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The role of the Maillard reaction in the formation of flavour compounds in dairy products – not only a deleterious reaction but also a rich source of flavour compounds
The role of the Maillard reaction in the formation of flavour compounds in dairy products – not only a deleterious reaction but also a rich source of flavour compounds

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Dairy products are heated both during processing and by consumers during food preparation; consumers place a high level of importance on flavour when assessing product acceptability. Of particular importance to the flavour of heated dairy products is the highly complex network of Maillard reactions. Much focus has been placed on the undesirable flavours generated through the Maillard reaction and how to minimise the formation of these flavours. However, beneficial flavours can also be formed by the Maillard reaction; dairy products, such as ghee, are formed by heating and are characterised by the unique flavour generated by this chemistry. This review looks at the Maillard reaction as a source of beneficial flavours for cooked dairy products and the application of models to the study of flavour formation in food systems. Models are typically used to study complex reactions in a simplified way; however, they are not always applicable to food systems.

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Antony Fairbanks undertook both his first degree and DPhil in Chemistry at Oxford University (Wadham College), for the latter working with Professor George Fleet. After Postdocs with Professor Pierre Sinay (Ecole Normale Superieure, Paris) and Professor Steve Ley (Cambridge), he moved back to Oxford to as University Lecturer in 1996. In 2009 he moved to the University of Canterbury in Christchurch, where he was appointed as Head of the Department of Chemistry in November 2010. His research interests focus on synthetic carbohydrate chemistry, the stereocontrol of glycosylation reactions, and the synthesis of glycoconjugates and glycomimetics as potential therapeutic agents.
Introduction

The flavour of dairy products can be particularly important to consumers. Milk that is fresh and of high quality typically has a characteristic mild flavour, consequently any deviation in flavour will be obvious. Whilst a major source of flavour components is the milk itself, the degradation of milk constituents during processing can also have a significant impact on the final flavour profile.

The quality of many foods, including dairy products, is affected by the Maillard reaction, and this becomes more significant when those foods are heated. The highly complex network of reactions can produce an attractive taste, appearance and aroma for the consumer or it can develop undesirable colours, off-flavours and potentially harmful reaction products. Changes to functional properties of milk proteins can also occur. In the context of dairy foods, these undesirable flavours are of concern in both production and storage of UHT milks and dried milk powders, thus minimisation of Maillard chemistry in dairy products has been a priority in the field. However, these same flavours are desirable in ghee, brown butter, Ryazhenka Kefir, grilled cheese, condensed milk, toffees, fudges, dulce de leche and milk chocolate crumb. Thus, depending on the desired product quality, both minimising and enhancing the progress of the Maillard reaction may be of interest to dairy food processors. In this review, a brief overview of the Maillard reaction will be given before discussing the role of this chemistry in the flavour formation of dairy products, model systems that have been employed to understand the chemistry, and avenues that might be used to control the product formation to improve dairy product quality.

Maillard reaction

The Maillard reaction is named after Louis Camille Maillard, who first described the reaction that occurs between an amino group and a carbonyl moiety in 1912. The amino group can be part of an amino acid, peptide or protein, any of which can react with a variety of carbonyl-containing compounds, typically sugars (such as glucose, fructose or lactose) or their derivatives, or fat breakdown products. The Maillard reaction is a thermally induced reaction. In most dairy products the carbonyl compound will initially be the reducing sugar lactose (or its hydrolysis products, glucose and galactose) and the amino groups could be derived from either casein or whey proteins, which contain amino acid residues that have been shown to be reactive to Maillard chemistry. Other sources of amine groups include amino phospholipids or free amino acids, whilst milk fat provides another source of carbonyl compounds.

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Paul Andrewes is senior research scientist at Fonterra Cooperative Group Limited. He received his BSc degree in chemistry from Massey University (Palmerston North, New Zealand) and his PhD from the University of British Columbia (Vancouver, Canada) also in chemistry. He completed postdoctoral fellowships at Unilever Research (Vlaardingen, Netherlands) and the US Environmental Protection Agency (North Carolina, USA). His research interests include flavour chemistry of dairy products and mechanisms responsible for sensory attributes such as astringency.

Professor Juliet Gerrard trained at Oxford University, where she completed an Honours degree in Chemistry and a DPhil in Biological Chemistry. In 1993, she was appointed as a research scientist at Crop & Food Research, where her multidisciplinary research portfolio included a substantial element of applied research in the food science area. She was appointed as a Lecturer in Biochemistry at the University of Canterbury in 1998, where she is now Professor and Co-Director of the Biomolecular Interaction Centre. She has recently accepted an IRL Industry and Outreach Fellowship, and has over 100 publications, covering a broad range of interests including the Maillard reaction and bionanotechnology.
There are several stages to the Maillard reaction. The initial stage (Fig. 1) is typically a condensation reaction between the sugar and an amine to form an unstable glycosylamine (imine). This glycosylamine can then undergo rearrangement to form the Amadori compound, an aminodeoxyketose. This Amadori compound can react along multiple parallel pathways to form advanced Maillard reaction products, a selection of which are illustrated in Fig. 3 (see below).\textsuperscript{14,20} For a detailed treatment of the many and varied reaction pathways of Maillard chemistry see Nursten,\textsuperscript{14} Ledl and Schleicher,\textsuperscript{19} and Gerrard.\textsuperscript{21}

Factors influencing the Maillard reaction

In a food system, the Maillard reaction is dependent on several factors: the type of sugar, the type of amino acid residue, the temperature, the pH, the water activity, any buffers, the oxygen availability and the nature of the food matrix.\textsuperscript{2,3,21,22} These factors need to be considered during both food processing and food storage.\textsuperscript{3} The Maillard reaction system comprises multiple reaction pathways, each of which can be favoured relative to alternate pathways under different conditions, making optimisation of the reaction under a given set of conditions very challenging.\textsuperscript{22}

pH and buffers

The pH of the solution is highly important at the beginning of the reaction, when protonation of the amine group will slow the initial reaction, which yields the Amadori product (Fig. 1). The pH is also important after the formation of the Amadori compound, as it can determine which pathway the reaction then predominantly follows: e.g. 1,2-enolisation at low pH and a 2,3-enolisation pathway at high pH (Fig. 2).\textsuperscript{6} The different pathways give rise to different products, e.g. furanone via 2,3-enolisation and furfural and hydroxymethylfurfural (HMF) via 1,2-enolisation.\textsuperscript{4} There is a variety of mechanisms that have been proposed leading to a range of Maillard reaction compounds from the Amadori compound. Fig. 2 below outlines a possible mechanism in a dairy product.

In general, as the reaction progresses, carboxylic acids form, leading to a decrease in pH. In dairy foods, this pH decrease can be buffered by the components of the food matrix, e.g. the remaining lysine residues of milk proteins. However, in the absence of any buffering species, for example at later stages of the reaction when these lysine residues have been consumed, the pH drop can be large and significant.\textsuperscript{14} As the pH decreases, the rates of further alternative reaction pathways with acid-catalysed mechanisms will be increased.

The concentration of the open chain form of the sugar can also play a role in the overall reaction rate as it affects the reactivity of the sugar.\textsuperscript{22} The concentration of the open chain form sugar will increase with increasing pH. Furthermore, protonated and non-protonated forms of the amino compound are in a pH dependent equilibrium, with a higher portion being protonated at low pH. At pH 7, only approximately 1% of amine groups are non-protonated, which explains one facet of the dependence of reaction rate on the pH of the system.\textsuperscript{22} As the pH increases there will be less protonation, increasing the rate of reaction.

The presence of buffering agents in the reaction system will alter the rate of the Maillard reaction. Phosphate buffers have been seen to have a catalytic effect, leading to an increase in reaction rate. Other buffers, including citrate buffers, do not have this same effect. The concentration of the buffer is also important.\textsuperscript{23}

Temperature

The reaction temperature is also an important parameter, particularly above 100 °C. It is the driver behind the initiation of the Maillard reaction that is most often seen in food systems cooked at elevated temperatures.\textsuperscript{9} Not only the overall reaction rate, but the relative rates of different reaction pathways are also dependent on temperature.\textsuperscript{22} Generally, the amounts of the volatile compounds found in a sample increase with an increase in temperature.\textsuperscript{24} Pasteurisation and UHT processes are conducted at elevated temperatures as is the manufacture of products such as ghee and dulce de leche. Other cooking requirements such as pizza cheese and grilled products also results in exposure to elevated temperatures.\textsuperscript{9,14,25–27}

Consideration should also be given to the difference between the cooking temperature and the actual food temperature.\textsuperscript{28} Due to water evaporation, the temperature of the food could be significantly less than the cooking temperature during the early heating stages. This difference between the set temperature and the actual temperature means that while the oven may be set to, for example, 130 °C until the water has evaporated, at which point the temperature may rise to the set temperature. This also implies that the temperature throughout a food may not be uniform.\textsuperscript{28}

Type and identity of sugar

One of the reactant factors affecting the Maillard reaction is the type of sugar and the nature of its breakdown products. Aldose sugars will react differently to ketose sugars.\textsuperscript{29} Aldoses such as

![Fig. 1 Early Maillard reaction products of lactose](image-url)
glucose, mannose, galactose and ribose give rise to the Amadori intermediate, whilst the ketoses such as fructose, tagatose, ribulose and piscose give rise to the corresponding Heyns compound. Each individual sugar will exhibit a different rate of reaction with monosaccharides reacting faster than disaccharides. This is in part due to the position of the ring opening equilibrium; if the equilibrium favours the open chain form, the rate of reaction will be faster. From each of these intermediate products (Heyns and Amadori) the mechanism moves towards different carbonyl compounds and advanced reaction products, the formation of which can significantly alter the flavour and aroma profile. The yields, product compositions and rates of these steps are largely dependent on the pH: slightly acidic, neutral and/or slightly basic conditions will all yield different products. Most dairy products will contain significant quantities of lactose, a disaccharide of glucose and galactose, but there is also ascorbic acid present that can itself react to form Maillard compounds. The addition of other sugars to a dairy food product might significantly alter the flavour profile.

Transformation of lactose

In dairy products the prominent sugar is lactose. Lactose participates in the Maillard reaction as a reducing sugar but also undergoes degradation by a second pathway. At high temperatures (usually >100 °C) lactose is isomerised to lactulose which subsequently degrades to galactose, formic acid and a range of C5/C6 compounds. These transformation reactions in which amino compounds are not involved, form a subset of non-enzymatic browning reactions referred to as caramelisation reactions. The rate of transformation and the rate of the caramelisation reaction are dependent on the type of sugar in a similar manner as the Maillard reaction as addressed above.

Type and identity of amine

The use of different compounds containing amino groups can lead to a range of alternate flavour profiles as a result of different compounds that can be formed. Table 1 shows the range of flavours possible by changing the amino acid heated with glucose; a variety of compounds are responsible for these flavour profiles as shown in Fig. 3. Dairy proteins contain a range of amino acids, some of which have residues able to participate in the Maillard reaction without breakdown of the protein. Hydrolysis of the protein results in increased amino group availability for the Maillard reaction. As demonstrated in Table 1 the amino acids present and available can lead to a range of flavour properties.

Lipid degradation compounds

Many dairy products contain lipid components as either part of the matrix (cream, milk, cheese) or as a major component (butter, ghee) placing importance on the flavour imparted by the lipid. Carbonyl compounds are formed during the oxidation of lipids and are also intermediates of Maillard reaction products. The degradation and oxidation of lipids are important to the flavour of food, as these breakdown products can react with other Maillard reactants, leading either to deterioration or improvement of food quality. Volatile compounds such as methyl ketones, aldehydes and free fatty acids are formed when fats are heated. These volatile compounds can then go on to react with amino acids or Maillard reaction products. A higher degree

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**Table 1** Possible flavours arising from heating different amino acids with glucose under various conditions

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Odour of product formed on heating with glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>Fruity, flowery, sweet</td>
</tr>
<tr>
<td>Arginine</td>
<td>Bitter, sour, fruity</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>Fruity, sweet</td>
</tr>
<tr>
<td>Cysteine</td>
<td>Sulphur, meaty</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>Sour</td>
</tr>
<tr>
<td>Glycine</td>
<td>Caramel, sweet, flowery</td>
</tr>
<tr>
<td>Histidine</td>
<td>Sour</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>Burnt, caramel</td>
</tr>
<tr>
<td>Leucine</td>
<td>Burnt, caramel</td>
</tr>
<tr>
<td>Lysine</td>
<td>Pleasant/sweet, caramel, cardboard, herbal tea</td>
</tr>
<tr>
<td>Methionine</td>
<td>Potatoes, prawn crackers</td>
</tr>
<tr>
<td>Threonine</td>
<td>Sweet, fruity, astringent</td>
</tr>
<tr>
<td>Serine</td>
<td>Fruity, sweet</td>
</tr>
<tr>
<td>Proline</td>
<td>Fruity, bitter</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>Flowery, almond, bitter</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>Fruity, flowery, tea-like</td>
</tr>
<tr>
<td>Valine</td>
<td>Caramel, biscuit, malty, chocolate, bitter</td>
</tr>
</tbody>
</table>
of browning and volatile formation has been seen in model systems containing lipid oxidation products when compared with a model system in which there were no lipid oxidation products, demonstrating that the lipid oxidation products are taking part in the Maillard reaction. Lipid oxidation reactions can also occur prior to the heat treatment, usually favoured under acidic conditions in the presence of oxygen. Lipid degradation leads to rancid flavours which can be of particular concern in dairy products, especially those with limited shelf life or high fat percentage; however, the Maillard reaction may reduce this phenomenon by removing rancid compounds via both the reaction itself and the ability of some Maillard reaction products to exert an antioxidant effect, which could prevent rancid flavour compounds from being produced.

**Water activity**

The water activity \( (a_w) \) of the reaction system is an index that describes the availability of water to participate in reactions. It is defined by the equation \( a_w = P/P_o \) where \( P \) is the partial pressure of the water in the system and \( P_o \) is the partial pressure of pure water. Many reactions occur with \( a_w \) values between 0.5 and 0.8.

Water activity varies widely within dairy products, ranging from very high values in products such as milk \( (a_w > 0.95) \), to very low values in products with low water content such as milk powder \( (a_w < 0.2) \) and ghee. The multiple possible dehydration processes along with many of the Maillard reaction pathways will each generate additional water molecules. In a system with excess water (dilute solution) a high \( a_w \) will hinder many steps of the Maillard reaction due to reactant dilution resulting in a decrease of reaction rate. If the water activity \( (a_w) \) is lowered, the concentration of reactants will increase, but they may begin to lose mobility essential for reaction resulting in a lower rate of reaction. For example, in milk powder, low water activity is important to flavour and preservation of quality. The effect of \( a_w \) may thus be a combination of a concentration and diffusion effect. At low \( a_w \), the system is very concentrated and diffusion is difficult, producing a slow reaction rate. Note that there is no effect from concentration or diffusion on unimolecular reaction steps.

**Influence of metals**

The Maillard reaction can also be influenced by the formation of metal complexes between amino acids and available metals. The reaction can be catalysed by copper and iron but inhibited by manganese and zinc. Calcium has also been shown to delay the Maillard reaction by forming complexes with certain sugars. Dairy products contain calcium and traces of other metals which can complex with the amino acids and influence the reaction.

**The impact of emulsion structure**

Microemulsions are a dispersion of either water in oil or oil in water. They are uniform in structure, have low viscosity and are thermodynamically stable. They have a particle size in the order of nanometers (5–100). In contrast, an emulsion such as cream or butter has a much larger particle size, is not transparent and is kinetically, not thermodynamically, stable.

In an aqueous reaction system the reactants are free to interact with each other; whereas in a structured fluid they are confined to droplets (emulsions/microemulsions) or channels (bicontinuous phase). When the concentration of reactants is kept constant across aqueous, emulsion and cubic (bicontinuous) systems, the rates of product formation were found to be different. The effective partitioning of the reactants within the emulsion structure creates a localised concentration gradient that increases the proximity of reactants in certain system locations, thereby increasing the frequency of collisions between reactants and so the overall reaction rate. The localised concentration gradient arises because although the overall amount of each reactant has been kept the same, the phase that it occupies has a smaller volume and therefore the reactant concentration is increased within that phase.

**Studying the Maillard reactions with a view to flavour control**

**Model studies**

A considerable amount of information about the Maillard reaction has been collected using model studies, rather than within the complexity of the reaction systems in food. The food matrix itself can have a large effect due to pH, water content/activity and other influencing factors, as discussed above. Models attempt to predict the rates of formation of Maillard reaction products as a function of these factors and can be empirical (mathematical) or mechanistic (based on the knowledge of the chemical reaction and system). The use of a model can allow testing of mechanistic predictions and provide insights by simplifying a problem to its basic components. However, the translation to real food systems can be problematic. When the experiments are carried out on real food the results can be conflicting as there are confounding factors influencing the results. Typical model systems for the Maillard reaction contain an individual amino acid and sugar – the simplest starting materials. Such studies/models can be extended to proteins and sugars and further layers of complexity such as emulsion structure can be added to the model system in a controlled manner as the complexity begins approaching that in the actual food system.

There are various parameters to consider when setting up a model system: the sugar, the amino compound, the reaction matrix (aqueous, lipids, emulsion) and the reaction conditions (pH, water activity, time, and temperature). Various
experimental temperatures and times have been used in model studies: low (37–80 °C) \(^{24,51,55}\) moderate (100–150 °C) \(^{30,33,58–60}\) and high (>200 °C) \(^{59}\) with times for experiments ranging from minutes to hours. \(^{52,58,61,62}\)

**Examples of models and their uses**

There are a wide range of model systems that could be applied to dairy products, depending on the nature of the study being carried out. \(^{20,45,63–66}\) These studies haven’t currently been applied to addressing the impact on flavour of the products or utilised to study the flavour of dairy products. They focus on how the reaction compounds resulting from the Maillard reaction change when parameters associated with the system are changed.

A simple model that has been used to study the Maillard reaction in dairy systems comprised a monosaccharide (e.g. glucose, galactose, fructose, tagatose) with casein \(^{29}\) in an aqueous phosphate buffer. This system contained the sugar (150 mM) with sodium caseinate (3% w/w) in aqueous phosphate buffer (0.1 M, pH 6.8). This gave a molar ratio of sugar to lysine residues of 10 : 1. The model reaction system was heated to 120 °C. The purpose of this model was to demonstrate the differences in reaction mechanisms between an aldose sugar (glucose, galactose) and a ketose sugar (fructose, tagatose) in the same system, under the same conditions. \(^{29}\) The sugars were also heated in the system in the absence of sodium caseinate to allow the separation of caramelisation products and pathways from those that were Maillard products and pathways. The study demonstrated that there was a difference in the results for aldose sugars and ketose sugars. The researchers observed that the ketoses had a faster rate of reaction than the aldoses \(^{29}\) and that these sugars also followed different Maillard reaction pathways that led to different colours, flavours and nutritive damage in the final products. This model system and the reaction conditions are similar to those involved in heating milk (pH 6.7), with caseins, sugars, and high temperature leading to coloured and flavoured products. Thus there are similarities between the products formed in this system and those reportedly formed in heated milk. \(^{29,34}\) These product similarities include furfuryl alcohol, acetic acid, formic acid and various Maillard intermediates \(^{29}\) identified in the model system which were identified in milk alongside HMF and furfural. \(^{14}\) The addition of lactose to the list of sugars studied would allow greater similarity to the reaction occurring in dairy products at high temperatures. The degradation of lactose in milk was studied using a model system consisting of lactose and sodium caseinate dissolved in a milk salt solution. \(^{14}\)

Model systems have been developed that allow the tracking of heat treatment markers in milk. Homogenised lactose and sodium caseinate have been used to model milk in an effort to develop an assay to detect HMF formed during heat treatment. \(^{67}\) This study was also used to look at the impact of fat content on formation of heat markers in milk, namely HMF.

A simple model system of lactose and lysine has also been used to develop a method to identify heat treatment markers in milk products. \(^{11,67}\) The yield, composition and rates of the initial Amadori compound formation depended mainly on the system pH. To allow control over the pH, buffers such as sodium bicarbonate (NaHCO\(_3\)) \(^{62}\) are often used. The desired pH influences which buffer is used; care must be taken to avoid using buffers that contain reactive amine moieties (such as Tris), but sodium acetate, sodium phosphate can successfully be used in conjunction with HCl or NaOH to adjust the final pH. \(^{44}\) The lactose-lysine model system \(^{51}\) utilised aqueous solutions of lactose and lysine without pH control. The change in pH was used to monitor the progress of the reaction, together with relative antioxidative efficiency and optical density as the brown colour developed. \(^{34}\) Relative antioxidative efficiency is a parameter that has been measured in numerous studies involving the Maillard reaction \(^{41,62,69,70}\) and has potential relevance in dairy systems, such as chocolate, grilled cheese and ghee, where advanced Maillard chemistry is likely to have generated a large number of anti-oxidant compounds. These studies are focused on finding the flavour compounds that form and discovering markers for the Maillard reaction, rather than the impact of these compounds on the flavour of the product.

Models have also been used to study specific compounds generated by the Maillard reaction and the mechanistic pathways by which they are formed, using isotope-labelled starting materials. In a dairy system this method could be used to investigate formation pathways of flavour compounds found in heated dairy products such as furfural, and flavours associated with off-flavours. Fig. 4 illustrates the formation of furan and the different positions of the label in the final product. Isotope positions in the final product are dependent on the mechanism of

![Fig. 4 Summary schematic of potential mechanistic routes to furan from glucose.\(^{58}\)](image-url)
The formation of furan and methylfuran in model systems and food systems has been studied using isotopically labelled ascorbic acid\(^{53}\) and \(^{13}\)C labelled sugars.\(^{58}\) These models were used both under dry roasting conditions and aqueous conditions, and food systems were monitored by spiking pumpkin puree with the labelled compounds and then heating under the same conditions as were used in the model system.\(^{58}\) This allowed the influence of a food matrix on the formation mechanisms to be assessed and clearly demonstrated the relative importance of the pathways highlighted below and that the furan formation from sugars and amino acids represented only a minor route. Other routes involve recombination of fragments originating from sugar and protein fragments.\(^{58}\)

The use of labelled sugars has also been applied to the study of specific pathways such as enolisation\(^{71}\) by analysing where the labelled fragments are located at the end of the reaction. The formation of acetic acid during the Maillard reaction under various conditions has been studied in this way\(^ {73}\) as it is a common product of the reaction of hexose sugars in alkaline conditions. The amount of acetic acid formation was studied to allow bicontinuous microemulsion structures to form. The transition between microemulsion structures is continuous, therefore be altered by adjusting the amount of water in the system. The same cannot be said for emulsions whose structures are discrete from one another; in order to transition from o/w to w/o there must be a phase inversion which is transitional rather than catastrophic.\(^ {73}\)

With the exception of using novel double emulsions to form processed cheeses\(^ {72}\) there has been little research published into the possibilities of altering the structures of dairy products such as milk, cream and butter.

### Analysis of Flavours

The analysis of the products formed is an important aspect of the model studies and studies involving real food systems. A range of techniques are available to study the end products of the studies depending on the questions being asked; chemical analysis\(^ {74–79}\) is used to identify the reaction compounds that form during the course of the reaction, physical analysis has been used to study the texture, rheology\(^ {79}\) and colour, while sensory\(^ {16,80–82}\) analysis is used to determine the flavour and texture along with the acceptability of these parameters by the consumer. Most studies focus on one form of analysis, either identifying what the reaction products are, or how the colour changed over the course of the reaction, or whether the consumer find the product acceptable. To gain a full understanding of dairy product flavour more than one set of analysis is required.

### Flavours in dairy products

In addition to the mild dairy flavours derived from the milk itself, specific dairy products will have characteristic flavours derived from their method of manufacture, which may influence either the pathways of the Maillard reaction, or the subsequent perception of any Maillard reaction products. The heat processes used in dairy food processing are generally for pasteurisation or water removal. This application of heat initiates the Maillard reaction, which generates additional flavour compounds, resulting either in flavours being produced or the generation of flavour precursor compounds that go on to react during subsequent cooking. In either scenario, these compounds may be off-flavours or beneficial to product quality.

#### Fluid milks

In milk, there are over 200 volatile components that contribute to the overall flavour.\(^ {80}\) Several of these components are present in very small amounts (\(<400 \, \text{µg kg}^{-1}\) ) but still impact the overall flavour profile. Maillard reaction products have been identified in heat damaged milk\(^ {84,85}\) as a result of pasteurisation. The presence of these products even at small levels can alter the flavour of the milk producing an off-flavour. There have been many analytical studies focusing on identifying the flavour compounds of milk.\(^ {1,26,17,77,86,87}\)

UHT milk is heat treated at ultra high temperatures.\(^ {27}\) This brief but intense heating occurs in a temperature range of 135–140 °C. The heating can be either direct (steam injection or milk infusion into steam) or indirect (heating and cooling using heat exchangers). This heat treatment destroys pathogens, but can also cause chemical changes in the milk leading to off-flavours. Ideally, UHT milk would have the same flavour as fresh milk: namely only a minimal aroma, with a slightly sweet but relatively bland flavour. This flavour profile can be greatly influenced by the presence of volatile compounds, in particular sulphur containing compounds. While adding desirable flavour to cheeses and butter, these sulphur compounds, including hydrogen sulphide, dimethyl sulphide and methanethiol, which can all be derived from Maillard chemistry, are often responsible for the off-flavours in UHT milk.\(^ {26}\)

#### Milk powders

Whilst most Maillard reactions are initiated by heat, it has also been demonstrated that Maillard chemistry is an important factor in the development of off-flavours and browning in milk powders during storage.\(^ {37,57,86}\) These reactions also result in
nutritive damage to the product and therefore the conditions of storage are important to minimise these deleterious effects. Any off-flavours, such as nitrogen containing indole compounds, are very noticeable and objectionable in the final product.

Likewise, the temperature of milk powder storage can influence the Maillard reaction; samples stored at a higher temperature (50 °C) exhibit accelerated Maillard reaction product formation. Increased humidity has also been observed to accelerate the Maillard reaction during storage, if the aw was increased into the range appropriate for this chemistry to become significant.

The furan derivatives furfural and furfuryl alcohol (see Fig. 3) are Maillard reaction products produced by sugar degradation and dehydration. These compounds were identified in skim milk powder but their levels were below the perception threshold. However, they have a sweet, nutty, caramel odour that could be important for condensed milk. The Maillard reaction also leads to the development of colour in sweetened condensed milk.

The formation of compounds such as hydroxymethylfurfural (HMF) and furfurose (see Fig. 3) along with browning of the powders are indicators of the Maillard reaction during storage. HMF is commonly used in dairy products but is not suitable for all food types. The monitoring of HMF is often done using colorimetric techniques or fluorescence. An enzyme link immunosorbant assay is currently being developed to monitor HMF in a wide range of carbohydrate containing foods.

Cheese

The flavour of cheese is derived from the activities and interactions of starter bacteria, rennet, milk enzymes and also from any secondary flora present. The flavour compounds of impact include methyl ketones formed via fat oxidation that is initiated by bacteria, fatty acids formed from the lipolysis of the milk fat, sulphur compounds generated by bacteria, α-dicarbonyl and related compounds that can also react with amino acids to generate Strecker aldehydes (a known Maillard reaction pathway) and amine compounds, e.g., the amino termini of peptides generated by enzymatic hydrolysis, which may also participate in Maillard chemistry.

The use of cheese on pizza and in prepared foods requires a cheese with desirable attributes, including colour, after cooking. The browning of cheese during baking can be attributed to the Maillard reaction. When tested by sensory panellists, the cooked brown colour and flavour of the cooked cheese were not seen as undesirable, although a less coloured cooked cheese was favoured by pizza manufacturers.

The manufacture of processed cheese involves heating the cheese products with other materials to yield a homogeneous product. The temperature of processing steps can cause colour defects (browning) that have been linked to the Maillard reaction. Aroma defects are also generated giving rise to an ‘overcooked’ aroma. These defects depend on the heating time and temperature and the product composition. There were several compounds identified in a model cheese system that are Maillard reaction products: furfuryl alcohol, furfural, furaneol and maltol. This model system demonstrated that these compounds played a major role in the ‘overcooked’ defect.

Cooking

The heating of dairy products is not limited to manufacturing, as it is also a common household process. Flavour is an important attribute of food, both prior to and after heating. Many dairy products are cooked, such as cheeses, cream and butter. There are also other dairy products that are made by cooking other dairy ingredients, including ghee, milk chocolate crumb, Ryazhenka Kefir and browned butter. The effects of the Maillard reaction are often seen when these products are cooked, providing a desired change to the product, including grilled cheese such as on pizza, browned butter often used in making roux or baking, milk chocolate crumb or block milk.

Halloumi is a cheese that is eaten after frying or grilling, developing a browned outer layer. Although little sensory analysis has been carried out on this cheese, it is known that the volatile flavour compounds differ between the raw and cooked cheese. Moreover, given that this cheese is most commonly consumed in cooked form, the change in flavour can be assumed to be desirable. Another cheese commonly cooked for consumption is mozzarella; there were no undesirable flavours noted when mozzarella was cooked.

Cream, milk and butter are also commonly used in baked goods such as scones, shortbreads and other sweet items, where they are subjected to high temperatures, in the presence of sugar, for cooking; many Maillard reaction products are thus generated that are associated with the favourable aroma of these products. A further use of the Maillard reaction in cooking is during the making of ghee. Ghee is an example of a product in which the flavour compounds generated via the Maillard reaction are desirable. The flavour in ghee is generated from multiple sources: compounds found naturally in the starting material, Maillard browning reaction compounds, free fatty acids, lipid oxidation and fermentation. Dulce de leche is another product which requires the Maillard reaction to generate the characteristic colour and flavour. The consumer acceptability relies on the flavour and colour.

Low fat dairy products

The current consumer driven market is searching for low fat food alternatives, including dairy products, without compromising on food flavour; however, low fat products such as cheeses, milk, ice cream and yoghurts often lack flavour. Fat can be replaced with protein, carbohydrates, other fat based products, or a combination of all three. Low fat cheese can lose up to 50% of its flavour with a reduction in fat, which, coupled with associated changes in texture and other sensory attributes, can lead to an inferior product. For example, low fat chocolate ice-cream made with 2.5% milk fat plus low fat cocoa powder instead of cocoa butter had a less intense flavour.

It is essential to control Maillard reactions in low fat dairy products to avoid off-flavours and compensate for lost flavour. For example, ghee is a fat product with potential for use in flavour replacement. The highly flavoured nature of ghee relative to products such as butter oil or anhydrous milk fat (AMF) makes it an alternative that would add flavour, even at low fat content.
Ghee

Ghee is a product that is made by indigenous methods in many countries around the world, largely in Asia, the Middle East and Africa. It is known by various other names such as maslee in the Middle East where ghee is derived from goat, sheep or camel milk and roghan in Iran. Ghee is used in cooking, as a condiment and for religious purposes. The cooking methods vary along with the unique individual flavours.

By definition, ghee is a product exclusively obtained from milk, cream or butter by means of processes which result in almost total removal of water and non-fat solids, with an especially developed flavour and physical structure; the flavour is ‘acceptable for market requirements after heating a sample to 40–45 °C’. A good ghee has been defined as having a pleasant, nutty, lightly cooked or caramelised flavour. It was said that the flavour can best be described as a lack of oiliness or blandness, sweetly rather than sharply acidic, but it is objectionable to have any suggestion of rancidity. The flavour of ghee cannot be attributed to a single compound, but rather to a large range of compounds. This group of compounds includes aldehydes, ketones, fatty acids, carboxylic acids, lactones and alcohols. These flavours are generated during the heating process by reactions between protein and lactose, protein and lactose degradation products, lipid oxidation and degradation of free fatty acids.

There are several methods of making indigenous ghee; all have a common element of heating to high temperature (110–140 °C). The different methods of making ghee all start from fermented milk, cream (often soured to 0.5–1% acidity), butter or a combination of butter and buttermilk. After the heat clarification, the remaining product is filtered to remove any remaining solids.

The presence of maltol and furans has been linked to significant differences in flavours. These products, along with other pyrans, various ketones and aldehydes are known Maillard reaction products. Maltol and furans are products of sugar degradation, and the initial reducing sugar concentration can greatly influence the amount of each compound formed. Important flavour compounds are considered to be aldehydes, ketones and lactones.

There are commercial products that fit the definition of ghee based solely on physical characteristics. These products include AMF (anhydrous milk fat), butter ghee and butter oil. Whilst they are similar with respect to some of their characteristics, these products do not display the same flavour profile as traditional indigenous ghee: butter oil and AMF are particularly lacking in flavour. The production of synthetic ghee flavours has been attempted in the past using a formulation of synthetic flavouring compounds to create a ghee flavour in butter oil. The synthetic flavourings used were based on analytical data for ghee flavour constituents. There are several papers that outline the flavour constituents that have been identified in ghee. Efforts made to reconstitute the flavours focused on a mixture of lactones, free fatty acids and carbonyl compounds; however, as not all of the ghee constituents had been identified, and their exact proportions were not known, it was difficult to formulate a synthetic ghee flavour in the butteroil. A better understanding of high temperature Maillard chemistry may therefore inform the development of this type of product.

Conclusion

Some dairy foods have very little in common with the model systems identified for studying the Maillard reaction. The use of models to study the influence of microemulsion structures on the Maillard reaction has demonstrated that different microemulsion structures can lead to different reaction product profiles. However, many food systems are emulsions (cream and butter) rather than microemulsions, leaving a significant gap between models and food, which needs to be bridged.

Many of the flavour studies are conducted with the purpose of identifying marker compounds found in the products. There is a lack of studies which systematically identify the flavour compounds in dairy products and link this with the impact of the compounds on flavour.

In the majority of dairy products the Maillard reaction is often an undesirable source of flavours, which has led to a focus by the dairy industry on reducing the extent of the reaction. However, in cooked cream products, such as ghee and dulce de leche, Maillard reactions are desirable and indeed essential. Numerous flavour compounds have been found in ghee, but little work has been done to determine the origin of these compounds, the mechanisms by which they form, and the influence of the emulsion structure on the final product ratios. More work is certainly required to understand the mechanisms of flavour formation in cooked cream products, in particular, so that the flavour can be manipulated to enhance it and make the final product more desirable.

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