Effect of Inorganic Salts on Acrylamide Formation in Cereal Matrices

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Abstract: The aim of the work was to compare the impact of different salts such as monovalent and divalent chlorides, hydrogencarbonates, phosphates and lactate on acrylamide formation in cereal model system during baking at 190°C for 9 min. Ammonium hydrogencarbonate promoted acrylamide production significantly. On the other hand, other inorganic salts lowered acrylamide content. Calcium chloride was the most effective with near to 90% acrylamide elimination ability. Sodium acid pyrophosphate, sodium as well as potassium dihydrogen phosphate were also very effective and brought about 75% acrylamide content decrease, followed by calcium lactate, sodium chloride and potassium chloride causing 40–45% of acrylamide elimination and finally sodium and potassium hydrogen carbonates that achieved 30% reduction of acrylamide.

Keywords: acrylamide; cereals; raising agents

INTRODUCTION

Acrylamide presence in food attracts a major concern due to its potential health impact.

Acrylamide formation was found to occur during a thermal process, by Maillard reaction, of reducing sugars with asparagine at temperatures above 120°C (Stadler *et al.* 2002).

Ammonium-based raising agents are widely used in biscuit manufacture, either individually or as part of a mixed raising system providing browning, crisp and porous crumb (Sadd *et al.* 2008). Nevertheless, there is a deficiency of ammonium hydrogen carbonate in significant encouragement of acrylamide formation in bakery products. On the other hand, metal ions in salts that is added in to cereals as a raising agents, preservatives or fortificants was demonstrated to cause a reduction of acrylamide. For example, the fortification of flour in U.K. with 0.3% calcium carbonate gave the acrylamide reduction of about 30% (a similar effect was obtained using calcium chloride or magnesium addition). It is noteworthy that not only cations but also anions play an important role in effect on acrylamide formation during food processing. Calcium causes an acrylamide reduction if is added as a carbonate or chloride. However, calcium propionate which is added as a preservative (up to 0.2%) resulted in more than 90% increase in acrylamide (Gökmen & Şenyuva 2007*;* Sadd *et al.* 2008; CIAA Toolbox 2009). The aim of presented study was to compare selected salts on acrylamide formation in cereal model system.

MATERIAL AND METHODS

A cereal model system consisted of 0.38 g of wheat starch, 57 mg of fructose, 63 mg of glucose monohydrate, 0.38 mg of L-asparagine monohydrate and 380 µl of water to simulate the main composition of acrylamide precursors in dough. Reactants were combined in a closed glass test vials with PTFE lined storage caps and mixed well using vortex. Selected salts, NaCl, $CaCl_2 \cdot 2H_2O$, $KHCO_3$, $NaH_2PO_4 \cdot 2H_2O$, KH_2PO_4, $NaHCO_3$, NH_4HCO_3, $Ca(C_3H_5O_3)_2 \cdot 5H_2O$ (marked as: CaL_2), $Na_2H_2P_2O_7$ and KCl were added in concentrations 0.01, 0.05 and 0.1 µmol/g into model system. Impact of salts on pH value of system was measured in the highest concentration. Baking conditions were tested at 190°C during 30 min to find out the maximum of acrylamide formation. All samples were prepared in triplicate. Acrylamide was extracted by acetic acid with further pre-extraction to ethylacetate to avoid the negative impact of salts reported by Gökmen and Şenyuva (2006) using the chromatography system published earlier (Ciesarová *et al.* 2009).

RESULTS AND DISCUSSION

Free amino acid asparagine in combination with reducing sugars generates significant amounts of acrylamide when heated at temperatures greater than 120°C (Mottram *et al.* 2002; Stadler *et al.* 2002). The generation of acrylamide in the cereal model system at customary baking temperature of 190°C was characterised by very fast acrylamide formation in first 7 min followed by a short interval of relative stabile acrylamide concentration up to 10 min and subsequent an acrylamide decrement (Figure 1). The decline of the curves was most likely due to polymerisation as recently reported (Stadler *et al.* 2004; Kolek *et al.* 2007). Reasonably, 9 min of baking was selected as a suitable time for thermal input in experiment for the determination of concurrent formation and degradation of acrylamide in the presence of selected salts.

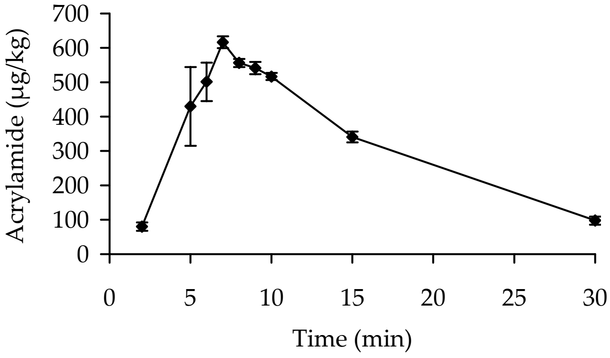

Figure 1. Formation of acrylamide in cereal model system during baking at 190°C

When the cereal model system without the presence of salt was heated, the yield of (603 ± 29) µg/kg of acrylamide was achieved at 190°C after 9 minutes. The presence of salts in the reaction mixture resulted in a decrease of acrylamide concentration (Figures 2 and 3) with exception of ammonium hydrogen carbonate NH_4HCO_3, a well-known accelerator of acrylamide formation, since the highest content of acrylamide was detected (1488 ± 130 µg/kg, Figure 2). As it has been published, NH_4HCO_3 increased the formation of sugar fragments (glyoxal and methylglyoxal) that reacted rapidly with asparagine to furnish acrylamide in higher yield than the native reducing sugars under mild conditions. To achieve the correct balance of gas release during baking and optimum texture, flavour and colour, combinations of NH_4HCO_3, $NaHCO_3$ and acidulant are often required (CIAA Toolbox 2009). On the other hand, it has been suggested that adding of divalent metal ions could give additional high-temperature stability to asparagine matrix interactions (stable polymer network), thereby rendering the latter species unavailable for reaction with carbonyl precursors to produce acrylamide (Sadd *et al.* 2008). Gökmen and Şenyuva (2007) showed that the presence of cations in the reaction mixture

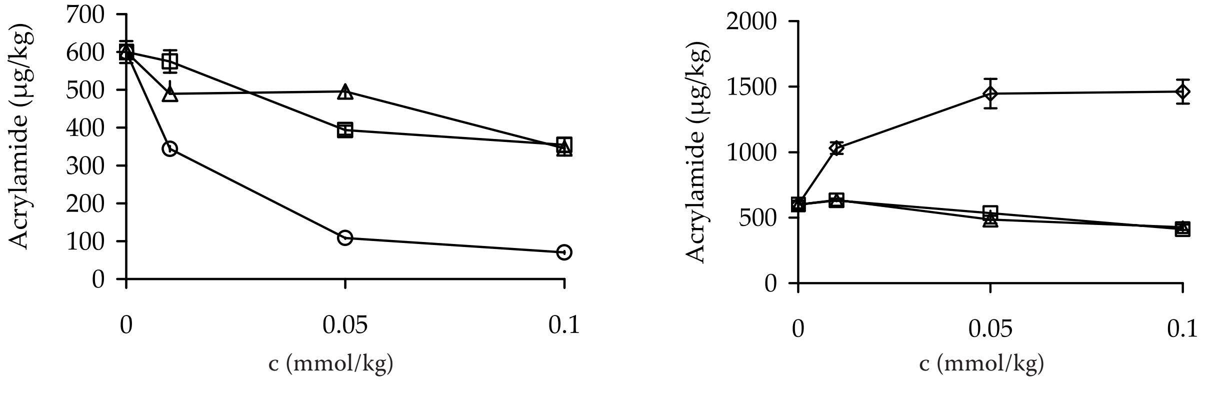

Figure 2. Effect of chloride (A – □ NaCl, pH 6.42, △ KCl, pH 6.32, ○ $CaCl_2$, pH 6.24) and hydrogen carbonate anions (B – □ $NaHCO_3$, pH 7.67, △ $KHCO_3$, pH 7.74, ○ NH_4NCO_3, pH 7.76) of sodium, calcium, potassium and ammonium salts on acrylamide formation in cereal model system (190°C/9 min)

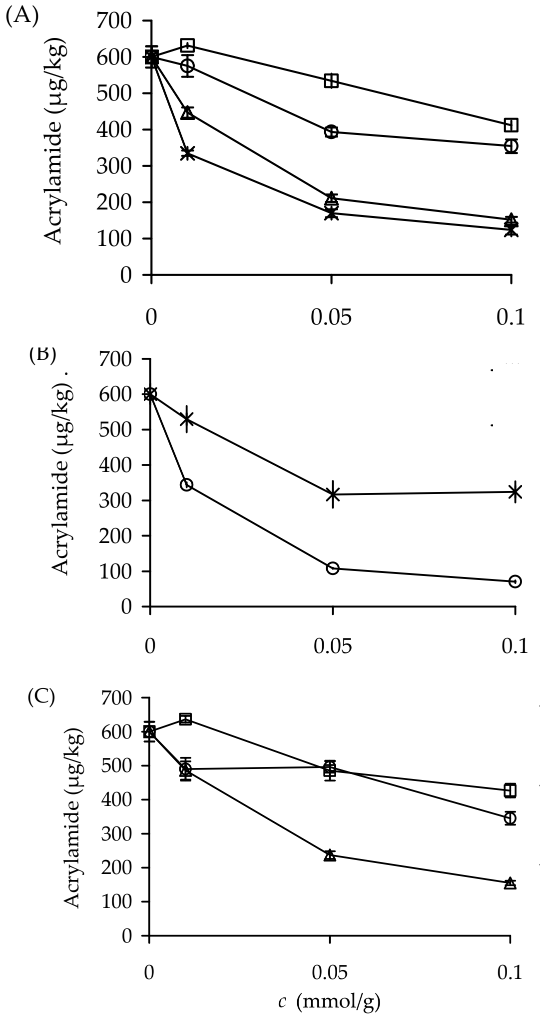

Figure 3. Effect of sodium (A – □ $NaHCO_3$, pH 7.67, ○ NaCl, pH 6.42, △ KH_2PO_4, pH 4.90, ✱ $Na_2H_2P_2O_7$, pH 7.76), calcium (B – □ $KHCO_3$, pH 7.74, ○ KCl, pH 6.32, △ KH_2PO_4, pH 4.88), and potassium cations (C – ✱ CaL_2, pH 6.45, ○ $CaCl_2$, pH 6.24) of different salts on acrylamide formation in cereal model system (190°C/9 min)

influenced the rate of decomposition of acrylamide precursors significantly, mainly glucose, while the most asparagine remained unreacted. It was confirmed by mass spectrometric analyses of pyrolysates that the formation of the Schiff base of asparagine, which is the key intermediate leading to acrylamide, was prevented; meanwhile the reaction proceeded to form brown coloured products. Although the monovalent cations prevented from the formation of acrylamide in a certain extent, it was less efficient than the divalent cations (Gökmen & Şenyuva 2007). It was confirmed also in the presented study (Figure 2) where NaCl and KCl caused the comparable acrylamide mitigation from (603 ± 29) μg/kg up to (345 ± 19) μg/kg whereas $CaCl_2$ resulted in the final acrylamide concentration of (70 ± 4) μg/kg. The effect of the non-ammonium-based raising agents could be explained entirely in terms of shifts in pH that is obvious from results in Figure 3 depicting different sodium, calcium and potassium salts. Nevertheless, there is a need to take into account that low pH is beneficial for acrylamide, but is limited in practice by dough buffering and the risk of promoting other contaminats such as 3-monochloropropane-1,2-diol (3-MCPD) (Sadd *et al.* 2008).

Gökmen and Şenyuva (2007) successfully applied chlorides to reach an acrylamide mitigation in potato strips by dipping into the 0. M solution of $CaCl_2$ as well as NaCl. The results confirmed that divalent cations were capable of inhibiting the formation of acrylamide. Despite the promising efficiency of $CaCl_2$ in acrylamide reduction strategy in food, trials at benchscale have given variable results, strongly affecting a product quality where calcium chloride hindered the rise of sweet biscuits and the products were unpalatable when tasted. For that reason, this approach have not been commercialised yet (CIAA Toolbox 2009).

It can be concluded that using inorganic salts is effective acrylamide mitigation strategy. $CaCl_2$ was the most effective in acryalmide mitigation in cereal model system followed by pyrophosphates and phosphates such as $Na_2H_2P_2O_7$, $NaH_2P_2O_4$ and $KH_2P_2O_4$.

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