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Non-enzymatic browning and estimated acrylamide in roots, tubers and plantain products

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Abstract

Acrylamide has been discovered in foods, especially high carbohydrate foods that are dry-cooked (baked, fried or roasted) at high temperatures which also create the conditions for non-enzymatic browning. Baking, frying and roasting are common food preparation methods in Ghana. Fifteen different high carbohydrate foods in Ghana, that undergo dry-cooking, have been investigated for non-enzymatic browning and acrylamide production. The products that showed notable non-enzymatic browning and acrylamide levels include fried sweet potato, plantain chips from the fresh produce, with their respective non-enzymatic browning and acrylamide values as 0.095 ± 0.006 optical density (OD), 1043 ± 47.6 parts per billion (ppb); 0.034 ± 0.03 OD, 568 ± 22.9 ppb. Roots and tuber products had relatively high non-enzymatic browning and acrylamide levels while plantain products showed low levels of non-enzymatic browning and acrylamide.

Keywords: Acrylamide; Non-enzymatic browning; Dry-cooking

1. Introduction

Non-enzymatic browning of foods is the term given to the processes that finally result in the browning of food products without the involvement of enzymes, during and after processing. There are several reactions that could result in this; two such reactions are caramelisation (browning due to sugar–sugar reactions when heated at high temperatures) and the Maillard reaction (Maillard, 1912), which results from reactions between reducing sugars such as fructose and glucose on one hand, and protein and its derivatives (amino acids and amides) on the other. Although the two reactions result in the production of some acceptable organoleptic and aesthetic qualities in foods, particular attention has often been focused on the Maillard reaction and its associated end products. This is because it is believed to produce deleterious effects on the nutritional quality of foods, as a result of the involvement of amino acids and protein derivatives, resulting in a loss in the availability of essential amino acids, such as lysine. More recently, non-enzymatic browning, by the Maillard reaction mechanism, in carbohydrate foods has been brought under much scrutiny, because of the reported production of acrylamide (Troxell & Posnick, 2003) as one of its end products. It has been reported that when starchy foods are cooked at high temperatures, such as in frying, roasting or baking, the Maillard reaction occurs and an amino acid, particularly asparagine, reacts with sugars to produce acrylamide. Asparagine is a common amino acid in the proteins of potatoes, cereals, and many other foods (Becalski, Lau, Lewis, & Seaman, 2003; Mottram, Wedzicha, & Dodson, 2002).

Although much work has been done on non-enzymatic browning in foods, especially in Europe and the Americas, such as for potato (Marquez & Añon, 1986), Kiwifruit (Wong & Stanton, 1989), pear (Cornwell & Wrolstad, 1981) and apple (Babsky, Toribio, & Lozano, 1986; O'Beirne, 1986; Toribio & Lazano, 1984), not much has been done on foods in Africa in general and Ghana in particular. The only reported work on non-enzymatic browning in

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Ghanaian foods was by Rohan and Stewart (1966) on cocoa beans, and this is probably, because of its economic value and inherent health benefits. Recent studies on non-enzymatic browning in foods have focused on the effect of water activity and its related effects (Bell, White, & Cheu, 1998; Bell, 1995; Buera & Karel, 1995; Karmas, Buera, & Karel, 1992; Karmas & Karel, 1994). The recent discovery of acrylamide in foods (Hagner et al., 2001) has made it imperative for scientists to refocus research efforts on non-enzymatic browning and its associated products.

Acrylamide is a potential carcinogen, with known neurotoxic effects in animals and humans. In humans, for example, studies done by US EPA, 1985 have indicated that toxicity from acrylamide includes signs and symptoms like paresthesias in the fingers, coldness, numbness in the lower limbs, and weakness of the hands and feet. Moreover, exposure of acrylamide to humans in drinking water has resulted in drowsiness, disturbances of balance, confusion, memory loss and hallucinations (HSDB, 1994). Although the studies carried out so far could not indicate conclusively that the occurrence of some cancers is due to food acrylamide (Mucci, Dickman, Steineck, Adami, & Augustsson, 2003), there is the need for more work, since acrylamide has not been tested for "no observable adverse effect level" in toxicological studies (Lutzow, 2002). Coughling (2003), states that the reported levels of acrylamide are higher than those of other contaminants that have been known to occur in foods over the past thirty years. In all this however, the Food and Drug Administration (FDA) of the US, and other regulatory bodies all over the world, have not yet arrived at specific acceptable levels for acrylamide in foods, except to caution that they should be eaten in moderation, at least for now.

Most of the staple foods in Ghana are derived from high carbohydrate crops such as cassava, yam, cocoyam, sweet potato, plantain, maize and several others that are locally cultivated. They are frequently processed using simple traditional means, such as boiling, deep fat frying, roasting and baking. Baking, roasting and deep fat frying are high temperature processes that have been confirmed to induce non-enzymatic browning and acrylamide formation. For the health and well being of the consumers, it is important to establish a baseline database for the occurrence of acrylamide in the dry processed foods in Ghana, commonly eaten at high temperature. Consequently, the objective of this work is to study the occurrence of non-enzymatic browning in Ghanaian traditional foods derived from roots, tubers and plantain, through high temperature cooking methods, and to estimate the levels of acrylamide in them.

2. Materials and methods

2.1. Materials

Fifteen different dry processed food samples (baked, fried or roasted) were bought from various markets, street vendors and restaurants within the city of Accra. The samples were processed foods from cassava (*Manihot esculenta*), yam (*Dioscorea rotundata*), cocoyam (*Xanthosoma mafaffa*), sweet potatoes (*Ipomoea batatas*) and plantain (*Musa paradisiaca*). Freshly processed French fries were also bought from a popular food service centre.

2.2. Sample preparation

The baked/roasted or fried foods were ground to fine particle sizes using a laboratory mortar and pestle. The grinding was done for the whole and crust of some foods and only the whole for some others. The ground samples were packaged in polyethylene bags and stored at freezing temperature (−18 °C) until ready for use. Fresh potatoes were either roasted or fried according to the dry-cooking conditions employed by Troxell and Posnick (2003). These were also ground to a fine powder and stored as described above.

2.3. Solvent selection

In order to select the best solvent for the extraction of non-enzymatic browning products, various solvents were tested for their ability to extract browning products. The tested solvents included distilled water, 50% ethanol, dilute base (NaOH), dilute acid (HCl) and hexane/acetone (1:4).

2.4. Determination of non-enzymatic browning

The method of Hendel, Bailey, and Taylor (1950) was adopted with little modification. One gram of each sample flour was measured into a 250 ml Erlemenyer flask and 50 ml of distilled water added to each sample. The samples were allowed to stand for 1 h and filtered using 595 Rundfilter filter paper. The filtered extracts were centrifuged (TOMY CX 250 model) for 30 min at 23,000*g*. The clear supernatants were acidified with 0.5 ml of 40% v/v acetic acid. The non-enzymatic browning was measured at a wavelength of 420 nm in the Shimadzu spectrophotometer UV-120 against a blank. Sample lots were triplicated with five spectrophotometric readings per replicate.

2.5. Estimation of acrylamide

Frozen French fry potato samples were prepared according to Troxell and Posnick (2003) and the non-enzymatic browning determined using the method of Hendel et al. (1950) with the modification as described above. The values obtained for the non-enzymatic browning for the processed potatoes were plotted against their corresponding acrylamide values as reported by Troxell and Posnick (2003). The graph obtained was used to estimate the acrylamide values of the test samples.

2.6. Statistical analysis

The means and standard deviation of the values for non-enzymatic browning and acrylamide were calculated using

Microsoft Excel 2003. Graphs were drawn using Microsoft Excel 2003.

3. Results and discussion

3.1. Solvent selection

From Fig. 1, distilled water was the singular solvent that gave the highest spectrophotometric reading at 420 nm. This finding is consistent with the report of Spark (1969) that melanoidins and, for that matter, non-enzymatic browning products are best extracted using water. This might also explain why in the method of Hendel et al. (1950), water was used as the solvent for extraction. However, since non-enzymatic browning products are organic in nature, it was expected that organic solvents would extract best, but the results proved otherwise.

3.2. Non-enzymatic browning levels

Table 1 shows the non-enzymatic browning (420 nm absorbance) values of products from cassava (*M. esculenta*), cocoyam (*X. mafaffa*), yam (*D. rotundata*) and plantain (*M. paradisiacal*). It is not quite clear which of the processes (frying or roasting) caused more non-enzymatic browning. It is, however, clear that the type of product and processing method collectively contributed to the intensity of non-enzymatic browning. For example, fried whole cassava (*M. esculenta*) paste "*agbele krakro*" had a value of 0.021 optical density (OD) at 420 nm while fried sweet potato (*I. batatas*) recorded a value of 0.095 O.D. This variation in browning levels is also evident in the roasted products.

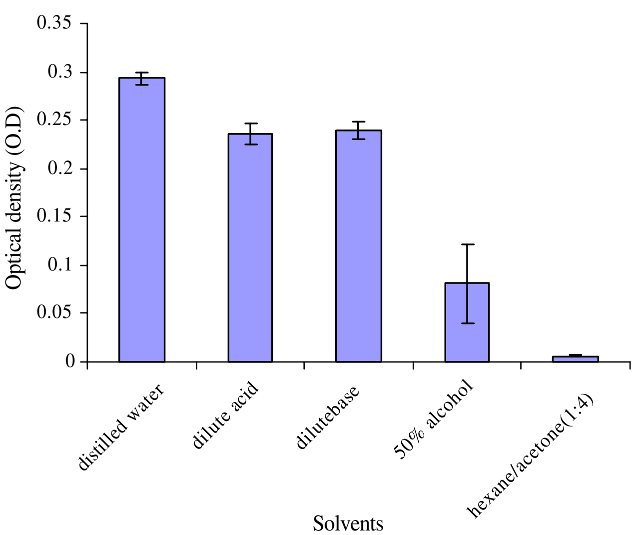

Fig. 1. Non-enzymatic browning extraction efficacy at 420 nm.

In Table 1, the general observation is that the products from unripe plantain browned more than those from ripened plantain. For example, plantain chips made from unripe pulp recorded 0.034 OD while the chips from ripened pulp had 0.019 OD. This is a reduction of about 44%. This may be due to presence of sugars which contribute to browning through pyrolysis (Mazza, 1983; Schallenberger, Smith, & Treadway, 1959) or reaction with amino acids. The increased non-enzymatic browning in the unripe plantain could also be due to the additive effect from enzymatic browning, which is more pronounced in unripe plantain than ripe. As the processes are not standardised, most of the processors used crispness or browning intensity as an index for completion of cooking. The unripe pulp will therefore be cooked for a relatively longer time and hence the relatively higher non-enzymatic browning value. For the ripened plantain, the breakdown of starch and sugars may have decreased the water activity, resulting in decreased non-enzymatic browning (Karmas & Karel, 1994). In addition, the sugars naturally undergo non-enzymatic browning (caramelisation) when heated, and since in most of the plantain products, the browning level is an index for cooking, the high sugar levels resulting from ripening will result in high browning intensity at the surface as opposed to little or no browning at all at the core. This is seen in fried plantain paste (krakro), where the crust recorded a very high value for browning, but the 'whole' recorded a value comparable with those of the other ripened products.

Table 1
Browning levels in some foods in the market (roots, tubers and plantain products)

Food item	Browning at 420 nm	Food item	Browning at 420 nm
Roasted yam whole	0.027 ± 0.004	Fried agbele krakro crust	0.025 ± 0.002
Roasted yam whole	0.068 ± 0.005	Pringles original (potato)	0.053 ± 0.006
Roasted cocoyam whole	0.016 ± 0.004	Plantain chips – fresh	0.034 ± 0.003
Roasted cocoyam crust	0.043 ± 0.010	Plantain chips – ripened	0.019 ± 0.003
Fried yam whole 1	0.035 ± 0.011	Fried ripe plantain	0.017 ± 0.002
Potato chips (Papaye)	0.005 ± 0.002	Roasted ripe plantain	0.024 ± 0.003
Potato chips (Tacobel)	0.009 ± 0.002	Krakro whole	0.022 ± 0.003
Fried sweet potato whole	0.095 ± 0.006	Krakro crust	0.064 ± 0.003
Fried yam whole 2	0.057 ± 0.004	Kalawele	0.024 ± 0.003
Fried agbele krarkro whole	0.021 ± 0.002		

Values are means of fifteen readings from three replicate determinations ($n = 3$) $\pm$ SD.

3.3. Acrylamide

Fig. 2 shows the acrylamide estimation curve, based on the regression of non-enzymatic browning on acrylamide formation. In the roots and tubers (Fig. 3) the highest estimated acrylamide was found in sweet potato (*I. batatas*), with a value of 1043 ± 47.6 ppb. Almost all the products in this category recorded high values, with most of them recording values more than 500 ppb. This value is a thousand times higher than the levels of acrylamide allowable, in bench marked products such as tap water (0.5 μg/l), as suggested by the World Head Organization (WHO, 1993). However, the estimated low values of potato chips, from restaurants, are notable. These low values are far less than what has been found for potato chips in similar studies (FDA, 2003; SCF, 2002; SNFA, 2002; Troxell & Posnick, 2003). The value obtained for "Pringles" potato chips, compares very well with reported values (SCF, 2002; Troxell & Posnick, 2003), suggesting that the method used for the estimation of acrylamide was appropriate. Fig. 4 shows that the acrylamide levels in plantain products were lower in comparison to those of the other products (Fig. 3). Most of the plantain products had acrylamide values close to 500 ppb.

It is important to note that when comparing the levels of acrylamide allowable in drinking water with the levels allowable in food, the values estimated for foods collected in restaurants and streets should not necessarily be a source of public health concern and outcry. There is still much to be learned about acrylamide in foods, including the toxicity and safety levels, since the metabolic fate of the chemical in food is still a subject for research. The conclusions and observations made on acrylamide in foods in other studies (Troxell & Posnick, 2003) also hold true in this study, that is, among similar categories of foods, there are differences in acrylamide levels.

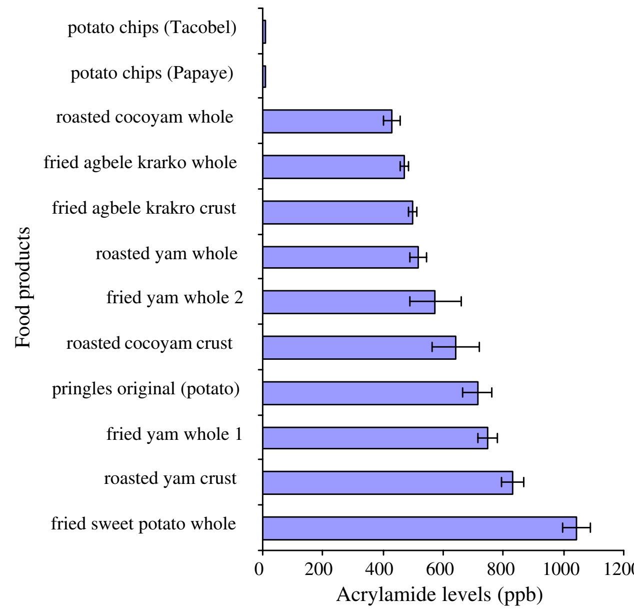

Fig. 3. Comparative histogram of estimated acrylamide levels in products from roots and tubers.

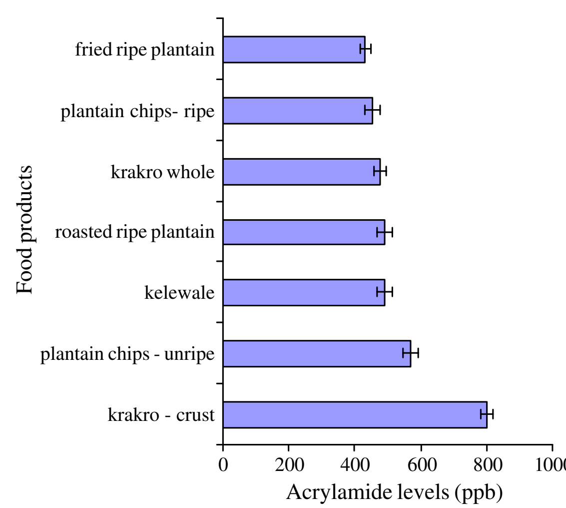

Fig. 4. Comparative histogram of estimated acrylamide levels in plantain products.

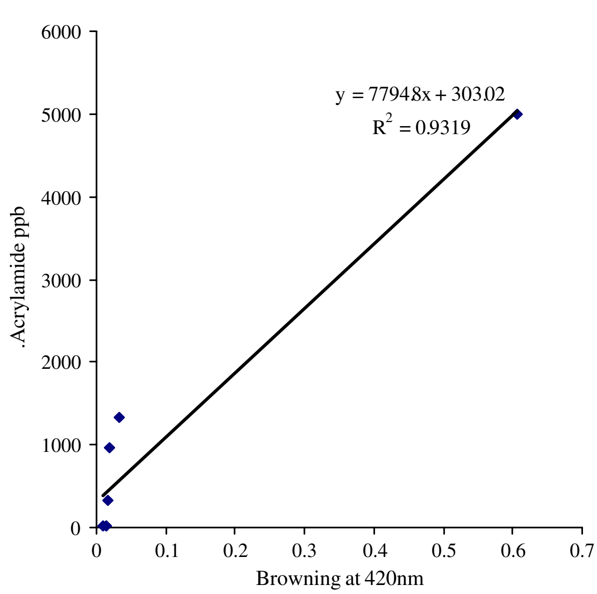

Fig. 2. Acrylamide estimation curve.

3.4. Conclusion

Dry processed (deep fat fried, roasted, baked) foods, commonly sold in restaurants or on the streets in Ghana, have varying degrees of browning with corresponding acrylamide concentrations. The browning intensity of products from root crops and tubers was high, and so was the acrylamide level. Plantain products had relatively low acrylamide and non-enzymatic browning values.

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