anthocyanins in both pure black carrot juice and concentrates during heating and storage at various temperatures, soluble solids and pHs and the stability of black carrot anthocyanins in citrate–phosphate buffer solutions at different pHs during heating. They concluded that increasing solid content, pH and temperature, during both

heating and storage, increased the degradation rates of anthocyanins. To minimize anthocyanin degradation, they recommended that black carrot concentrates be cooled, possibly to refrigeration temperatures, as soon as produced. Compared to the stability of anthocyanins from other sources in the literature, anthocyanins from black carrot showed greater stability to heat and pH changes. Such high stability may be attributed to the diacylation of the anthocyanin structure.

Regarding the thermal processing treatments (blanching, boiling and steaming), Volden et al. [156] studied their effects on red cabbage. The investigations of Volden et al. have shown that all manners of processing affected anthocyanins significantly ($p < 0.05$) with reductions of 59, 41 and 29 % for blanching, boiling and steaming, respectively. The reductions observed in the processed cabbage were not fully recovered in the processing waters, fitting the notion that anthocyanins are degraded by heat [86]. However, the extent of heat degradation might depend on various factors related to anthocyanin structure and the pH value. The more stable red-colored structure exists at $\text{pH} < 3$ and, as the pH is raised to 4–6, the colorless structures predominate.

Betalains

Betalains pigments are also water-soluble and usually localized in a unique organelle of plant cell: the vacuole. So far, betalain synthesis has only been observed in plants belonging to the taxonomic group of Centrospermae (red beet, etc.) [122]. The pH-dependent ionization of betalains provided the rationale for the release technique described by Mukundan et al. [94]: Betacyanins and betaxanthins are cations below pH 2.0, zwitterions at pH 2.0, monoanions between pH 2.0 and pH 3.5 and bisanions above pH 3.5 and 7.5 [114]. At pH 2, the zwitterionic state might permit diffusion and release from the vacuole. This behavior is similar to ion trapping where metabolites, such as alkaloids, are retained within the vacuole as a result of acquiring a net charge at the acidic vacuolar pH [112]. The observed release kinetics of betalains extends well beyond the low-pH treatment, which suggests that the observed mechanism involves an alteration in membrane properties and possibly preferential death of the pigment-containing cortical cells. This release kinetics is actually fortuitous in terms of recovery since betalains are most stable between pH 3.5–6.5 and have limited stability at pH 2 [98]. Therefore, the procedure of acidic exposure followed by release of the pigments into B5 medium [46] of pH 5.5 facilitates recovery under stable conditions. In this regard, the low-pH-mediated release of betalains is substantially different from that reported previously, where alterations of medium pH have been used to facilitate release of

secondary metabolites from plant tissue culture [64, 118]. For alkaloids in particular, the acid dissociation constant (pK_a) is sufficiently close to the physiological pH for the medium pH to be altered without necessarily disrupting the tissue. Under these conditions, concepts of equilibrium partitioning can be useful to describe release [112], and the acidified medium pH must be maintained throughout the release period.

Moßhammer et al. [93] investigated the visual appearance and pigment stability of fruit juice blends from *Opuntia* and *Hylocereus cacti* and of betalain-containing model solutions derived therefrom at pH values ranging from 3 to 7. Results revealed that highest betalain stability at pH 5 coming close to the pH values of cactus pear (pH 5.8) and purple pitaya juice (pH 4.5), respectively. This result is concordant with previous findings of Cai et al. [20], Cai et al. [21], Castellar et al. [24], Coskuner et al. [31], Huang and von Elbe [62], Pátkai and Barta [103], Von Elbe et al. [157] providing evidence of maximum betalain stability at pH values close to the natural pH values of the respective betalain-containing plant tissue.

Carotenes

Carotenoids are a class of natural pigments mainly found in fruits and vegetables that typically have 40-carbon molecules and multiple conjugated double bonds [40]. Carotenoids are usually divided into two categories: (1) carotenes comprised entirely of carbon and hydrogen, for example, α -carotene, β -carotene and lycopene; and (2) xanthophylls comprised of carbon, hydrogen and oxygen, for example, lutein and zeaxanthin [40]. Carotenoids may be beneficial to human health when consumed at appropriate levels [69]. The relatively low bioavailability of carotenoids from natural sources has been attributed to the fact that they exist as either crystals or within protein complexes in fruit and vegetables that are not fully released during digestion within the gastrointestinal tract [164]. A number of studies have shown that carotenoid bioavailability depends strongly on the composition and structure of the food matrix in which they are dispersed [39, 140, 146, 147]. Carotenoids are also strongly colored (red/orange/yellow), which limits the types of foods that they can be incorporated into. Finally, carotenoids are highly prone to chemical degradation during food processing and storage due to the effects of chemical, mechanical and thermal stresses [85, 97, 139, 167].

Qian et al. [109] studied the physical and chemical stability of β -carotene-enriched nanoemulsions and the influence of pH, ionic strength, temperature and emulsifier type. The emulsion samples were prepared in aqueous buffer solutions, and then, the pH was adjusted to the desired final value (pH 3–8) using either NaOH and/or HCl

solution. Emulsion samples (20 mL) were then transferred into glass tubes, stored in a dark place at ambient temperature (≈ 25 °C) for 5 days and total color difference (ΔE^*) was measured each day. They concluded that the rate of color degradation was appreciably faster at pH 3 than at higher pH values, since the overall change in color during storage was relatively small in the samples with pH values 4–8 ($\Delta E^* < 10$). Additionally, the rate of color fading increased with increasing storage temperature, was fastest at the most acidic pH value (pH 3) and was largely independent of salt concentration (0–500 mM NaCl). Previous studies have also found that the rate of carotenoid (lycopene) degradation in O/W emulsions was higher at acidic pH values [12]. Studies carried out to determine the mechanism of carotenoid instability in the presence of acids have shown that carotenoids are protonated and then undergo cis–trans isomerisation and additional degradation reactions [91, 92].

Zechmeister [168] has been reported that a high concentration of acid can result in isomerization of β -carotene. However, in some other papers, pH has been reported to have only a minor effect of β -carotene isomerization in solvents or in food systems [124, 128]. Apparently, the effect of pH on β -carotene stability can be attributed to time of exposure to acid, concentration of acid, and the system in which β -carotene exists.

Chen et al. [29] studied the effect of processing methods on changes of color, carotenoids and vitamin A contents in carrot juice. As carrots are low-acid (pH 5.5–6.5) foods, the sterilization of carrot juice under high temperature is often required. However, this treatment can result in great loss of color [135]. To minimize loss of color and carotenoid content, the raw carrot juice is often acidified before processing so that the sterilization can be lowered. Results indicated that after the carrot juice was heated immediately following acidification, the short exposure time of β -carotene to acid did not result in isomerization. It has been reported that blanching carrots with acid can increase the brightness of carrot juice and decrease the precipitation of carrot juice during processing [135]. Sims et al. [131] also demonstrated that blanching carrots with acid can improve the color and turbidity of heated or canned juice.

Myoglobin

Muscle pH has been shown to be primarily related to the biochemical state of the muscle at time of slaughter and following rigor mortis development. Both of these factors contribute to meat color and the occurrence of meat color defects [42]. The appearance of cooked meat can be influenced by pH, meat source, packaging conditions, freezing history, fat content, added ingredients and preservation treatments such as irradiation and pressure. These

factors change the ratio of different forms of myoglobin; the main pigments responsible for the ultimate color of meat [70].

The amount of ferrihemochrome formation from myoglobin during cooking is affected by initial meat pH. While mammalian muscle has a pH of around 7, normal fresh meat has a pH ranging from 5.4 to 5.6 [153]. The carbohydrate glycogen is held in the muscles, but with post-mortem reduction in oxygen supply, the glycogen is broken down to lactic acid, lowering the pH. This acidification process will continue until either the glycogen is consumed or the low pH inactivates glycolytic enzymes. Where glycogen is limited, such as in animals that are very active, stressed or exposed to cold over a long period prior to slaughter, the ultimate pH of the meat is higher. Meat with a pH above 6.2 tends to have tightly packed water-retaining fibers that impede oxygen transfer and promote longer survival of oxygen-scavenging enzymes, favoring deoxyMb rather than oxyMb. The purple-red myoglobin combines with the closed structure of the muscle to absorb rather than reflect light, making the meat appear dark. This condition is commonly known as dark, firm, dry (DFD) [1, 159].

Several studies have identified a correlation between raw beef pH and the amount of undenatured myoglobin remaining in the cooked product, which itself correlates with red color. When compared normal pH beef with high-pH beef the proportion of myoglobin denatured during cooking is less in high-pH beef samples and a more intense red color is measurable [70].

In ground beef with the pH artificially adjusted, patties with elevated pH required higher final endpoint temperatures to denature similar amounts of myoglobin than patties with lower pH [14].

Schmidt and Trout [121] demonstrated that even when cooked to the same internal temperature, high-pH beef, pork and turkey muscle (pH > 6.0) was redder than low-pH muscle (pH > 5.5) and appeared undercooked. These authors suggested that the high-pH muscle reduced the amount of myoglobin denatured at a given temperature. Trout [144] reported that at temperatures from 55 to 83 °C, the presence of sodium chloride and sodium tripolyphosphate increased the percentage of myoglobin denatured. High-pH muscle markedly decreased the percentage of myoglobin denatured producing obvious color differences in the cooked muscles. Trout [144] concluded that the pink color found in fully cooked high-pH meat products appeared to be due to: (1) incomplete myoglobin denaturation at low temperatures (<70 °C) and (2) formation of a pink hemochrome at higher temperatures (>76 °C).

The effect of pH on meat color is complex. One effect, as noted earlier, is that many of the haem-associated reactions are pH dependent. In addition, muscle pH affects the water binding nature of the proteins and therefore

directly affects the physical structure of the meat and its light reflecting properties [16]. Also, pH affects enzymatic activity of the mitochondrial system thereby altering the oxygen availability for haem reactivity [5, 30].

The Influence of pH on Texture

Texture of food products is one of the most important quality attributes, as it influences consumer acceptability. Texture in vegetables is often related to cell wall structure and composition but also to other factors, including cell morphology, size, shape, packing, contents and turgor [56]. In meat and fish, the texture is associated with the rate of glycolysis, the decrease in temperature post-mortem and the ultimate pH in the muscles, as suggested in the studies with bovine muscles reported by Koohmaraie [74] and Pérez et al. [106].

Fruits and Vegetables

Texture changes in fruits and vegetables can be related to transformations in cell wall and middle lamella polysaccharides due to enzymatic and non-enzymatic reactions [129]. Most of these changes are strongly influenced by the raw material properties, the (pre-) processing steps and conditions. Substrates, ions and enzymes which are located in different compartments in the cells can be liberated and interact with each other during heat treatment. Since pectic substances make up about 30 % of the dry matter in the primary cell wall and are the primary macromolecules of the middle lamella, chemical pectin changes play a role in process-induced textural changes: (1) enzymatic degradation by the successive demethoxylation and depolymerisation by pectin methylesterase and polygalacturonase, respectively, and (2) chemical degradation via a β -elimination reaction or acid hydrolysis [150].

In vegetables and fruits, thermal processing causes a pronounced degradation of the pectic polysaccharides resulting in reduced intercellular adhesion and consequently in increased softening. At $\text{pH} \geq 4.5$, softening is consistent with a depolymerisation reaction that has the characteristics of a beta-elimination reaction catalyzed by hydroxyl ions and inhibited by demethoxylation of pectin [130].

Pectin shows a high stability in aqueous solutions at pH 3.0–4.0. Nonetheless, three processes are known so far that lead to non-enzymatic pectin degradation. First, the fragmentation of the polymer can occur *in planta* due to highly reactive hydroxyl radicals [45]. Increasing evidence suggests that these reactions are part of the mechanisms that drive wall restructuring. During thermal processing, pectin may undergo either acid or base catalyzed depolymerization. At low pH (≤ 3.5), acid hydrolysis is proposed despite

some doubts [76]. Under these conditions, which are not common during regular food handling and processing, low methoxy pectin depolymerizes faster than high methoxy pectin. At higher pHs (≥ 4.5) and at elevated temperatures ($>80^\circ\text{C}$), a prevalent condition in most thermally processed plant-based foods, base catalyzed depolymerization (β -elimination reaction) of pectin is quite relevant [3, 51].

Brandt et al. [13] measured the effects of cooking vegetables at various pHs on the individual dietary fiber components of those vegetables using a stepwise extraction technique and to relate these changes to the resulting textural changes.

They found that in the raw state, the firmness was found to decrease in the following order: cauliflower, beans, potatoes, peas and corn. All of the vegetables were firmest at pH 4 in the cooked state. In general, the vegetables were softest at pH 10; at pH 2, the firmness was only surpassed by the results of pH 4. These results agree favorably with those of Doesburg [34] who showed that plant tissues possess maximum firmness at pH 4.0–4.5. He observed decreased firmness at pH values both higher and lower than pH 4. Beans and cauliflower showed the most dramatic changes due to cooking media. They exhibited significant linear effects since their firmness decreased as pH increased. In general, the most cooking solution fiber was extracted at pH 10, the lowest amount at pH 4. Those vegetables which showed the largest changes in shear values upon cooking also showed the greatest amount of material extracted into the cooking media. Cauliflower and peas showed the most material extracted into the cooking media, followed by beans, potatoes and corn. Pectin is usually thought to be stable in acid and unstable in alkali [68]. Corn and potatoes displayed no significant changes in water-insoluble hemicellulose from pH 2 to pH 10. Van Soest and Robertson [152] and Heller et al. [59] found that most plant tissues show increased soluble hemicellulose at both high- and low-pH values; at neutral pH, hemicellulose is the least soluble. The data showed no significant changes in cellulose with cooking which correlated with the strongly acidic conditions needed to degrade cellulose.

Ben-Shalom et al. [8] studied the effect of acidification (pH values: 6.2, 4.4 and 3.9) following blanching on the firmness of the carrot tissue. Blanching the carrot tissue at pH 6.2 caused a significant reduction (about 70 %) in the firmness of the carrot tissue. Acidifying and blanching the tissue at pH 4.4 improved the firmness almost 50 %, as compared with blanching the tissue at pH 6.2. But acidifying the tissue to pH 3.9 and blanching it decreased its firmness to the same value as at pH 6.2. It appeared that the degradation of firmness in carrot tissue during heat treatment occurred by two different mechanisms—one at neutral pH and another at pH 3.9 since at an intermediate pH the degradation was much less. They concluded that

reducing the pH of the carrot tissue before blanching at 4.4, the loss of tissue firmness was reduced.

Meat and Fish

Muscle pH has been associated with numerous other meat quality attributes including tenderness, water-holding capacity, cooking loss and microbial stability (shelf life) [42]. Texture (tenderness) has been identified as the most important factor determining the consumer-eating satisfaction of beef. Meat tenderness depends on a number of biological (e.g., species, age, sex and muscle type) and environmental (nutrition, ante-mortem stress, slaughter and chilling conditions, aging) factors [132].

Texture is associated with the rate of glycolysis, the decrease in temperature post-mortem and the ultimate pH in bovine muscles that may vary between 5.4 and 7.2 [74, 106]. The relationship between ultimate pH and tenderness is controversial. Some authors indicate a linear dependence between these two parameters, but more found a curvilinear dependence with maximal toughness for meat with pH values in the range 5.8–6.3. It can be explained on the basis of different proteolytic activity that leads to the lowest tenderisation during aging [106, 108, 160]. Thus, the increasing tenderness found as the pH rises from 6 to 7 is attributed to greater calpain activity, which is maximal at neutral pH.

In contrast, the increasing tenderness as pH falls below 6.0 has been attributed to enhanced acidic protease activity. Watanabe et al. [160] also suggested non-enzymatic causes of the increased meat toughness at pH values in the range 5.8–6.3. The authors recognized that reduced sarcomere length is an important cause of increased toughness in meat, and it appears that sarcomeres increase in length as the ultimate pH decreases below 6.2. Alternatively, tenderisation has been attributed to the direct effect of calcium ions on myofibrillar proteins, without involvement of enzymatic proteolysis, and this process has been shown to be pH dependent. The toughness of meat immediately post-mortem is the same whether the meat is of low, medium or high pH, when the aging is inhibited by $ZnCl_2$. Following limited aging, Watanabe et al. [160] found a curvilinear relationship between pH and shear force values, with a toughness peak at pH 6.07. However, the authors concluded that continued aging eventually achieves the same degree of tenderness at all pH values.

Marination is widely used by consumers to improve meat tenderness and flavor [163]. Artificial tenderization by acid marination, the soaking of meat in acid solution, is a commonly used culinary technique [2]. Marination affects tenderness in 3 ways, potentially: (1) pH-induced swelling of muscle fibers and/or connective tissue; (2) accelerated or additional proteolytic weakening of muscle structure and (3) increased solubilization of collagen upon

cooking [38, 100, 101]. Howat et al. [61] reported that meat tenderness was not increased by marination in weak acid (pH 2.56). However, Wenham and Locker [161] and Gault [47, 48] showed that tenderness of meats marinated with acid solutions (pH 2.58–3.17) increased, while Seuss and Martin [127] showed that meat became somewhat more tender as acid concentration increased at pH values between 1.8 and 3.0. The tenderization observed at pH values below 5.0 was believed to be caused mainly by the effects of acid pH on the water-holding capacity of muscle proteins. Oreskovich et al. [102] marinated meat with 0.1 M phosphate buffers ranging in pH from 3.25 to 10.15, 0.1 M sodium chloride, 0.4 M phosphoric acid or 0.7 M acetic acid. They reported that low muscle pH after marination had positive effects on texture and resulted in increased water-binding capacity, moisture content and decreased cooking losses.

Results showed that acid injection and marination improve the water-holding capacity and tenderness of muscle foods, as many researchers have observed that the water-holding capacity of muscle and the tenderness increases when the pH is below the isoelectric point of the major myofibrillar proteins [47, 55, 111].

Aktas et al. [2] studied the effect of organic acid marination on tenderness, cooking loss and bound water content of beef, using 0.5, 1.0 and 1.5 % of lactic and citric acid solutions. Beef was marinated in these solutions for 72 h at 4 °C into plastic bags. They reported that acid type and concentration had significant effects on pH values and moisture content. Compared to citric acid (pH: 2.67, 2.52 and 2.4), samples marinated with lactic acid (pH: 2.73, 2.50 and 2.40) had lower pH values, probably due to the different pH values of the individual acids, resulting in stronger acidification of the solutions and subsequently, of the muscles themselves. Additionally, the authors found that low muscle pH induced by marination resulted in increased binding of water, as the percentage of bound water decreased when muscle pH was lower than that of normal muscle. Results suggested that substantial changes in meat tenderness can be achieved by altering the pH of the meat. The tenderization mechanism is likely to involve pH-induced swelling of the muscle structure.

While acidification of meat could improve texture, it might adversely impact flavor. Factors such as pre-slaughter stress and physical damage, post-slaughter carcass temperature, pH value, extent of thermal processing, grinding, deboning, and the use of additives such as salt, nitrite and antioxidants can all affect the rate and extent of lipid oxidation in muscle foods [88]. Tichivangana and Morrissey [141] found that pH had a significant effect on lipid oxidation in cooked minced muscle systems. Lipid oxidation at pH 7.0 was much slower than pH 3 or 5 in all

muscle systems including fish, turkey, chicken, pork, beef and lamb.

Ke et al. [67] investigated the impact of citric acid on the tenderness, microstructure and oxidative stability of beef muscle. They initially reduced raw beef muscle pH with citric acid below the post-mortem pH (pH 5.5–3.5) to alter texture, followed by an increase in pH to reduce sourness while leaving citric acid in the muscle to inhibit lipid oxidation. Decreasing pH in beef with citric acid did not result in an increase in lipid oxidation rates when the beef was cooked. In addition, when the pH of the beef containing citric acid was increased back to the pH of the control meat lipid oxidation rates remained low compared to beef without citric acid, suggesting that the citric acid and not pH variations were responsible for decreasing lipid oxidation in cooked beef. Citrate can inhibit lipid oxidation by binding prooxidant metals via bonds formed between the metal and the carbonyl or hydroxyl groups of the citric acid molecule [43]. The citric acid acidification not only improved the water-holding capacity and tenderness of beef muscle, but also inhibited lipid oxidation induced by a combination of oxidative stress factors (e.g., acid pH, grinding, tumbling and heating).

Gelification, based in gelation that is an important functional property of fish muscle protein, is another common used culinary technique. Gel formation involves partial denaturation of protein followed by irreversible aggregation which results in a three-dimensional network [81]. Different structural changes and protein–protein interactions of myofibrillar proteins occurred during gelation [27]. These protein–protein interactions are influenced by several factors including protein concentration, pH, temperature, pressure, ionic strength and type of ion [143].

Although fish protein gels are commonly produced using heat treatment, myofibrillar proteins were reported to undergo gelation under mild acidic conditions [27, 44, 95, 96, 116, 120, 154, 155]. Glucono- δ -lactone (GDL) as an acidulant has been widely used in acidified gel food products to improve product texture, which can be slowly hydrolyzed into gluconic acid in the present of water, resulting in a slow lowering in pH of the products [4, 36, 145]. Lowering the pH slowly allows for a slower rate of denaturation and aggregation of the protein molecules, favoring the ordered protein–protein interactions required for strong gel formation [96, 143, 154].

Myosin is abundant in muscle protein and plays a key role in gel development in fish and meat products. Altering the pH of meat products could result in the attainment of the desired gel strength at a given temperature [162]. For instance, textural development of fermented fish and meat products was associated with lowering pH during fermentation [115]. Subjecting catfish myosin to pH 11.0–12.0 and subsequent readjustment to pH 7.3 increased the elastic

modulus of thermally treated myosin [110]. In addition, alkaline solubilization processing could also produce higher gelling quality than conventionally washed surimi from Atlantic menhaden [79, 105]. Some researchers suggested that conformational changes in the myofibrillar proteins during alkaline processing may expose more functional groups for transglutaminase-induced crosslinking and other protein–protein interactions [77, 78, 104]. Nevertheless, the initial washing at pH 5.5 was beneficial for suitable treatment for kamaboko gels from sardine [66].

Conclusions

This review shows several studies that exhibit the influence and the effect of pH on some physico-chemical changes and the importance of their control in food process. pH affects the color and texture of food products and understanding the direction of the change is very important to modify the final result.

Nevertheless, the effect of pH on physico-chemical properties cannot be generalized since the study on basic insight into this subject is still limited and the physico-chemical properties are product dependent. This issue is interesting and important for further investigation.

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