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Review

Reducing the potential for processing contaminant formation in cereal products☆

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ABSTRACT

Processing contaminants may be defined as substances that are produced in a food when it is cooked or processed, are not present or are present at much lower concentrations in the raw, unprocessed food, and are undesirable either because they have an adverse effect on product quality or because they are potentially harmful. The presence of very low levels of processing contaminants in common foods is becoming an increasingly important issue for the food industry, as developments in analytical techniques and equipment bring foods under closer and closer scrutiny. This review considers the formation of lipid oxidation products, hydrogenation of polyunsaturated fatty acids to prevent lipid oxidation and the associated risk of *trans* fatty acid formation. The formation of acrylamide in the Maillard reaction is described, as well as the genetic and agronomic approaches being taken to reduce the acrylamide-forming potential of cereal grain. The multiple routes for the formation of furan and associated chemicals, including hydroxymethylfurfuryl, are also described. The evolving regulatory and public perception situations for these processing contaminants and their implications for the cereal supply chain are discussed, emphasising the need for cereal breeders to engage with the contaminants issue.

1. Introduction

A food contaminant, based on dictionary definitions, may be described as a substance that makes a food impure. Foods are complex mixtures, of course, so it may be more useful to define a contaminant as something that would not normally be present in the food, has been introduced inadvertently from an external source or as a result of microbial, fungal or animal activity, or even just as something undesirable. Mycotoxins produced by fungal activity are an obvious example and are dealt with in another article in this volume. The issue becomes more complicated when food processing and cooking are involved, as these may bring about substantial changes in composition, including the production of substances that are not present in the raw food. Of course, these changes may be necessary to make the food edible and/or palatable, and when these substances are responsible for the colour, flavour and aroma of a food and have no negative effect on human health they are certainly not described as contaminants. Some of these compounds, however, do have the potential to have a negative effect on product quality, or even to cause harm, and therefore fall into the category of processing contaminant. We may therefore describe a processing contaminant as a substance that is produced in a food when it is cooked or processed, is not present or is present at much lower concentrations in the raw, unprocessed food, and is undesirable either because it has an adverse effect on product quality or because it is potentially harmful.

In this review, we describe four processing contaminants, *trans* fatty acids, acrylamide, furan and hydroxymethylfurfuryl, their implications for the cereal food supply chain, and the strategies that are being or could be developed to reduce their levels in cereal-derived products.

2. Thermal oxidation of lipids and the production of *trans* fatty acids

Wheat (*Triticum aestivum*), barley (*Hordeum vulgare*) and rye (*Secale cereale*) grain contains only approximately 1% oil and it is not worth extracting the oil for commercial use. Maize (*Zea mays*)

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and oat (*Avena sativa*) grain, however, contain around 5% and 7% oil, respectively. There is some commercial use of oat oil in cosmetics and skin moisturisers, but maize oil is a much more important commodity, with, for example, 1.3 billion litres of it being used in the USA in 2012, mostly for margarine and cooking oil (data from United States Department of Agriculture). Maize oil is made up of linoleic acid (54%), oleic acid (30%) and palmitic acid (12%), with stearic acid and α-linolenic acid making up the rest. Linoleic acid is an 18-carbon, omega-6 (18:2 n-6) polyunsaturated fatty acid, while oleic acid is an 18-carbon, omega-9 (18:1 n-9) monounsaturated fatty acid and palmitic acid is a 16-carbon saturated fatty acid (16:0). Polyunsaturated fatty acids are prone to oxidation during cooking and high-temperature processing, giving rise to lipid peroxides. These can form polymers that give a dark colouration and may be toxic. They can also breakdown to form various ketones, alcohols, hydrocarbons, acids and epoxides. These breakdown products cause a rancid, 'off' flavour and odour and can give rise to the formation of furans (Section 4).

Traditionally, food processors have avoided polyunsaturated fatty acid oxidation by chemical hydrogenation of the double bonds, converting the fatty acids to monounsaturates and saturates. Saturation of the fatty acids in plant oils also solidifies them, making them suitable for the production of margarines. The problem with the process is that some of the double bonds remain unsaturated but change from the *cis* form, which is present in the naturally-occurring molecule, to the *trans* form. In the *cis* form, the two hydrogen atoms attached to the carbon atoms involved in the double bond are on the same side of the double bond, while in the *trans* arrangement they are on opposite sides. The molecule is therefore identical to the naturally-occurring polyunsaturate in terms of length and number of double bonds but has a more linear shape. Nevertheless, it is regarded as so different from the *cis* form of the molecule that in the USA and Europe it cannot legally be designated as a polyunsaturate in food. This is partly because *trans* fatty acids arising from partial hydrogenation of plant oils are now regarded as being as harmful as saturated fatty acids in raising the level of low-density lipoprotein (LDL) cholesterol when consumed (reviewed by Brouwer et al., 2010) (it should be noted here that, in contrast to *trans* fatty acids produced in this way, vaccenic acid, a *trans* fatty acid found naturally in beef and dairy products, has been claimed to have health benefits (Bassett et al., 2010; Wang et al., 2010)).

The US government introduced legislation requiring information on the *trans* fat content of food products to be included in the Nutrition Facts panel of food labels in 2008 and, while there is no European Union legislation on *trans* fats, some Member States have acted independently. Denmark, for example, introduced legislation in 2003 limiting the *trans* fat content of fats and oils to 2%, with the limit applying to ingredients, not finished foods. The United Kingdom government, on the other hand, has not introduced legislation but there is a voluntary pledge from all major food manufacturers to remove *trans* fats from their products.

Soybean oil also contains a lot of linoleic acid and a genetically modified (GM) variety, Plenish, in which the activity of a gene encoding a *delta-12* desaturase enzyme that converts oleic acid to linoleic acid is reduced, has been produced by PBI, a subsidiary of DuPont. This variety accumulates oleic acid to approximately 80% of its total oil content, compared with 20% in non-GM varieties (Kinney, 1997), making the oil more stable during frying and cooking, less prone to oxidation and therefore less likely to form compounds that affect flavour (Mounts et al., 1994; Cahoon, 2003). Hydrogenation, with its risk of *trans* fatty acid formation, is not required. Monsanto also has a high oleic acid variety, Vistive, on the market; in this variety the high oleic acid trait was developed by mutagenesis, not GM, although the variety also carries a GM trait for tolerance of the herbicide, glyphosate. The technology has attracted some controversy because linoleic acid and its further desaturated derivative, α-linolenic acid, are important dietary fatty acids and consumers may not understand the significance of the changes that have been made. There are currently no reports of it being transferred to maize, despite the established market for biotech maize varieties in the USA and many other parts of the world. Nor are we aware of other non-GM approaches to reducing the risk of *trans* fatty acid formation.

3. Acrylamide

3.1. Chemistry of the Maillard reaction and formation of acrylamide

The Maillard reaction, which was named after the French chemist, Louis Camille Maillard, who first described it in 1912 (Maillard, 1912), comprises a series of non-enzymic reactions between sugars and amino groups, principally those of amino acids. It takes place only at high temperatures and occurs mainly in cooked foods prepared by frying, baking and roasting. The reaction requires a reducing sugar such as glucose, fructose or maltose, although sucrose can participate if it is first hydrolysed through enzymic, thermal or acid-catalysed reaction (De Vleeschouwer et al., 2009). The products of the reaction include melanoidin pigments, which are complex polymers that are responsible for the brown colour in fried, baked and roasted foods, including bread crust, biscuits, crackers, cakes, tortillas, fried tortilla chips and other snacks, and toasted grains. The reaction also provides complex mixtures of compounds that impart flavour and aroma, including pyrazines, pyrroles, furan (a contaminant described in Section 4), oxazoles, thiazoles and thiophenes (Mottram, 2007). The particular compounds formed give different cooked foods and brands their defining characteristics, and depend on the amino acid and sugar composition of the raw material and the processing conditions.

The reaction is initiated by the condensation of the carbonyl (C═O) group of a reducing sugar with the amino group of an amino acid or other amino compound, producing a Schiff base. The Schiff base cyclises, in the case of an aldose to produce an N-substituted aldosylamine, such as glucosylamine from glucose, then undergoes acid-catalysed rearrangement to an Amadori rearrangement product (or a related Heynes rearrangement product if the sugar is a ketose), followed by enolisation, deamination, dehydration and fragmentation to give rise to sugar dehydration and fragmentation products. These intermediates include furfurals, furanones and pyranones. They contain one or more carbonyl groups and are therefore highly reactive and can undergo further condensation reactions with amino groups and other species.

The Maillard reaction is very complex and more information can be found in reviews by Halford et al. (2011), Mottram (2007) and Nursten (2005). While many of its products contribute to the flavour, colour and aroma of food, some are undesirable (Friedman, 2005). Indeed, as long ago as 1980, it was noted that the nutritional value of foods decreased after browning and that this must be caused by the generation of undesirable compounds (Yannai, 1980). It has since been discovered that one of the reactions of carbonyl compounds is Strecker degradation, whereby an amino acid is deaminated and decarboxylated to give an aldehyde and an α-aminoketone, and that a Strecker-type reaction involving asparagine results in the formation of acrylamide (Mottram et al., 2002; Stadler et al., 2002; Zyzak et al., 2003). This appears to be the major route for acrylamide formation, but others have been proposed, for example with 3-aminopropionamide as a possible transient intermediate (Granvogl and Schieberle, 2006) or through pyrolysis of gluten (Claus et al., 2006).