

Effects of Fermentation and Roasting on Natural Antioxidants in Maize

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ABSTRACT

Natural antioxidants in foods are well appreciated for preserving foods and had been shown to have beneficial effects against oxidative stress-induced degenerative and age-related diseases, cancer, and aging. This chapter reviewed the effects of two major primary processing methods; fermentation and roasting on the antioxidant properties of maize and its products. The effect of fermentation and roasting on the chemical active compounds including carotenoids, vitamin C, phenolics, and flavonoids, and the scavenging antioxidants power of both aqueous and organic extracts of fermented and roasted maize using DPPH and ABTS assays were reported. Fermentation results in the modification of cereals' phytochemicals; carotenoids content of maize increases due to fermentation with improved scavenging power of fermented maize extract. The effect of roasting includes increased antioxidant activity and content, development of brown colouration and improved flavour due to the presence of Maillard reaction products. These changes contribute to better health benefits by enhancing the digestibility of nutrients and the activity of available antioxidants. Intakes of roasted fresh or dried maize varieties; especially, QPM are highly recommended to ameliorate the causes of night blindness, lung and prostate cancers.

Keywords: antioxidant power, croteniods, fermentation, maize, phenolic, roasting.

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I. INTRODUCTION

Naturally occurring antioxidants are simply body's detoxifiers. They are chemical 'free radicals' that give away no electrons because of their stable state in their own way. They are capable of converting the body's toxins into harmless waste products that are removed from the body as excreta [1]. The importance of naturally occurring antioxidants in foods is well appreciated in supplying of essential antioxidants *in vivo* and for food preservation [2]. The early antioxidants were natural substances but were soon replaced by synthetic substances, which are cheaper, of more consistent purity, and possessed more uniform antioxidant properties [2]. Also, there has been a renewed attention to *in vitro* and *in vivo* studies that show the beneficial effects of antioxidants against free radicals induced degenerative diseases, cancer, aging, and age-related diseases [2], [3].

Recently, cereal crops and their components have been focused on functional food and nutraceuticals due to the presence of dietary fibre, protein, energy, minerals, vitamins, and other phytochemicals needed for healthy growth in good amount in them [4]. Ferulic and its derivatives are one of the phenolic acids which contribute to the antioxidant properties of cereal grains [5]. And so, a diet containing whole grains is now recommended for health reasons because they are a rich source of antioxidants.

Maize (*Zea mays*) is the American Indian word for corn, which is literally interpreted as "that which sustains life". It is, after wheat and rice, the most World's important cereal

grain, providing nutrients in food and feeds and serving as a basic raw material for the production of starch, oil and protein, alcoholic beverages, food sweeteners, and more recently, fuel [6]. It was reported by FAO [6] that, there are a number of grain types, distinguished by differences in the chemical compounds deposited in the kernel. Special grain types grown primarily for food include sweet corn and popcorn. The problem of limiting amino acid composition in normal endosperm maize (Plate 1a) had been solved by the development of quality protein maize (QPM) shown on plate 1b which contains 30% more lysine, 55% more tryptophan, and 38% less leucine compared to normal maize. Also, the biological value of protein of QPM is 80% while that of normal maize is 40% according to Bressani [7]. The origin of Maize's cultivation is Central America, particularly in Mexico, from where it spread to Canada and south-ward to Argentina. Its cultivation, consumption, and uses are worldwide and form one of the staple food commodities in many continents including Africa [8], [9].

Maize is an essential source of carbohydrate, protein, some vitamins, and phytochemicals, including lignans, phenolic acid, carotenoids; it also possesses antioxidant properties [10]. Health benefits of maize include prevention of heart ailments, controlling diabetes, lowering hypertension and avoidance of neural-tube defects during birth. Yellow maize contains three carotenoids, namely α -carotene, β -carotene, β -cryptoxanthin which are precursors for vitamin A. It is also a super source of non provitamin, carotenoids, including zeaxanthin and lutein that has beneficial functions in human health [11].



Plate 1a. Normal maize grains - Suwan -ISR.



Plate 1b. QPM grains -TZE Y POP DT STR QPM (Source: Oladeji [16]).

There are different ways of preparing and consuming maize depending on ethnic groups and locality; it may be boiled, roasted, pounded, fermented (ogi), sun-dried, and milled to flour [12]. According to researches, the way and manner maize is processed and/or prepared may increase or decrease its nutritive and health benefits [12], [13], [9]. Obizoba and Atii [14] observed that a combination of cooking and fermentation improved the nutrient quality of cereal crops and reduced antinutritional contents to a safe level when compared with some other processing methods. The digestibility value of maize grains as well as some B vitamins contents increased by malting or fermentation. Milling operation reduces the fats and proteins content as well as fiber, and cooking was found to improve the antioxidant capacity of maize [9]. This paper, therefore, looks at the effects of two primary processing: fermentation and roasting on the antioxidant properties of maize.

II. EFFECTS OF FERMENTATION ON NATURAL ANTIOXIDANTS IN MAIZE

Fermentation is a widely practiced unit operation in Africa because of its contribution to improved physicochemical properties and nutritional composition of food products [15], [16]. According to Obadinna *et al.* [17], it is one of the household food technologies by which the nutritive value of plant foods could be improved as well as reduce their anti-nutritional factors. According to WHO [18], cereal crops such as maize, rice, sorghum, and millet, can be fermented to improve the nutrient content, energy density of gruels, carbohydrate digestibility, increase the bio-availability of amino acids and also improve their shelf life under controlled environment.

Apart from improving the functional, nutritional, and safety parameters of food products, fermentation had been proved through many studies to have the potential of affecting the antioxidant properties as well as health-promoting usage of plant foods. Oladeji *et al.* [16] studied the effect of fermentation on chemically active antioxidants; ascorbic acid, total carotenoids, total phenol, and total flavonoids of two yellow coloured maize varieties. The ability of the fermented maize extracts to scavenge free radicals using DPPH and ABTS assays was also studied in the same work. It was found out that fermentation significantly affects these parameters.

A. Fermentation Effects on Chemically Active Antioxidants in Maize

Plant foods are essentially contained antioxidant-rich phytochemicals such as phenolic compounds, ascorbic acid, carotenoids, anthocyanins, phytosterols, and policosanols,

which play a major role in human health by combating the adverse effect of free radicals. The more they increased in consumption of fruits, vegetables, or cereal grains, the lesser is the risk of chronic diseases [3]. Naturally occurring antioxidants in maize are unique due to the fact that they contain carotenoids, with carotenes constituting eight percent of the total carotenoids [3].

Oladeji *et al.* [16] determined the total carotenoid content of fermented and unfermented maize flour; the values were between 35.48 and 56.69 mg/100 g of the samples. This corroborates the report that yellow maize contains a significant amount of carotenoids [10]. The carotenoid content of unfermented normal maize flour extracts was lower; 35.48 and 46.85 mg/100g for UFNM and UFQPM, respectively indicating that QPM flour had higher carotenoid content than normal endosperm (Table I). Fermentation generally had an improvement effect on the total carotenoid content of the maize flour extracts. Better total carotenoids of fermented samples as compared with unfermented flours indicate that fermentation had increased the availability of total carotenoid in the maize flour samples. Similarly, fermentation increased the vitamin C content of the two maize varieties studies which is in agreement with earlier reports about fermentation increasing the vitamin C content of maize flour products [19], [20].

TABLE I: TOTAL CAROTENOID AND VITAMIN C CONTENTS (MG/100 G) OF MAIZE /MAIZE PRODUCT

Samples	Total carotenoid	Vitamin C
Unfermented Maize flour	35.48±0.33d	11.33±1.05c
Unfermented QPM	46.85±0.88c	12.67±1.15bc
Fermented maize flour	50.70±0.70b	14.67±0.58ab
Fermented QPM flour	56.69±0.27a	15.33±1.10ab

Values are reported as means ± standard deviation.

Mean values followed by different letters are significantly different ($p \leq 0.05$).

Source: Oladeji [15] and Oladeji *et al.* [16].

Both methanol and aqueous extracts of fermented and unfermented flours from the maize varieties were examined by Oladeji *et al.* [16]. It was observed that the total phenol of methanolic extract was between 0.564 and 0.702 mg/100 g TAE while that of aqueous was between 0.266 and 0.408 mg/100 g TAE (Table II). Fermentation had a reducing effect on the total phenol content of both the aqueous and methanolic extracts. This corroborates an earlier observation by Ellong *et al.* [21] that processing treatments had a reducing effect on various nutrient contents in plants. Across varieties, the reducing effect of fermentation was milder on FNM than in the FQPM in an aqueous medium; 0.275 and 0.266 mg/100 g TAE for FNM and FQPM flour samples, respectively, though without any significant difference. On the other hand, total phenol is more stable in FQPM flour than in FNM when in a methanol medium [16]. Ogunmoyole *et al.* [22] also agreed that methanolic extracts values of total phenol are higher than those of aqueous extracts.

In Oladeji *et al.* [16], flavonoids contents were reported to be reduced due to fermentation in flours from QPM and normal maize varieties. Sample FQPM contained 56.72 and 2.32 mg/g QE for methanolic and aqueous extract, respectively while FNM contained 1.72 and 56.06 mg/g QE flavonoid for aqueous and methanolic extract, respectively (Table II).

TABLE II: TOTAL PHENOL AND FLAVONOIDS CONTENTS, DPPH AND ABTS SCAVENGING POWER OF SOME MAIZE PRODUCTS

Samples		UFN	UFQ	FN	FQ
Total Phenol (mg/g TAE)	Aqueous Extract	0.408±0.006a	0.411±0.016a	0.275±0.005b	0.266±0.023b
	Methanol Extract	0.581±0.02d	0.702±0.01abc	0.564±0.06d	0.596±0.01cd
Total Flavonoid (mg/g Quercetin equivalent)	Aqueous Extract	19.51±1.88b	31.35±3.59a	1.72±0.21d	2.32±1.22cd
	Methanol Extract	42.09±3.25c	47.91±4.06b	56.06±0.24a	56.72±0.30a
DPPH Scavenging power (%)	Aqueous Extract	47.10	25.91	32.59	26.81
	Methanol Extract	20.70	17.13	18.96	15.32
ABTS scavenging Power (%)	Aqueous Extract	73.99	60.28	44.32	39.28
	Methanol Extract	58.27	61.44	43.85	40.33

Key: UFN – Unfermented decorticated normal maize, UFQ – Unfermented decorticated quality protein maize, FN – Fermented normal maize, FQ – Fermented quality protein Maize. Adapted from Oladeji [15] and Oladeji *et al.* [16].

The values reported for methanol extracts are similar to 58.22 mg/g QE earlier reported for Iranian Corn Silk [23]. Fermentation increased the flavonoid content of methanolic extract but showed a negative effect on the aqueous extracts. Also, Oladeji [15] noted that the fact that flavonoid content of the methanolic extracts was conspicuously higher than that of the aqueous extracts may be due to the solubility difference of phytochemicals depending on the solvent of extraction or/and polarity of the solvent. For instance, quercetin is soluble in ethanol but insoluble in water [24].

B. Effect of Fermentation on Scavenging Power of Maize Products

The scavenging power of some fermented and unfermented normal maize and QPM varieties was determined by Oladeji [15] using DPPH and ABTS assays. The DPPH radical is commonly adapted in evaluating the free radical scavenging activity of hydrogen donating antioxidants in plant extracts [25]. The ability of the different flour to scavenge DPPH shown in Table II differed significantly from one another. The DPPH scavenging power of aqueous extracts is within the range of 20.28 and 41.79% while that of methanol extracts is within the range of 11.38 to 20.70% (Table II). This result is lower compared to the report on fruit extract earlier reported possibly because fruits naturally possess higher antioxidant capacity than grains [26]. However, the result is close to 12.85% reported for *Kunu* without sugar- a Nigerian beverage made from corn [3]. Generally, fermentation had a reducing power on DPPH scavenging ability of all the flour extracts except for methanol extract of QPM which showed a little increase from the unfermented extract. It is possible that the gene modification done in developing QPM improves its constituent's stability during processing. However, the ability of the aqueous extracts of the maize flour samples to scavenge DPPH radical was higher than those of the methanol extract (Table II). This means that antioxidant with the ability to scavenge DPPH in the flour extracts was less soluble in the organic medium than in water; an advantage in product development as these flours are meant to be reconstituted in water before consumption. Therefore, this gives assurance of higher antioxidant benefits when consumed.

According to Awika *et al.* [27], ABTS assay was found to be superior because it is more rapid, cost effective, and can be operated over a wide range of pH. It was found out by Oladeji *et al.* [16] that the ability of aqueous and methanolic extracts of maize flours to decolourise ABTS is similar except for the unfermented normal maize UFN flour which is significantly higher than the aqueous (73.99%) and methanolic extract (58.27%) shown in Table 2. Normal

maize's extracts flour decolourised ABTS better than the extracts of QPM. In the study, the result of the aqueous extract showed that 73.99 and 60.28% of ABTS were decolourised by UFN and UFQPM flours, respectively (Table II). This was reduced by fermentation to 44.23 and 39.28% for FNM and FQPM flour extracts, respectively [15].

III. EFFECTS OF ROASTING ON NATURAL ANTIOXIDANTS IN MAIZE

Roasting is one of the popular primary processing applied to maize or corn as the case may be in most African countries. It is a processing method that employs the use of dry heat. It aids increase in the shelf life of foods and enhances the efficiency of the next processing steps [28]. Both fresh matured maize on the cob as well as dried maize grain is roasted before consumption or further processing. While the latter is used for food and feed, the former is used for food without further processing; a product which is popularly nicknamed 'mouth organ' in Nigeria. It is commonly eaten like a snack during maize peak season. Roasting of maize is not just fashionable but improves digestibility, increase energy supply, remove toxin, impact flavours and increase the availability of natural antioxidant compounds present in maize, thereby impacting digestive health, improving skin health, and so on [28], [29].

A. Roasting Effects on Chemically Active Antioxidants

Antioxidant activities cum health benefits of plant foods are chiefly determined by their phytochemical components. Some phytochemicals are common in many plant foods, while others are present solely in cereal grain products [30]. Significant antioxidant active phytochemicals found in maize include carotenoids, vitamin C and phenolics. Whole grains are specifically rich in phytochemicals and some of these occur with dietary fiber. These are released during digestion from the fiber complex due to the action of enzymes [31]. This may be the reason why the digestive enzyme-treated fiber-rich fractions of cereal flours exhibited higher antioxidant components and activity than untreated counterparts indicating that cereals may have fiber-bound phenolics which are released during digestion [32].

During processing, roasting resulted in to increase in the content and activity of antioxidants, development of brown colouration and enhanced flavour of end-products due to the presence of Maillard reaction products (MRPs) [33]. These changes impart better health benefits by helping the digestibility of nutrients and activity of available antioxidants [34].

TABLE III: EFFECT OF ROASTING ON ANTIOXIDANT CONTENT OF SOME MAIZE/MAIZE PRODUCT

Miaze/ Maize product	Type of roaster	Roasting condition	Effects	References
QPM grains (on cob)	Charcoal fire roasting	Local roasting	Phytate content reduced by 5.8% upon roasting when compare with raw	Omenna <i>et al.</i> , [29].
Corn local population (10 varieties)	Stainless pot roaster	150-190 °C for 20 mins	Total Phenol content (mgGAE/gDW) increased between 2.3 and 15.6% after roasting	Aramiuc [48].
Corn local population (10 varieties)	Stainless pot roaster	150-190 °C for 20 mins	Phytic acid content reduced in the of 15.6 and 23.2% in roasted seeds when compare with raw seeds	Aramiuc [48].
Maize grain	Electric rotary roaster (DR 1)	160-240 °C for 10-50 mins	Antioxidant activities and phenolic compounds increased with increase in temperature and time	Youn and Chung [49].
Maize grain	Electric rotary roaster (DR 1)	160-240 °C for 10-50 mins	Increase in phenolic compound is proportional to increase in roasting temperature and time	Chung <i>et al</i> [50].
Maize grain	Sand bath roaster	Local roasting	Phytic acid content decreased by 23.7 and 41.6% for dried and fresh grain, respectively.	Khan <i>et al.</i> , [51].

Summa *et al.* [35] reported that MRPs which are formed as a result of high heat treatment have molecular weights of less than 30 kDa and their antioxidant activity is strong. Disruption of the cell wall and cell membrane due to the thermal processing of grains is responsible for the release of soluble phenolics from the bonds of insoluble esters [36]. It was also reported that an increased quantity of solubilized ferulic acid (a phenolic acid) in roasted maize results in increase in total antioxidant activity which occurs significantly only at temperatures above 180 °C. In a study on the effect of forced convection roasting (FCCTR) on antioxidant properties of whole grain maize by Bala [30], it was found out that roasted S28 and S33 had total phenolics content in the range of 1.42 to 1.73 and 1.08 to 1.46 g GAE/100 g with R2 values of 0.59 and 0.75, respectively (Table III).

However, the quality, health benefit, and utilization of roasted corn may be dependent on the roasting conditions. Table 3 shows some roasting methods and condition and their effect on antioxidants. Roasting causes significant changes in the availability of their naturally occurring antioxidant compounds. Oboh *et al.* [3] reported that roasting reduces significantly at 95% confidence limit the extractable phenols of Maize varieties (yellow and white) roasted for 17 min; and allowed to cool, and later milled into powder. However, roasting caused a significant increase in the ferric reducing the antioxidant power of the maize varieties. The heat-processing method employed affects the decrease or increase in phenolic compounds and antioxidant activity in various types of foods. Roasting of barley using Sand and microwave oven at 280±5 °C for 20 seconds reduced total phenolics content by 8.5 to 49.6% and total flavonoids by 24.5 to 53.2%, and increased antioxidant activity by 16.8 to 108.2% [38].

Roasting results in chemical degradation and modification of phenolic compounds. It was reported that the modified phenolic compounds such as phenylindans demonstrated high antioxidant capacity [39]. Therefore, the ability of FCCTR in preventing significant loss of antioxidant activity and content might be ascribed to the use of superheated steam and rotation movement during the roasting process. This must have reduced the influence of dry heat (responsible for the Maillard reaction) on the maize grains. It is noteworthy that most phenolic compounds (phenolic acids and flavonoids) present in cereal grains are concentrated in the bran. [40]. Thus, consumption of whole grain maize flour of the roasted maize cultivars would be of immense health benefits due to the presence of bran and germ.

Carotenoid content of maize is highly variable among different strains; some varieties can contain as much as 80 µg total carotenoids/g dry weight [41], while white maize contains little to no retinol activity [42], [43]. In a study conducted by Omenna *et al* [29], it was reported that roasting had improved the bioavailability of vitamin A, which acts as the precursor of visual pigment 11-cis-retinal. The effect of roasting on vitamin A could be extrapolated to be the same on the total carotenoids content of maize. Vitamin A is essential in maintaining healthy vision and play. Also, it was observed by Wang and Russell [44] that the level of 9-Cis β-carotene is increased during heat processing. However, β-carotene has been shown to act as quench singlet oxygen, an immune modulator, and reduce peroxy radicals at a low partial oxygen pressure [44]. Various *in vivo* and *in vitro* studies have confirmed β-carotene's ability to prevent tumor cell growth and the progression of carcinogenesis [45]. To this end, regular intake of roasted quality protein maize reduces the risk of prostate and lung cancers and therefore, this is recommended for smokers [29].

B. Effect of Roasting on Scavenging Power of Maize Products

The chemical - 1, 1- diphenyl -2-picrylhydrazyl (DPPH) is a stable radical having a deep purple colour when reacting with other radicals, reducing agents, or compounds, it is capable of HAT leads to loss of colour which occurs at 515 nm as well as loss of its electron paramagnetic resonance (EPR) free radical signal [46]. Similarly, ABTS^{•+}, reacts with both hydrogen donors and electron [47]. Studies established the fact that roasting at high temperatures especially increases the DPPH scavenging ability of maize and maize products. Khongpan and Anprung [48] opined that the roasting temperature was the main factor affecting the bioactive compounds. In their study, the contour plots indicated that the optimum roasting temperature and time were 160 °C and 25 mins., respectively. The effects of roasting on the nutritional and antioxidant properties of yellow and white maize variety were determined by Oboh *et al.* [49]. A significant decrease in the phytate content was observed but the reduced phytate content did not have sparing effect on Zn bioavailability. The antioxidant properties (DPPH free radical scavenging ability and Fe²⁺ chelating ability) were reduced. However ferric reducing power of the maize varieties under study has increased significantly by roasting. Thus, roasting increased the energy value and antioxidant capacity as exemplified by high reducing power [49]. The DPPH antioxidant activity of

S28 and S33 ranged from 606.30 to 699.17 and 508.26 to 708.63 mM AAE/g with R² values of 0.26 and 0.70, respectively [50].

IV. CONCLUSION

Maize and other cereal crops are made to pass through different primary processing to enable their further use for product manufacture as food or feeds. It is an established fact the effects of processing and method of preparation of maize may increase or decrease its nutritive and health-promoting values depending upon the processing. As long as the whole grain is used, all nutrients and photochemical are retained; however, the gravity of alteration in the nutrients and phytochemicals in maize is dependent on the type and mode of processing the food material is subjected to. Fermentation results in the modification of cereals' phytochemicals; carotenoids content of maize increases due to fermentation, phenols, and flavonoids are reduced when subjected to the wild fermentation process. However, the scavenging power of fermented maize increased significantly after fermentation, especially the DPPH scavenging power of aqueous maize extract.

The effect of roasting includes increased antioxidant activity and content, development of brown colouration and improved flavour due to the presence of Maillard reaction products. These changes contribute to better health benefits by enhancing the digestibility of nutrients and activity of available antioxidants. However, the quality, health benefits and utilization of roasted corn may be dependent on the roasting conditions. Roasting causes significant changes in the availability of their naturally occurring antioxidant compounds; an increase in the ferric reducing antioxidant power of the maize varieties has been established, while some roasting methods had been implicated with a reduction in the phenolic contents of maize, FCCTR method of roasting had been reported to cause degradation and modification of phenolic compounds. The modified phenolic compounds such as phenylindans demonstrated high antioxidant capacity. Roasting had improved the bioavailability of vitamin A which acts as the precursor of visual pigment 11-cis-retinal had been improved due to roasting, and β -carotene significantly increased. Vitamin A is essential in maintaining healthy vision and play.

Therefore, intakes of roasted fresh or dried maize varieties; especially, QPM are highly recommended to ameliorate the causes of night blindness and blindness. Also, regular intake of roasted quality protein maize decreases the risk of lung and prostate cancers, and therefore, this is recommended for people who smoke. Overall, control fermentation processes raise the antioxidant capacity of maize products. Likewise, maize roasting using appropriate temperature conditions is advisable to optimize the health benefits of maize and its products.

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CONFLICT OF INTEREST

Author declares that they do not have any conflict of interest.

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