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Review Article

Nonenzymatic Browning and Antioxidant Properties of Thermally Treated Cereal Grains and End Products

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Thermal treatment can be applied to cereal grains as a pretreatment or processing step in the form of either hydrothermal or dry thermal treatment. These heat treatments result in the occurrence of nonenzymatic browning reactions by means of the Maillard reaction and caramelisation. Nonenzymatic browning is influenced by the type and concentration of sugars and proteins, and the presence of bran. Aside from increasing nonenzymatic browning, thermal treatment increases the antioxidant capacity of cereals and baked goods through the release of bound phenolics. The degree of nonenzymatic browning and antioxidant content in cereal-based products depend on the thermal treatment intensity. Some studies found a decrease in total phenolic content after thermal treatment, due to loss of thermally labile compounds. High-intensity treatment has been shown to produce 5-hydroxymethylfurfural (HMF), furfural, and potentially carcinogenic acrylamide. Acrylamide formation can be mitigated by altering the ingredient composition and the degree of thermal treatment. This review discusses the chemistry of nonenzymatic browning reactions, factors influencing the degree of these reactions, and mitigation strategies for acrylamide. An overview of the effect of dry thermal treatment on nonenzymatic browning and antioxidants in wheat and wheat-based products as well as other cereals is provided. Before concluding with perspectives, a discussion of the relationship between nonenzymatic browning and antioxidant properties is presented. This review of the published literature was conducted using two electronic databases and varying combinations of search terms related to the scope of the review.

1. Introduction

Cereal grains may be subjected to thermal treatment as a pretreatment of the whole grain to modify flour properties or as a processing step during the production of end products. There are two types of thermal treatments, categorised as either hydrothermal [1] or dry thermal [2], depending on whether water is added. During both treatments, the grains, flour, or products are exposed to temperatures high enough to cause nonenzymatic browning [3]. High moisture levels, however, prevent these reactions in hydrothermal treatment. Dry thermal treatment, on the other hand, provides ideal conditions for the occurrence of nonenzymatic browning reactions [4]. As the moisture content decreases, the concentration of reactants (amino acids and reducing sugars) increases and the elevated temperatures increase the rate of reaction between these compounds [5].

Nonenzymatic browning reactions occur during heat treatment of foods as either the Maillard reaction, caramelisation, or ascorbic acid browning, depending on the involvement of nitrogen-containing compounds such as amino acids [4]. The Maillard reaction, first discovered in 1912 by French chemist Louis Camille Maillard, involves a reaction between amino acids and reducing sugars at high temperatures [6]. In contrast, caramelisation involves both reducing and nonreducing sugars in the absence of amino compounds when food is heated in either acidic or alkaline conditions [4]. The Maillard reaction and caramelisation are important in thermally treated grains and final products as both result in changes to the colour, texture [7], and sensory acceptability [8]. The Maillard reaction may also occur in food and food products during storage at low temperatures for extended periods.

Nonenzymatic browning reactions have been shown to also produce the toxic compounds 5-hydroxymethylfurfural

(HMF), furfural, and potentially carcinogenic acrylamide [6, 9]. Despite this drawback, it has been reported that formation of melanoidins and Maillard reaction products during nonenzymatic browning [10] resulted in an increase in antioxidant content and activity in barley [11], rye [12], and wheat bread [13–15]. Additionally, the formation of acrylamide can be reduced by applying mitigation strategies such as modified baking atmospheres to slow the rate of reaction [16] and enzyme treatment to reduce the availability of reactants [17].

In cereal grains, antioxidants are concentrated in the bran and consist of phenolic compounds, pigments, flavonoids, and vitamin E [18]. These compounds exhibit different mechanisms of antioxidant activity [19] and generally have a low bioavailability due to covalent bonds between the antioxidants and indigestible polysaccharides of the cell walls [20]. Exposure to thermal treatment increases antioxidant activity by releasing bound compounds and increasing the extractability as well as the production of new compounds which have antioxidant properties [14, 15, 21, 22].

This review aimed to provide an overview of thermal treatment, nonenzymatic browning, and antioxidants in cereal grains and cereal-based products. The review of the current literature focused on dry thermal treatment, factors influencing the degree of nonenzymatic browning, changes in antioxidant activity and total phenolic content, and acrylamide mitigation. Following the description of the research methodology, a brief discussion of hydrothermal and dry thermal treatments is provided by means of an overview of nonenzymatic browning and antioxidant properties of cereals. Published research related to the effect of dry thermal treatment on nonenzymatic browning and antioxidants are summarised and critically reviewed. Furthermore, mitigation strategies for acrylamide, HMF, and furfural, and the Maillard reaction products of concern for food producers, are reviewed. The relationship between nonenzymatic browning and antioxidant properties is discussed before concluding with perspectives.

2. Literature Review Research Methodology

Two electronic databases, i.e., Google Scholar and ScienceDirect were used to search for publications related to thermal treatment, nonenzymatic browning, and antioxidant properties of cereal grains. This review was not systematic in nature, however, the following search terms were used to obtain published articles between the years of 2005 and 2023 related to the objectives of this review: ("non-enzymatic browning" OR "Maillard") AND ("wheat" OR "cereal" OR "cereal grains"); ("thermal treatment" OR "dry thermal treatment" OR "roasting") AND ("non-enzymatic browning" OR "Maillard") AND ("wheat" OR "cereal" OR "cereal grains"); ("thermal treatment" OR "dry thermal treatment" OR "roasting") AND ("non-enzymatic browning" OR "Maillard") AND ("wheat" OR "cereal" OR "cereal grains") AND ("antioxidants" OR "antioxidant properties" OR "phenolics"); ("acrylamide") AND ("mitigation"); ("non-enzymatic browning" or "Maillard") AND ("acrylamide") AND ("mitigation"); ("HMF" or "hydroxymethylfurfural") AND ("mitigation").

3. Thermal Treatment of Cereal Grains

Thermal treatment of cereal grains, before and/or during processing, comprises hydrothermal [1] and dry thermal [2] treatment. Studies on dry thermal treatment, causing nonenzymatic browning, are however more extensive [23].

3.1. Hydrothermal Treatment. Hydrothermal treatment is mainly applied as a pretreatment to modify starch properties of flours, such as improving the water absorption capacity [24] and thermal stability [25], increasing the pasting and gelatinisation temperature [26], and decreasing starch retrogradation [24]. The two types of hydrothermal treatments typically applied to cereals, i.e., annealing (ANN) and heat moisture treatment (HMT), differ in moisture content and the temperature applied [1]. During ANN, the grains are exposed to temperatures between the glass transition temperature (Tg) and the onset temperature of gelatinisation (To) with excess (>60%) or intermediate (>40%) moisture levels for a set period [27]. The Tg is a narrow range of temperatures in which the glassy, rigid amorphous regions of the starch change to a more flexible state [28, 29]. The To represents the temperature at which the starch granules in excess water swell irreversibly and start to lose its crystalline structure [30]. HMT, on the other hand, uses low moisture levels (<35%) at temperatures above Tg and below To (84–120°C) for specified periods of time. This combination of temperature and moisture levels is insufficient for starch gelatinisation [25, 27, 31] and results in only partial gelatinisation.

Both ANN and HMT have been applied to different cereals to improve starch properties and functionality. In the case of rice, maize, and millet, it has been used to modify properties such as gelatinisation, pasting, and retrogradation [31]. This has been investigated specifically for end uses such as noodle production [32], breadmaking [33], and biscuit and gluten-free cake production [34].

3.2. Dry Thermal Treatment. Dry thermal treatment involves the simultaneous occurrence of heat and mass transfer, leading to changes in physicochemical and functional properties of the grains by increasing the temperature and reducing its moisture content [35]. These methods include roasting, radiation, and methods using pressure change [2].

For dry thermal pretreatment of grains and flours, roasting methods comprise conventional sand, pan, oven, forced convection continuous tumble (FCCT), and fluidised bed roasting [36]. Roasting has been applied to improve the rheological and functional properties of sorghum [8], sensory properties of soybean [7], physicochemical, structural, and functional properties of wheat [37], as well as nutritional and antioxidant properties of barley [11, 38] and maize [39]. Microwave and infrared radiation were applied to improve functional and rheological properties of wheat [37] and sorghum [40] as well as increase the antioxidant properties of buckwheat [41] and maize [42]. Pressure change methods, including superheated steam, vacuum steam, and gun puffing [2], have been applied to wheat to combat microbial growth [43] and improve cake volume, and sensory properties [44], respectively. Dry thermal treatment can therefore be applied to improve safety and shelf life by inactivating pathogenic microorganisms [43].

Inactivation of the endogenous enzymes associated with lipid oxidation as well as protein and starch degradation [45] has been observed in highland barley without significant changes to flour functionality. The enzymes were inactivated by roasting the barley at 20% moisture content, as the presence of water increases the sensitivity of the enzymes to thermal inactivation [45, 46]. Thermal inactivation of enzymes involves protein denaturation, resulting in a loss of the ability to catalyse reactions [47].

Dry thermal treatment was also shown to cause changes in the antioxidant properties of barley [48], sorghum [40], wheat bread [14, 15], and maize biscuits [49]. These changes included increased free phenolic and total phenolic content and an increased antioxidant activity, attributed to the release of bound phenolic compounds because of thermal damage to cell structures [50]. Moreover, dry thermal treatment enabled the occurrence of nonenzymatic browning reactions, which led to the production of new antioxidant compounds [22, 51].

In addition to the influence of the type and concentration of amino acids as well as the reducing sugars available, the rate of nonenzymatic browning reactions also depends on the temperature and time of exposure to dry thermal treatment [6]. Therefore, changing the time-temperature conditions will greatly influence the extent of the nonenzymatic browning reactions. When nonenzymatic browning reactions occur, colour and flavour compounds are formed which affect the sensory attributes of end products produced from thermally treated grains [8]. The products of the nonenzymatic browning reactions have been shown to contribute to increased antioxidant activity and phenolic content [13–15]. In contrast, the increase of nonenzymatic browning reactions also resulted in a decrease in protein digestibility and the production of the carcinogenic compound acrylamide [6].

4. Chemistry of Nonenzymatic Browning in Cereal Grains

Nonenzymatic browning refers to the chemical reactions that occur during the heat treatment of foods. Three types of nonenzymatic browning that can occur during thermal treatment or prolonged storage of food include the Maillard reaction, caramelisation, and ascorbic acid browning. The two main types that occur simultaneously in cereal grains and cereal-based products are the Maillard reaction and caramelisation [4].

4.1. Maillard Reaction. The Maillard reaction starts with a condensation reaction between the carbonyl group of a reducing sugar and a free amine group of an amino acid, peptide, or protein when exposed to high temperatures such as during baking, roasting, and extrusion [52]. This is followed by a series of complex chemical reactions which result in the formation of colour and flavour compounds [53]. A detailed schematic of the chemical reactions, intermediates, and end products of the Maillard reaction is shown in Figure 1.

During the initial stage of the Maillard reaction, the carbonyl group from a reducing sugar and the amine group from an amino compound undergo a dehydration reaction. This is followed by the Amadori rearrangement reaction, yielding the Amadori compound [4]. After the initial phase, the Amadori compound and reducing sugars undergo dehydration, fragmentation, Strecker degradation, and aldol condensation to form the end products of the Maillard reaction [52]. These compounds are biopolymers known as melanoidins and are responsible for the desirable changes to colour [54] and flavour [55]. They also have antimicrobial, antiallergenic, and antioxidant properties [6].

Under controlled conditions, the Maillard reaction is desirable as it improves sensory properties through the production of Amadori rearrangement products, melanoidins, and other reaction products such as pyrazines [56], contributing to colour, flavour, and aroma [57]. However, despite these beneficial changes, the involvement of proteins in this reaction results in a loss of the biological value of essential amino acids, causing undesirable changes to the nutritional profile [6]. In addition to melanoidin formation, the Maillard reaction also leads to the formation of potentially toxic and carcinogenic compounds such as 5-hydroxymethylfurfural (HMF) and acrylamide [6, 53, 58]. Although HMF has been shown to provide beneficial effects such as antioxidant activity [59], antiallergy [60], and anti-inflammatory properties [61], it has also been described as having mutagenic, genotoxic, and carcinogenic effects [62, 63]. As reviewed by Capuano and Fogliano [64], the toxicity and carcinogenic effects have been widely studied in rats and rodents. In these studies, the animals were exposed to HMF concentrations of 188 to 750 mg/kg, which is much higher than the estimated dietary HMF intake of 1.6 mg/person per day in humans. Therefore, the safe consumption levels of HMF for humans are still unclear, since HMF metabolism varies between individuals [65].

Acrylamide has been classified as a possible carcinogen to humans [9] and has shown the risk of inducing cancers including prostate cancer [66], breast cancer [67], lymphoma [68], and lung cancer [69] among others. Although the European Food Safety Authority could not establish a tolerable dose of acrylamide, the average chronic dietary exposure of adults is estimated to be between 0.4 and 0.9 μg/kg body weight per day. Cereal-based products are the second main contributor to dietary acrylamide exposure following potato products. The main precursor for acrylamide formation is free asparagine (in the presence of reducing sugars), which is concentrated in the aleurone layer and remains attached to the bran during milling [70]. Following the formation of the Amadori compound in the initial stages of the Maillard reaction, two pathways exist for acrylamide formation [71], either via the Schiff base or a carbanion intermediate. A schematic of these two pathways, leading to acrylamide formation, is shown in Figure 2.

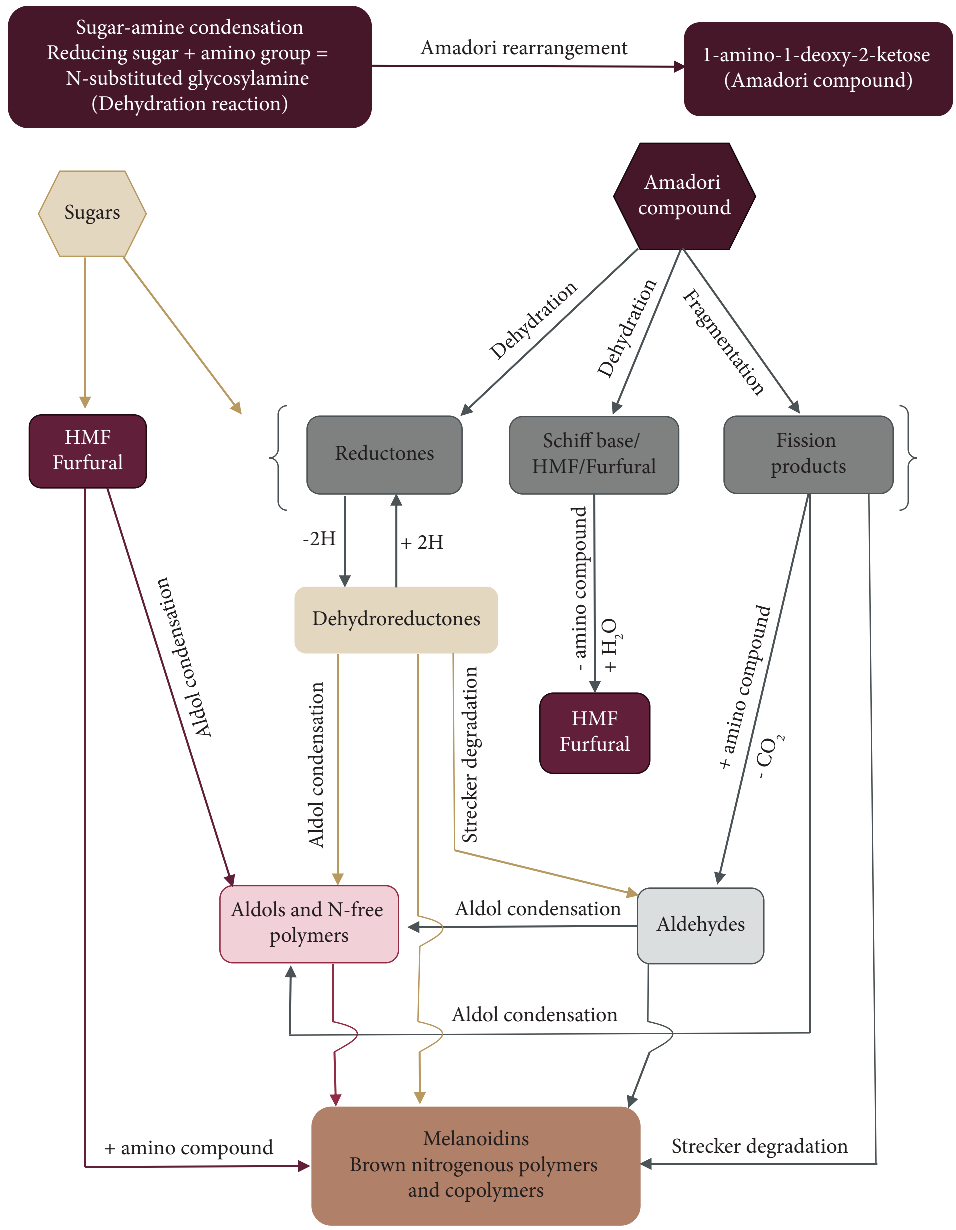

Figure 1: Schematic of the chemical reactions, intermediates, and end products of the Maillard reaction (based on Nursten [52]).

4.2. Caramelisation. Caramelisation involves the degradation and isomerisation of sugars when heated to high temperatures in the absence of nitrogen-containing compounds in either acidic or alkaline conditions [4]. These reactions can follow many different pathways depending on the environmental conditions such as pH, temperature, sucrose concentration, and the presence of impurities [72]. As represented in Figure 3, caramelisation starts with the hydrolysis of the glycosidic bonds of sucrose to yield D-glucose and fructose when exposed to high temperatures [72]. Following sucrose decomposition, glucose and fructose take part in further reaction pathways which produce compounds responsible for the characteristic colour, flavours, and aromas associated with caramelisation [53].

4.3. Indicators of Degree of Nonenzymatic Browning. Nonenzymatic browning reactions can be characterised by several of their intermediate and end products. Therefore, these compounds can be used as indicators of the occurrence and degree of nonenzymatic browning reactions. The most prominent indicator of the degree of nonenzymatic

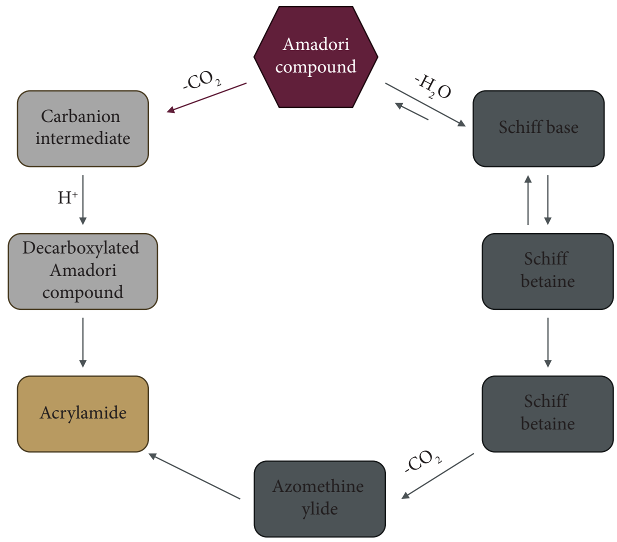

Figure 2: Schematic of the pathways leading to acrylamide formation via either the Schiff base or carbanion intermediate (based on Yaylayan and Stadler [71]).

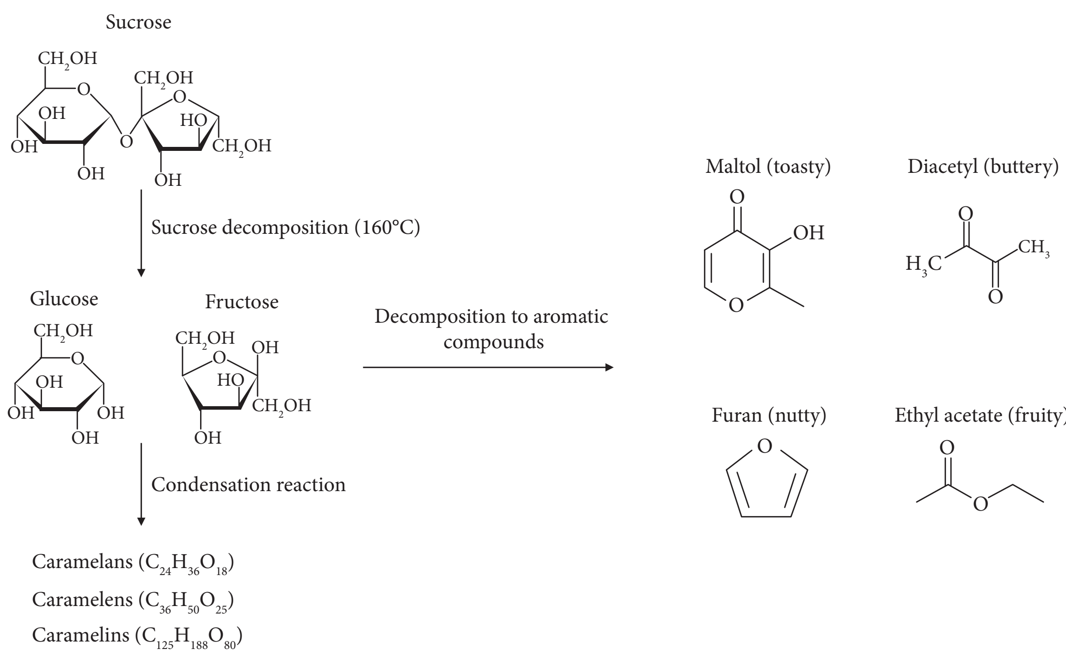

Figure 3: Schematic of the chemical reactions, intermediates, and end products involved in caramelisation (based on Belitz et al. [53]).

browning is HMF, which is produced by both the Maillard reaction and caramelisation [53]. In addition, furfural and acrylamide are indicators for the Maillard reaction, alongside furosine which is an indicator for the formation of the Amadori compound [4].

5. Factors Influencing Nonenzymatic Browning

The occurrence and degree of nonenzymatic browning is highly dependent on the amount and type of substrate available (sugars and proteins) and moisture content as well as time-temperature combinations of the heat treatment [6]. The use of high temperature treatment for extended periods increases the degree of nonenzymatic browning by reducing the moisture content [73]. The degree of Maillard browning is also influenced by both the amount and types of reducing sugars and amino acids available for reaction [74]. During caramelisation, the type of reducing sugars influences the formation of indicator compounds. For example, HMF production is favoured by fructose rather than glucose using a multiresponse modelling [75]. Whole grain cereals are high in dietary fibre and therefore have a higher content of free asparagine which is concentrated in the aleurone layer. This results in an increase in acrylamide production during the thermal treatment of whole grain cereals [70].

A summary of studies that investigated the effects of thermal treatment as either a pretreatment or processing step on nonenzymatic browning of cereal grains and end products is shown in Table 1. Some of these studies are discussed in more detail in the sections to follow. Most of these studies investigated the impact of heat treatment during baking with only a few considering pretreatment of whole grains and flour. There is, therefore, a need for further studies investigating thermal treatment of cereals as a pretreatment rather than a processing step.

5.1. Time-Temperature Combinations of Heat Treatment. The effect of time-temperature conditions of thermal treatment on the degree of nonenzymatic browning has mostly been investigated in cereal-based baked products. It has been found that an increase in the intensity of baking conditions, e.g., during bread [78, 79] and biscuit production [49], resulted in increased levels of HMF due to nonenzymatic browning. The formation of nonenzymatic browning indicators increased 4-fold with a 6 min extension of heating was observed in sweet biscuits made from different cereal flours [49] as well as in bread crisp models [78]. Similarly, a recent study investigating the effect of fermentation and baking parameters on HMF and acrylamide formation in bread [85] showed that an increase in fermentation time (10–30 min) and baking time (20–30 min) resulted in an increase in HMF and acrylamide. An increase in the intensity of time-temperature conditions coincide with an increase in reactivity between the carbonyl groups of reducing sugars and amino groups of proteins, increasing the rate of the reaction between them and the production of HMF via the Maillard reaction [86]. A summary of observed HMF and acrylamide levels in cereal products, with heat treatment as a processing step, is shown in Table 2.

Two studies on the effect of infrared (IR) heat treatment on the formation of Maillard reaction products in maize [42] and buckwheat [41] found that acrylamide and HMF formation doubled with the thermal load of heat treatment [41, 42]. As a result of IR treatment (38°C for 48 h) of dried maize samples, furosine was formed indicating the occurrence of the Maillard reaction at lower temperatures and longer exposure. Moisture content was found to be highly correlated ($R^2 = 0.71$) with furosine content, suggesting that moisture levels have a significant impact on the Maillard reaction [42]. The formation of furosine is also dependent on the amount of lysine available for the formation of the Amadori compound, as observed by Rufián-Henares et al. [76].

5.2. Type and Concentration of Reactants. Given that reducing sugars and proteins are the reactants involved in nonenzymatic browning reactions, observed correlations between the amount and type of reactants and the degree of nonenzymatic browning were to be expected. The effect of the type and concentration of reactants on the degree of nonenzymatic browning has been illustrated in several published studies. The results of these studies are, however, difficult to compare because each study used a different type and intensity of thermal treatment as well as different samples or raw materials, all of which would influence the degree of nonenzymatic browning.

It was found that increased contents of reducing sugars and proteins resulted in an increased production of HMF and furosine in wheat-based sweet biscuits [49] and bakery products [49, 77]. In these studies, the HMF content of the wheat biscuits (30.7 ± 0.6 mg/kg) made with added sugar [49] was almost ten times higher than that in wheat bread (3.21 ± 0.02 mg/kg) when exposed to the same intensity of thermal treatment [78], emphasising the effect of formulation on the degree of nonenzymatic browning. Additionally, high furosine contents (10670.3 mg/kg) were observed in whole grain biscuits with high lysine and protein content, with a significant positive correlation between Maillard reaction products and total protein as well as lysine contents. In contrast, Mesías and Morales [77] found no correlation between HMF and reducing sugar content in flours from different cereal sources; however, the HMF content correlated significantly with the ratio of reducing sugar to protein content [77]. The lack of correlation between protein content and HMF suggests that HMF is formed via caramelisation rather than the Maillard reaction. Similarly, Ghazouani et al. [83] found a negative correlation between protein content and HMF production in the wheat-based traditional Mediterranean breakfast cereal, Bsissa. The formulation of Bsissa was completely different than the wheat-based bakery products investigated by Mesías and Morales [77] and Žilić et al. [49]. The produced Bsissa comprised different combinations of roasted wheat, legumes (chickpeas, lentils, and Fava beans), and spices without added sugars and fats [83]. It was also exposed to a more intense heat treatment (roasting at 230°C) compared to the bakery products which were baked at 150–180°C for short periods [49, 77, 83].

Rufián-Henares et al. [76] found that different contents of reducing sugars and proteins in heat-treated cereal flours resulted in different levels of HMF production. Maize and soybean flours, which contain higher levels of reducing sugars and proteins, showed significantly higher HMF content ($P < 0.05$) after heat treatment compared to wheat flour. Consistent with this, no HMF could be detected in rice flour which had the lowest protein and very low reducing sugar contents. It was also found that the level of heat damage, as indicated by HMF content, depends on the protein content and the type of protein present, specifically the presence of lysine. Soybean flour had the highest lysine content (3.097%), favouring the formation of Maillard reaction products via the Amadori compound [76]. Similarly, Žilić et al. [49] investigated the effect of sugar biscuit formulation on the formation of Maillard reaction products and found that the initial content and type of reducing sugars in the different cereal flours impacted on the amount of HMF formed. Additionally, it was shown that both the free lysine and fibre contents correlated significantly with furosine content. As a result, biscuits made from whole grain flour resulted in an increased degree of Maillard browning.

5.3. Presence of Bran and Dietary Fibre. Whole wheat flour was found to be related to a higher degree of nonenzymatic browning compared to refined wheat flour [76, 78]. Whole

TABLE 1: An overview of studies on the effect of dry thermal treatment as pretreatment or processing step on nonenzymatic browning of cereal grains, flours, and end products.

Grain/flour/product	Thermal pretreatment	Research focus	Reference
Wheat and whole wheat flour	Oven roasting: 180°C for 3, 6 and 10 min	Development of the MR in dry-roasted flours	[76]
Wheat flour	Baking: 150°C for 30 min	Effect of flour type on formation of dicarbonyls and furfural during baking	[77]
Maize flour	IR radiation: 110, 115, 120, and 140°C for 50 to 100 s	ACR, HMF, and furosine formation in IR-heated maize flour	[42]
Maize, oats, rice, and soybean flour	Oven roasting: 180°C for 3, 6, and 10 min	MR development in dry-roasted flours	[76]
Tartary buckwheat	IR radiation: 130, 150, and 170°C for 10 min	MRP and antioxidant properties after IR heating on MRP and antioxidant properties	[41]
Wheat, spelt, oats, rye, and teff dough system	Baking: 150°C for 30 min	Effect of flour type on formation of HMF, furfural, and dicarbonyl compounds in dough model systems containing water or glucose	[77]
Bread crisp model (wheat, whole wheat, and rye)	Baking: 180°C for 35 min Toasting: 140°C, 160°C, and 180°C at five toasting times each	Effect of flour type and processing conditions on MR and ACR formation	[78]
Bread (wheat)	Baking: 200°C and 225°C for 20–60 min	HMF formation as a function of heat treatment intensity	[79]
Bread (wheat)	Baking (modified atmosphere) at 250°C for 20 min	ACR and HMF formation in different baking atmospheres	[16]
Bread (wheat)	Baking: 200°C for 35 min and 240°C for 30 min	ACR formation with different flour composition, extraction rate, and baking conditions	[13]
Bread (rye)	Baking: 260°C for 40 min	Effect of flour extraction rate and breadmaking on formation of Maillard reaction products	[12]
Bread (rye and spelt)	Baking: 200°C for 35 min and 240°C for 30 min	ACR formation with different flour composition, extraction rate, and baking conditions	[13]
Bread (barley, rye, triticale, oats, sorghum, and millet)	Dry heat treatment of flour: 140°C for 15 min hydrothermal treatment of flour: feeding zone 50°C, compression zone 120°C, and cooking zone 220°C Baking of breads: 160°C (upper heater) and 220°C (lower heater) for 65 min	HMF and ACR formation of flours and breads exposed to wet and dry heat treatment	[74]
Biscuits (wheat)	Baking: conditions not specified	HMF formation with the substitution of wheat flour with wheat germ	[80]
Biscuits (bread wheat, durum wheat, soft wheat, and hard wheat)	Baking: 180°C for 7, 10, and 13 min	Effect of flour type on the MR in sweet biscuits	[49]
Water biscuits	Baking: 205°C for 18 min	Heat damage and antioxidant capacity in water biscuits enriched with sprouted wheat and barley	[81]
Biscuits (triticale, rye, barley, oats, and maize [white, yellow and red standard and blue popping])	Baking: 180°C for 7, 10, and 13 min	Effect of flour type on the MR in sweet biscuits	[49]
Breakfast cereal (wheat, maize, and rice)	Commercial processing	Influence of breakfast cereal composition on head-damage indices. Relationship between HMF, furfural, and glucoisomaltol	[82]
North African breakfast cereal (Bsissa) made from wheat, barley, and sorghum	Roasting at 230°C (cereals and legumes for 30 min and spices for 3 min)	Levels of ACR, HMF, and furaldehyde in commercial Bsissa	[83]
Infant cereal (wheat, rice, maize, oats, barley, rye, sorghum, millet)	Toasting: conditions not specified	Effect of formulation on MRP and phenolic compounds	[84]
Maize snack	Oven roasting: 200–270°C for 7 and 12 min	Nonenzymatic browning development with different processing conditions	[73]

HMF, hydroxymethylfurfural; ACR, acrylamide; MR, Maillard reaction; MRPs, Maillard reaction products; IR, infrared.

Table 2: A summary of hydroxymethylfurfural and acrylamide levels in cereal products produced with thermal treatment as a processing step.

Product	Thermal treatment	HMF content (mg/kg)	Acrylamide (μg/kg)	Reference
Wheat-based Bsissa	Roasting at 230°C	$<6\times10^{-3}$	ND	[83]
Barley-based Bsissa		$>10\times10^{-3}$	ND	
Breakfast cereals	—	36.24	—	[82]
Hard wheat biscuits	Baking at 180°C for 7 min	1.0 ± 0.1	—	[49]
Rye biscuits		0.5 ± 0.1		
Hulless oats biscuits		1.4 ± 0.0		
Hard wheat biscuits	Baking at 180°C for 13 min	30.7 ± 0.6		
Rye biscuits		35.8 ± 1.1		
Hulless oats biscuits		48.0 ± 0.7		
Wheat bread	Toasting at 180°C for 13 min	3.21 ± 0.02	—	[78]
Whole wheat bread		0.78 ± 0.03		
Rye bread		4.38 ± 0.18		
Wheat bread	Baking at 200°C for 30 min	4–6	—	[79]
Barley flour	Dry thermal treatment at 140°C for 15 min	27.0 ± 0.5	516 ± 13	[74]
Rye flour		32.6 ± 0.5	1833 ± 96	
Oats flour		44.3 ± 1.6	1951 ± 4	
Maize grains	Infrared heating at 120°C for 85 s	21.25 ± 0.49	461.51 ± 2.89	[42]
	Infrared heating at 140°C for 100 s	46.88 ± 0.05	704.51 ± 26.24	
Wheat flour	Toasting at 180°C for 10 min	4.16 ± 0.01	—	[76]
Whole wheat flour		4.72 ± 0.06		
Oats flour		3.43 ± 0.02		
White wheat bread	Baking at 200°C for 35 min		9.68 ± 0.85	[13]
Whole grain dark wheat bread			7.06 ± 0.22	
White rye bread			50.73 ± 1.63	
Whole grain dark rye bread			58.13 ± 7.46	

HMF, hydroxymethylfurfural; ND, not detected; IR, infrared.

wheat flour contains more bran, dietary fibre, and ash, which increases the free acrylamide content and therefore acrylamide production [70]. This was confirmed in a study by Przygodzka et al. [13], who investigated the effect of flour composition and baking conditions on acrylamide formation. The authors showed an increase in acrylamide production in rye and spelt flours with higher dietary fibre and ash contents, compared to conventional wheat flour. This agrees with the results observed by Rufián-Henares et al. [82] and Delgado-Andrade et al. [87] showing that breakfast cereals enriched with dietary fibre had higher levels of nonenzymatic browning indicators compared to non-enriched cereals.

6. Mitigation of Acrylamide, HMF, and Heterocyclic Compounds

The production of the toxic and potentially carcinogenic compounds acrylamide, HMF, and other heterocyclic compounds such as furfural during nonenzymatic browning in thermally treated products is a concern for food producers. The potential of mitigation strategies to reduce the formation of acrylamide during thermal treatment when producing cereal-based products has been illustrated [62]. These include [1] the use of using oxygen-free baking atmospheres [2, 16], lowering the pH with lactic acid bacteria [3, 88], reducing heat loads [4, 89], enzymatic treatment with asparaginase [17, 90], and reducing the sugar content [91].

Gülcan et al. [16] investigated the use of modified baking gaseous atmospheres to prevent the formation of acrylamide, while the baking time and temperature were kept constant. The use of carbon dioxide and nitrogen atmospheres resulted in a 50% decrease in acrylamide production, while a sulphur dioxide atmosphere almost completely prevented acrylamide formation. The removal of oxygen from the baking atmosphere interferes with the heat distribution from the heat source to the bread, slowing down the rate of the Maillard reaction. The sulphur dioxide atmosphere achieves acrylamide mitigation via the sulphur atom binding to the carbonyl groups of reducing sugars more readily than the amino acids, limiting the Maillard reaction and therefore acrylamide formation [16].

After inoculating sourdough with lactic acid bacteria (LAB) strains, Nachi et al. [88] found that the sourdough breads produced significantly ($P < 0.05$) less acrylamide than those baked with baker's yeast only. Since the pH was lower due to the presence of the lactic acid bacteria, the Schiff base was not formed, and the formation of acrylamide was reduced [89].

During conventional and vacuum biscuit baking, Mogol and Gökmen [89] showed that lowering the heat load (lower temperatures and shorter times) decreased the acrylamide formation. Vacuum baking reduced the heat load, resulting in significantly lower acrylamide formation than with conventional baking at all the time-temperature combinations tested. When combining conventional baking (220°C, 2–4 min) for surface browning with vacuum baking (180°C, 500 mbar, 4–6 min) for moisture reduction, acrylamide formation was prevented while still producing a desirable colour [89].

Recent research found that using asparaginase and glycine combined in green malts to mitigate acrylamide formation reduced acrylamide levels by half [17]. The process of malting is used to prepare barley for brewing and involves the initiation of germination, followed by kilning or roasting. The germination process activates endogenous enzymes which hydrolyse carbohydrates and proteins, increasing the amount of reducing sugars and amino acids, including asparagine. Following germination, the malt is kilned or roasted to dry the wet malt and provide colour and flavour as well as to stop enzymatic reactions associated with germination. The increase in reducing sugars and amino acids during germination leads to an increase in the degree of Maillard browning and acrylamide formation during kilning. The formation of acrylamide can be limited with the addition of the enzyme asparaginase to green malts before kilning. This enzyme converts free asparagine into aspartic acid, decreasing the amount of acrylamide precursor. The addition of glycine maintains colour formation during kilning, as this amino acid takes part in the Maillard reaction without forming acrylamide.

Mitigation strategies for HMF, furfural, and other heterocyclic compounds [92] include changing the process parameters of thermal treatment such as baking time-temperature combinations [93] and the product formulation composition [94]. An increase in baking temperature and time resulted in a decrease in pH which led to increased levels of HMF and furfural in sponge cake models [92]. The use of glucose and fructose in sponge cakes also resulted in increased HMF levels compared to using sucrose, lactose, and maltose. In biscuits, lower baking temperature and less reducing sugars resulted in a decrease in the formation of HMF and acrylamide [95]. In addition, the use of sodium bicarbonate as leavening agent instead of ammonium bicarbonate limited the decomposition of sucrose, thus lowering the amount of reducing sugars available for HMF formation in biscuits [93].

7. Antioxidants in Cereal Grains

Whole grains are rich in antioxidants in the form of phenolic compounds such as phenolic acids, carotenoids, anthocyanins, tocopherols, and tocotrienols [18]. When milled, these compounds are unevenly distributed between the different milling fractions, with the bran and germ containing most of the antioxidants [96]. It was found that the phenolic content of the wheat depended on genotype and growing environment [96]. In a subsequent study, researchers observed that bran had a 28-fold higher total phenolic content (TPC) than white flour when comparing whole wheat, wheat bran, and wheat flour for antioxidant activity [97].

Bioactive compounds exhibit antioxidant activity through several mechanisms including the scavenging of free radicals, chelating metal ions, quenching singlet oxygen, and nitrogen radicals, and acting as reducing agents by donating electrons to free radicals [19]. Diets rich in whole grains, fruits, and vegetables have been associated with a reduced risk of chronic disease due to the radical scavenging properties of antioxidants [98]. Although whole grains are rich in antioxidant compounds, the latter are largely bound in the cell walls of the bran and therefore less available for absorption in the gastrointestinal tract once consumed [99]. Exposure to thermal pretreatment can improve antioxidant bioavailability due to the release of the bound antioxidant compounds [20, 100]. However, exposing the grain to thermal treatment also has the risk of losing antioxidant value due to thermal degradation [101]. Despite many laboratory studies showing beneficial health effects of antioxidants, more rigorous clinical and epidemiological studies are needed to assess their bioavailability [102, 103]. The bioavailability of cereal phenolics is determined as the concentration of absorbed phenolics that can reach the target organ [104]. Bioaccessibility is necessary for bioavailability and is described as the number of consumed antioxidants that has been released into the gut and would be available for intestinal absorption into the blood stream [105].

7.1. Phenolic Compounds. Cereal grains contain several phenolic compounds, mainly phenolic acids, flavonoids, and tannins as well as carotenoids, concentrated in the bran fraction [106]. Of these, ferulic acid and p-coumaric acid are the most abundant phenolic acids [107] and lutein and zeaxanthin the most abundant carotenoids [108]. Phenolic compounds can exist in either a free soluble, a conjugated soluble, or a bound insoluble state. Conjugated soluble phenolics couples to polysaccharides, proteins, or lipids and are easily absorbed through the gastrointestinal tract. Bound insoluble phenolics are less bioavailable because they are trapped in the plant cell walls by covalent bonds [99]. The bioavailability of cereal phenolics is also reduced due to interactions between the phenolics and the fibre matrix of the bran [20]. By exposing grains to thermal pretreatment, the accessibility of phenolics is improved by modification of the fibre matrix, releasing bound compounds [109].

Phenolic acids in wheat are mainly present in their insoluble bound state; however, thermal treatment can be applied as a pretreatment to release them into their free soluble state [19, 110]. Thermal pretreatment, therefore, improves the bioaccessibility of antioxidant compounds in wheat and causes an increase in antioxidant activity through the release of bound phenolics, destruction of thermally labile antioxidants, and the formation of new antioxidants through the Maillard reaction [11, 76, 111]. Several studies have been published recently on the effect of different types and intensities of thermal treatments, as pretreatment or processing step, on the antioxidant properties of cereal grains and products. The research focus and thermal treatments used in these studies are summarised in Table 3 and discussed in more detail in the following.

7.2. Effect of Time-Temperature Combination of Thermal Treatment. Table 4 shows the effect of thermal treatment as a pretreatment or processing step on the phenolic content

Table 3: An overview of studies on the effect of dry heat treatment as pretreatment or processing step on the antioxidant properties of cereals and end products.

Grain/flour/product	Thermal pretreatment	Research focus	Reference
Whole wheat kernels	FCCT roasting: 150–234°C at 30–90 Hz	FCCT roasting and AO properties of South African wheat	[112]
Highland barley	Heat fluidisation (170°C for 20 min) Microwave (700 W for 60 s) Baking (220°C for 170 s)	Physicochemical, ultrastructural, and nutritional characteristics after thermal treatment	[48]
Sorghum	Microwave heating: 350 and 500 W for 15, 30, and 45 s	AO properties after microwave heating	[40]
Sorghum	Wet cooking: 60, 80, and 95°C for 1 h Pressure cooking: 121°C for 15 min	AO capacity (ABTS and DPPH) of thermally treated sorghum	[113]
Maize	IR radiation: 50–100 s, 110, 115, 120, and 140°C	Level of phenolic compounds and total AO capacity of IR-heated samples	[42]
Millet	Parboiling: steaming of soaked grains for 5 min Roasting: pan roasting for 5 min	AO properties of porridge made from thermally treated millet	[100]
Teff	Microwave heating: 900 W for 5 min Oven roasting: 120°C for 40 min	Effect of heat treatment on total phenol, AO activity, fatty acid composition, and phenolic compounds	[114]
Mexican barley	Boiling: 60 min Sand roasting: 125°C for 30 min	AO capacity of barley after traditional cooking, roasting, and germination	[115]
Barley	Sand roasting: 280°C for 20 s Microwave cooking: 900 W for 120 s	AO properties and heat treatment	[11]
Barley	Oven toasting: 152°C for 3 h Sand roasting: 280°C for 15 s	AO properties of heat-treated barley cultivars	[116]
Tartary buckwheat	IR radiation: 130, 150, and 170°C for 10 min	AO activity, total phenolic content, and total flavonoid content after IR heating	[41]
Sorghum, fonio, and pearl millet	Boiling at 100°C: sorghum for 12 min, fonio for 21 min, and millet for 15 min	Total AO capacity and phenolic profile of whole-meal African cereals after cooking	[117]
Wheat germ	Heating in fluidised bed dryer: 180°C for 20 min Oven roasting: 180°C for 5, 10, and 20 min	AO activity and phenolic content of roasted wheat germ	[118]
Wheat germ	Hot air treatment: 150, 180, and 200°C for 40, 20, and 12 min, respectively Microwave heating: 50, 60, and 70°C for 5, 10, 15, and 20 min	AO activity of wheat germ treated with hot air and microwave heating	[101]
Wheat germ oil	Roasting of wheat germ: 180°C for 0–20 min	Effect of roasting on oxidative stability and AO capacity	[22]
Bread crust-like system (whole wheat and refined wheat)	Baking: 200°C for 5, 15, and 30 min	Concentration of bound ferulic acid and total AO capacity. Whole wheat flour contains more bran, dietary fibre, and ash, resulting in a higher content of free asparagine, and increased acrylamide production after fermentation and heating	[21]
Bread crust-like system (whole einkorn, whole rye, whole oats, and whole maize)	Baking: 200°C for 5, 15, and 30 min	Concentration of bound ferulic acid and total AO capacity after fermentation and heating	[21]
Bread (whole wheat)	Baking: 215°C for 24 min	Effect of breadmaking process on phenolic profile and AO activity of different hard wheat flour	[15]

Table 3: Continued.

Grain/flour/product	Thermal pretreatment	Research focus	Reference
White pan bread	Baking: 215°C or 230°C at 24 min or 30 min	Effect of sugar type and amount and baking conditions on physical properties, melanoidin content, and AO capacity	[14]
Rye bread	Baking: 260°C for 40 min	Effect of flour extraction rate and breadmaking on overall AO activity	[12]
Biscuits	Baking: 180–220°C for 10–25 min	AO activity with different recipe composition and baking conditions	[119]
Water biscuits	Baking: 205°C for 18 min (rotating oven)	Heat damage and AO capacity of water biscuits enriched with sprouted wheat and barley	[81]
Biscuits (maize)	Baking: 200°C for 7 and 10 min 150°C for 12 min	Effect of baking conditions and dough formulation on phenolic compounds, AO capacity, and colour of biscuits	[49]
Pasta (durum wheat—whole wheat flour and refined semolina)	Boiling for 7 or 8 min (al dente), 11 or 12 min (fully cooked), and 17 or 18 min (over cooked)	AO capacity and carotenoid content with different cooking times	[120]
Muffins (rice, wheat, oats, maize and barley)	Baking: 170°C for 13 min	Impact of flour type on starch digestibility and AO capacity of muffins	[121]

FCCT, forced convection continuous tumble; AO, antioxidant; IR, infrared.

Table 4: An overview of the effect of thermal treatment on total phenolic content and antioxidant activity of cereal grains and products.

Product	Thermal treatment	TPC (mg GAE/g)	DPPH	ABTS	Reference
Whole wheat kernels	Forced convection roasting at 136°C for 55 cycles/min	2.05	4.40 (μmol TE/g)	6.39 (μmol TE/g)	[112]
	FCCT roasting at 234°C for 55 cycles/min	1.73	5.77 (μmol TE/g)	5.44 (μmol TE/g)	
White wheat bread	Baking at 200°C for 35 min	0.26 ± 0.01*	—	1.71 ± 0.06 (μmol TE/g)	[13]
White spelt bread		0.25 ± 0.01*		1.12 ± 0.02 (μmol TE/g)	
White rye bread		0.42 ± 0.09*		3.42 ± 0.04 (μmol TE/g)	
White wheat bread	Baking at 240°C for 30 min	0.30 ± 0.01*		1.63 ± 0.11 (μmol TE/g)	
White spelt bread		0.32 ± 0.01*		1.31 ± 0.01 (μmol TE/g)	
White rye bread		0.52 ± 0.01*		3.54 ± 0.01 (μmol TE/g)	
Whole wheat bread crust	Baking at 200°C for 5 min	—	9.7 ± 0 (mmol TE/kg)	9.5 ± 0.4 (mmol TE/kg)	[21]
Whole rye bread crust			11.8 ± 0.3 (mmol TE/kg)	10.1 ± 0.1 (mmol TE/kg)	
Whole wheat bread crust	Baking at 200°C for 30 min		28.9 ± 0.5 (mmol TE/kg)	17.5 ± 0.1 (mmol TE/kg)	
Whole rye bread crust			22.4 ± 0.2 (mmol TE/kg)	12.4 ± 0.2 (mmol TE/kg)	
Wheat germ oil	Roasting at 180°C for: 5 min	0.0216 ± 0.75	3.59 ± 0.55 (μmol TE/100 g)	10.9 ± 0.64 (μmol TE/100 g)	[22]
	20 min	0.0583 ± 0.91	31.5 ± 0.85 (μmol TE/100 g)	14.6 ± 0.11 (μmol TE/100 g)	
Ethanol extract of wheat germ	Roasting at 180°C for: 5 min	17.53 ± 0.81	5.55 ± 0.18 (IC_{50}, mg/ml)	2.43 ± 0.15 (IC_{50}, mg/ml)	[118]
	20 min	30.24 ± 0.71	3.44 ± 0.29 (IC_{50}, mg/mL)	1.31 ± 0.07 (IC_{50}, mg/mL)	
Sorghum grain	Microwave treatment: 350 W, 15 s	41.5 ± 0.70	36.8 ± 1.89 (%)		[40]
	350 W, 45 s	47.1 ± 0.93	40.9 ± 3.00 (%)		
	500 W, 15 s	42.2 ± 1.72	50.1 ± 3.61 (%)		
	500 W, 45 s	50.8 ± 1.76	59.1 ± 4.07 (%)		

*mg FAE/g. TPC, total phenolic content; DPPH, 2,2-diphenyl-1-picrylhydrazyl; ABTS●+, 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) cation radical; GAE, gallic acid equivalent; TE, Trolox equivalent; FAE, ferulic acid equivalent.

and antioxidant capacity of cereal grains and end products. Antioxidant properties remained largely the same regardless of grain type or heat treatment. The use of high-temperature-short-time (HTST) treatment using heat fluidisation, baking, cooking, roasting, or microwave treatment resulted in an overall increase in the TPC, free phenolic content, and total antioxidant capacity in wheat [14, 15, 21, 112], barley [11, 48, 115], and sorghum [40].

Shen et al. [14] showed an 83% increase in antioxidant capacity, measured by the DPPH assay, in white pan bread after increasing the baking time by 16 min. Similarly, Çelik and Gökmen [21] observed that extending the baking time by 15 min increased the antioxidant capacity by 81%. An increase in antioxidant activity was found in barley after sand roasting (39.8% [11] and 73.7% [113]), toasting (33.3%), and microwave heating (34.1%) [11]. Similarly, the TPC and DPPH activity significantly ($P < 0.05$) increased by 13% and 56.45%, respectively, in finger millet flour after roasting [100]. Thermal treatment damages cell structures, releasing bound phenolic compounds into the free state, which contributes to increased antioxidant capacity and TPC levels [50].

Microwave heat treatment yielded the lowest increase in free phenolics in whole barley compared to baking and heat fluidisation as it caused less damage to the outer layer and endosperm structure [48]. Additionally, it is possible that the TPC increased because the exposure time was too short to cause the decomposition of a substantial number of thermally labile phenolic compounds. An earlier study showed that ferulic acid, the main phenolic compound in wheat, has a high thermal stability, contributing to the higher TPC at HTST treatment conditions [111]. This explains why baking did not significantly alter the ferulic acid contents or and its isomers in pan bread [15, 21]. By increasing the temperature, melanoidins would also be formed by the Maillard reaction, which have antioxidant properties [13, 20].

The antioxidant capacity (DPPH activity) of sorghum, exposed to both wet cooking and pressurised cooking, was significantly higher in the pressure-cooked sorghum compared to the wet-cooked sorghum [118]. However, both types of thermal treatments increased the antioxidant capacity compared to the uncooked samples. The increase in antioxidant capacity was attributed to the improved extractability of conjugated phenolics after thermal treatment, while the different types of cooking resulted in different compositions of phenolic compounds. Wet cooking increased the caffeic acid content while 3,4,5-trimethoxycinnamic acid and catechin, covalently bound to cell walls, were released by pressure cooking [113]. In contrast, it was found that exposure of wheat to high loads of thermal treatment can decrease the TPC due to the degradation of heat sensitive flavonoids and phenolic compounds [112]. Sharma and Gujral [11] observed a decreased of up to 49.6% in TPC in barley after microwave heating while Bai et al. [48] observed a 36.9% decrease after heat fluidisation treatment and a 14.02% decrease after microwave treatment.

7.3. Effect of Wheat Germ and Grain Sprouting. Wheat germ is well known for its high nutritional value and health benefits, which has prompted researchers to study the effects of thermal treatment on its stability and nutrients. Several studies investigated the effect of roasting and other thermal treatments on the antioxidant activity and phenolic compositions of wheat germ and wheat germ oil. Zou et al. [22, 118] found that roasting (180°C for 20 min) caused an overall increase in TPC in wheat germ (16.49 to 30.24 mg GAE/100 g) and wheat germ oil (10.7 to 58.3 mg GAE/100 g) as well as an increase in antioxidant content and capacity (2.17 to 31.5 μmol TE/100 g) in wheat germ oil. This was despite the decrease in certain individual antioxidant compounds such as tocopherols and carotenoids due to thermal degradation. Also, in this study, it was shown that thermal treatment at a lower temperature and shorter time (70°C for 10 min) resulted in an increase in total tocopherol content due to increased extraction capacity of these lipophilic compounds resulting from structural changes induced by mild heat treatment. The high time-temperature combination (180°C for 20 min) most likely led to damage of cell structures, releasing bound phenolic compounds, with an increase in TPC. The damage to the cell structure possibly allowed for more phenolic compounds to be extracted into the oil phase. The formation of Maillard reaction compounds with phenol-like structures would also have contributed to the increase in TPC [22]. Contrary to this, Meriles et al. [101] showed that roasting at 180°C for 20 min caused a decrease in TPC due to thermal degradation of phenolic compounds. This study also showed that microwave treatment at 70°C caused an increase in radical scavenging activity due to increased extractability of bioactive compounds through the release of bound phenolic compounds. The discrepancies in the results of these studies can be explained by the fact that wheat germ has a complex relationship between total phenolic content and antioxidant activity compared to the linear relationship seen in other plant extracts [122].

Hidalgo et al. [81] studied the effect of water biscuit enrichment with sprouted wheat and barley flour on heat stability and antioxidant capacity. Enrichment with sprouted grains resulted in an overall increase in the total carotenoids, tocols, conjugated phenolic compounds, and bound phenolic compounds. Tian et al. [123] found that germinating oats produced a fourfold increase in phenolic compounds. Germination causes several changes to the grain structure due to enzyme activity, which could be responsible for the release of bound and conjugated phenolic compounds. Despite the overall higher content of antioxidant compounds in enriched water biscuits, baking of the biscuits caused a decrease in the carotenoid and tocopherol levels due to thermal degradation. On the other hand, there was an increase in phenolic compounds such as ferulic acid because exposure to high temperatures destabilised certain molecular linkages, releasing conjugated and bound phenolic compounds.

8. Methods of Analysis

The antioxidant properties of cereal grains are analysed by quantifying either individual compounds using liquid chromatography or the total of a specific group of compounds using spectrophotometric techniques. Spectrophotometric assays used to determine antioxidant properties are based on different reaction mechanisms [6]. The Folin–Ciocalteu assay is used to measure the total phenolic content based on the reduction of the reagent by phenolic compounds resulting in a colour change [124]. The total phenolic content is then quantified using a standard curve of gallic acid to express TPC as gallic acid equivalents [125].

The antioxidant activity and capacity can be measured using (1) the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical; (2) 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) cation radical (ABTS•+) scavenging capacity; (3) ferric reducing/antioxidant power (FRAP); and (4) oxygen radical absorbing capacity (ORAC) assays. The DPPH assay is based on the reduction of the DPPH radical through hydrogen atom donation from antioxidant compounds, resulting in a colour change from violet to pale brown-yellow [126]. The capacity of the antioxidants to scavenge the DPPH radical is then quantified using a standard curve of Trolox ((±)-6-hydroxy-2,5,7,8-tetramethyl-chromane-2-carboxylic acid), an analogue of tocopherol, and the results expressed as Trolox equivalents [127]. The ABTS assay measures the ability of antioxidant compounds to scavenge the ABTS radical, quantified also using a Trolox standard curve [128]. FRAP measures the ability of antioxidants to reduce ferric iron relative to an antioxidant standard such as Trolox, ferrous iron (Fe^{2+}), or ascorbic acid [129]. In the ORAC assay, the ability of antioxidants to inhibit oxygen radical-induced oxidation is measured using a fluorescence probe [130]. These methods differ in reaction mechanisms, substrate type, reaction conditions, target compound, benefits, and limitations making direct comparison of results challenging [125]. The choice of assay will therefore depend on the sample composition, and it is generally recommended that two assays based on different reaction mechanisms are used to measure antioxidant activity [125, 131].

The extraction of antioxidants is required before any of these assays can be applied. Extraction methods differ in terms of the solvents and solvent ratios, extraction time, and temperature as well as the use of assisted methods such as sonication [112]. The most used solvents for antioxidant extraction include methanol, ethanol, acetone, and ethyl acetate [132]. These solvents are used in different concentrations depending on the solvent polarity. There is no universal solvent or extraction technique, and these depend on solvent and equipment availability, sample composition, and researcher preference.

9. Relationship between Nonenzymatic Browning and Antioxidant Properties

Nonenzymatic browning reactions, particularly the Maillard reaction, produce a myriad of compounds which have shown antioxidant activity [6]. Recent studies have demonstrated a link between nonenzymatic browning and antioxidant properties in wheat, cereal grains [11], and their products [15, 22]. During a study on the antioxidant properties of whole wheat bread, it was suggested that Maillard reaction products were responsible for increasing antioxidant activity and altering its phenolic composition [15]. Similarly, a study investigating the influence of roasting on the antioxidant capacity of wheat germ oil found that both the antioxidant capacity and HMF content increased with roasting time [22]. The same conclusion was made by Sharma and Gujral [11] while investigating the effect of heat treatment on the antioxidant properties of barley. The authors suggested that the production of melanoidins via the Maillard reaction contributed to the increase in antioxidants. However, none of these studies showed a statistically significant correlation between the antioxidant properties and Maillard reaction products.

Shen et al. [14] found browning intensity, measured as melanoidin content, contributed partially to antioxidant capacity in white pan bread, both of which increased with the intensity of heat treatment. This agrees with the findings of Przygodzka et al. [13] that showed a positive correlation between acrylamide formation and the antioxidant capacity ($r = 0.66$) and TPC ($r = 0.61$) of the bread crust of wheat bread. The darker breads with higher degrees of nonenzymatic browning had double the antioxidant capacity compared to lighter breads. A positive correlation between total antioxidant capacity and acrylamide ($r^2 = 0.98$) as well as HMF ($r^2 = 0.86$) was found to be true in maize flour after exposure to infrared radiation [42]. There is scope for more research into the relationship between nonenzymatic browning and antioxidant properties in thermally treated grains, as well as ways to minimise acrylamide and HMF formation while preserving the benefits of thermal treatment.

10. Practical Applications

This review emphasised the benefits of thermal pretreatment of cereal grains in terms of improved antioxidant properties. The exposure to high temperatures for improved antioxidant content could, however, impair protein functionality, and therefore the feasibility of using dry heat-treated wheat for breadmaking [133, 134]. Alternative applications of heat-treated wheat and other cereals with increased antioxidant properties could therefore include inclusion of such wheats in breakfast cereals [135] and cakes [134] which do not rely on the formation of gluten networks. Changes in starch functionality and protein denaturation in wheat flour because of thermal pretreatment have shown improvements in cake quality [134]. The formation of acrylamide and HMF can be mitigated by reducing baking temperature and time and the use of enzymes.

11. Conclusion and Perspectives

Dry thermal treatment can be applied as either a pretreatment of cereal grains or a processing step during the production of cereal-based products and provides ideal conditions for the occurrence of nonenzymatic browning reactions. The Maillard reaction is important in such thermally treated grains and final products as it contributes to colour, texture, and sensory acceptability. In addition, thermal treatment increases the antioxidant capacity of cereals and baked goods through the release of bound phenolics. These beneficial changes are mainly determined by thermal treatment intensity. Thermal treatment used as a pretreatment of whole grains has not been studied to the same extent as for cereal-based bakery products exposed to thermal treatment mainly due to a processing step.

The degree of nonenzymatic browning in cereal grains and products is related to the time-temperature conditions of thermal treatment. Increased thermal treatment intensity increases both the degree of nonenzymatic browning as well as the antioxidant content and capacity. Several studies speculate about the relationship between nonenzymatic browning reactions and antioxidant capacity; however, limited studies indicated a statistically significant correlation. This leaves room for further investigations.

As thermal treatment may impair protein functionality, and therefore the feasibility of using dry heat-treated wheat when gluten formation is required, wheat and other cereals with increased antioxidant properties due to thermal treatment could be used in, e.g., breakfast cereals and cakes. In addition to enhancing sensory acceptance and increasing antioxidant capacity, nonenzymatic browning also produces the toxic and potentially carcinogenic compounds HMF and acrylamide. The global concern over the levels of acrylamide in processed foods therefore motivates the need for further investigation of potential methods of reducing the formation of especially acrylamide in thermally treated cereal grains and their products.

Abbreviations

ABTS: 2,2′-Azinobis-(3-ethylbenzothiazoline-6-sulphonic acid)
ACR: Acrylamide
ANN: Annealing
DPPH: 2,2-Diphenyl-1-picrylhydrazyl
FAE: Ferulic acid equivalent
FCCT: Forced convection continuous tumble
FRAP: Ferric reducing/antioxidant power
GAE: Gallic acid equivalent
HAT: Hydrogen atom transfer
HMF: 5-Hydroxymethylfurfural
HMT: Heat moisture treatment
HTST: High temperature short time
IR: Infrared
MR: Maillard reaction
ORAC: Oxygen radical absorbing capacity
SET: Single electron transfer
TE: Trolox equivalent
TPC: Total phenolic content.

Data Availability

No underlying data were collected or produced in this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Mia Schutte conceptualized the study and wrote the original draft. Marena Manley conceptualized the study, reviewed and edited the manuscript, and supervised the study. Stefan Hayward reviewed and edited the manuscript.

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