The art and science of caramelization

CARAMEL & HEALTH

WHAT’S TODAY’S SITUATION?

Technical document intended for professionals
In the consumer’s mind, caramel is a product associated with taste, pleasure, childhood...

But what do we really know about caramel?

The term "caramel" is not limited to sweets, but refers to various products depending on their recipes and uses (food, ingredients for flavouring, additives for colouring).

Why is caramel a topic of particular interest?

Caramel is widely used in the food industry. Over time, the question of the link between caramel and consumer health has been raised.

This monograph presents an overview of current knowledge about caramel, and especially aromatic caramels and caramel colours.
**Summary**

**PART 1: Caramels... The basics!**
- 1.1 Aromatic caramels
- 1.2 Caramel colours
- 1.3 Burnt sugars
- 1.4 Caramel specialities

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**ApPENDIX 1: The supply chain for aromatic and colouring caramels**

**Glossary**

**AbbreViAtions**

**References**
To achieve a simple caramel, it is necessary to heat sugar in a saucepan with water and lemon juice. The more the sugar is heated, the more the caramel is dark and strong in flavour.

It is possible to add other ingredients like cream, butter, fruit extracts ... to make various delicious and original caramels.

Recipe of "homemade" caramel

**Ingredients**
1 kg of sugar  
1 glass of water (25 cl)  
1 teaspoon of vinegar or lemon juice

Put sugar, water and vinegar (or lemon juice) in a saucepan. Heat to boil and stir continuously. Wait until the water has completely evaporated. Remove from heat as soon as the desired colour is reached.
Introduction
The word "caramel" that seems so familiar, is actually used to define several types of products, all of whose secrets are still far from being revealed. Caramel is always a product obtained from the cooking of carbohydrates (sugars). However, according to recipes and uses, caramel falls into the category of food (example: toffee candy), ingredients used for flavouring (aromatic and speciality caramels) or additives (caramel colours).

**Part 1**
Caramels... The basics!

### 1.1 Aromatic caramels

**Aromatic caramel** is used to contribute to the taste of the food in which it is incorporated, and is defined in France by the norm AFNOR NF V00-100 as "a light brown to dark brown liquid or solid, soluble in water, obtained by the controlled action of heat on edible sugars. Small amounts of organic acids¹ may be added during the manufacturing process to promote the hydrolysis of sugars². The name caramel may refer to the original raw material if carbohydrate compounds are the only source materials" (example: caramel pure sugar).

Used as ingredients by the consumer or the food industry, aromatic caramels are identical to "homemade" caramels made by the gourmet in a saucepan or by the confectioner in his cauldron. Accurate temperature control by high-tech cooks and rigorous quality assurance, ensuring constant finished product specifications, are the advantages of an industrial process, compared to domestic or artisanal processes.

¹Examples of acids to promote hydrolysis: citric acid, acetic acid; ²Cleavage by the addition of water

### 1.2 Caramel colours

**Caramel colour** is defined in France by the AFNOR NF V00-100 as "a darker brown liquid or solid, soluble in water, obtained by the controlled action of heat on edible sugars, in the presence or not of chemical compounds which are promoters of caramelisation, and whose main destination is colouring of liquid foods."

Used as additives, these caramels can be manufactured with chemical caramelisation³ promoters to obtain high colouring power and stability of foods to which they are added. The safety of all food additives is demonstrated through toxicological studies validated by the European and international health authorities.

The wide variety of caramel colours has caused the competent authorities in food safety to produce classifications based on the reagents used and certain functional properties. At the international level, JECFA - Joint FAO / WHO Expert Committee on Food Additives - recognised since the 70s four classes of caramel colours, depending on the reagent used in their manufacturing process (ammonia, sulphite or no reagent).

The classes are known under the names 150a, b, c or d, in the JECFA International Numbering System (INS). According to the labelling rules in the European Union, they are named either E150a, b, c and d, or Class I, II, III and IV.

³Examples of caramelisation promoters: sodium sulphite, ammonia, ammonium sulphite
Both JEFCA and European Commission have standardised the properties of these 4 classes of caramel.

### Table 1: Classes of caramel colours

<table>
<thead>
<tr>
<th></th>
<th>Class I/E150a</th>
<th>Class II/E150b</th>
<th>Class III/E150c</th>
<th>Class IV/E150d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labelling</td>
<td>E150a Colour: Plain caramel</td>
<td>E150b Colour: Caustic sulphite caramel</td>
<td>E150c Colour: Ammonia caramel</td>
<td>E150d Colour: Sulphite ammonia caramel</td>
</tr>
<tr>
<td>Shade of colour</td>
<td>Brown-red</td>
<td>Brown-yellow-orange</td>
<td>Brown-black</td>
<td>Brown-grey</td>
</tr>
<tr>
<td>Sulphite compounds</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Ammonia compounds</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Characteristic caramelisation promoter</td>
<td>Soda /or any</td>
<td>Soda sulphite</td>
<td>Ammonia</td>
<td>Ammonium sulphite</td>
</tr>
<tr>
<td>Stability - Alcohol</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>- Tannin</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>- Acid</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Main uses</td>
<td>Alcoholic spirits, Coffee extracts, Petfood, Meat, Speciality breads</td>
<td>Vermouths, Brandies, Aromatic extracts</td>
<td>Beers, Vinegars, Biscuits, Sauces</td>
<td>Soft drinks, Petfood, Confectionery</td>
</tr>
</tbody>
</table>

- **Caramel Colours Class I/E150a** are "ordinary" caramels that contain no sulphites or ammonia compounds. They are mainly used in high alcohol drinks (whiskies, cognac, brandies ...).
- **Caramel Colours Class II/E150b**, using non-ammonia sulphites during the caramelisation process, are rather used in drinks, such as aperitifs.
- **Caramel Colours Class III/E150c** are obtained by heating sugars in the presence of ammonia or ammonia salts. More stable and soluble in saline solutions, they are used in soups, sauces, beers, cookies and pastries.
- **Caramel Colours Class IV/E150d** are produced in the presence of ammonia and sulphite compounds and are characterised by intense colouring power, promoting their use in soft drinks.
1.3 Burnt sugars

Some caramels, called "burnt sugars", correspond to the definition of both aromatic caramel and caramel colour. Produced only from sugars and water, without the use of caramelisation promoters, they bring a response to an increasing request for "natural" products. For clarity and to avoid misleading consumers, the European Technical Caramel Association (EUTECA) has published a decision tree about labelling. Burnt sugars that only bring colour to a finished product must be reported as E150a. If it is proved that the caramel brings taste to the product through a blind test, it is an aromatic caramel.

1.4 Caramel specialities

Caramel specialities are caramelised sugars, which incorporate milk products (milk powder or concentrated butter or cream), vegetable fats and sometimes other ingredients such as fruit extracts. The variety of names (hard or soft caramel, "fudge", "toffee") depends on the composition, the degree of cooking, the shape of the finished product and its taste. They are tasty products, made in accordance with traditional methods, like the famous salted butter caramels from French Brittany.

No specific regulations for caramel specialities but uses...

Sugar confectionery products are not defined by specific regulations regarding their composition, name or their method of manufacturing. Caramel, a French traditional product, however, was covered by a code of practice in 1953 by the Confectionery profession. This code is the result of a consensual and voluntary commitment of the profession, in order to preserve the tradition and quality of confectionery.

The "caramel" code of practice does not apply to caramels used as ingredients or additives but refers to sugar confectionery products presented to the final consumer.

*Confectionery Code. Confectionery National Chamber (France).
**Table 2: Overview of different types of caramels**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Aromatic caramels</th>
<th>Caramel colours</th>
<th>Burnt sugars</th>
<th>Caramel specialities</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Sucrose is often blended with glucose syrup, glucose-fructose syrup or invert sugar syrup in order to increase the stability of the product.</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ingredients</strong></td>
<td>Sugars*, catalysts (examples: lemon juice, vinegar)</td>
<td>Sugars*, chemical caramelisation promoters (examples: sulphite or ammoniacal compounds)</td>
<td>Sugars*, water</td>
<td>Sugars*, milk, butter, fats, honey, chocolate</td>
</tr>
<tr>
<td><strong>Foodstuff category</strong></td>
<td>Ingredient</td>
<td>Additive</td>
<td>Ingredient or additive</td>
<td>Confectionery</td>
</tr>
<tr>
<td><strong>Main uses</strong></td>
<td>Flavouring of foodstuffs</td>
<td>Colouring of foodstuffs</td>
<td>Flavouring or colouring of foodstuffs</td>
<td>Ready to eat candies Coating, filling, inclusions, topping</td>
</tr>
</tbody>
</table>

NB: The information provided in this monograph relates more specifically to aromatic caramels and caramel colours.
Aromatic caramels and caramel colours are classified respectively as ingredients or food additives.

2.1 Aromatic caramels and caramel specialities

From our earliest years, we eat caramel incorporated into many foods: rice pudding, puddings, custard, apple pies, beaten eggs, baked apples... Just hearing the word caramel makes us think about such sweet desserts!

Aromatic caramels and caramel specialities are ingredients used for flavouring, filling or topping. They are available in different ranges depending on intended applications: classic, textured, soft, full-bodied, bio, etc.

No longer limited to the traditional confectionery sector, caramel is now a popular ingredient found in many product categories, sweet and savory, including innovative products for athletes.

The diversity of uses of aromatic caramels and caramel specialities and the large number of manufacturers makes any estimate of their volume of production hazardous.
2.2 Caramel colours

Marketed for over 100 years, caramel colours would represent more than **80 % (by weight)** of all colours added to the foods we consume.

Annual world consumption of caramel colours is estimated to be **several hundred thousand tons**

Caramel colours are added to foods to provide them a yellow to brown colour and are widely used in a large range of foods such as flavoured soft drinks, alcoholic beverages, confectionery, soups or seasonings. Bakers have been using caramel to reinforce the colour of baked goods for decades. Caramel is much darker than other alternatives such as malt syrup or molasses. In comparison with other natural colours, caramel does not degrade at elevated temperatures or under pressures applied during extrusion processes for example [1].

In France, caramel E150b, E150c and E150d, used as brown pigments, would be present in 15.5% of soft drinks (cola type of products or tea drinks, for example). Caramel colour E150d (class IV) represents over 70% of the caramel colour market [2].
Focus on Non-alcoholic Soft Drinks

Sodas or soft drinks can significantly contribute to the consumption of caramel colours, particularly by big consumers. Sodas are part of the food classification group Refreshing Drinks Without Alcohol. This includes soft drinks and non-carbonated beverages.

Soft drink consumption reached **180 litres/inhabitant/year** in the US (the equivalent of 1.5 cans per day) and averaged **94 litres/inhabitant/year** in Europe. Children and young adults are the biggest consumers. The market is led by Coca-Cola Enterprises Inc. (CCE) which is the largest company in sales, distribution and production of non-alcoholic soft drinks in bottles and cans in the world [3].

The French are among the smallest consumers of such drinks in Europe: **60.8 litres/inhabitant/year**. They consume half the quantity consumed by the Belgians, the Germans and the Austrians.

In France, teenagers consume on average the equivalent of a half-can of non-alcoholic soft drinks per day and adults, a third of can. Since 2003, the consumption of non-alcoholic soft drinks in France has remained stable for children and teenagers (111 to 114 ml/day and 168 to 169 ml/day respectively) [4].

**Figure 1: Illustration of the daily average consumption of non-alcoholic soft drinks in France and in the United States**

1/2 can per day (teenagers)  1/3 can per day (adults)  1.5 can per day

Decreasing the consumption of simple carbohydrates is one of the nutritional objectives of public health policy in industrialised countries.

Prevention of overweight, obesity, diabetes and cardiovascular disease is not achieved only by reducing the intake of sugars, but also requires a diversified diet and regular practice of physical activity. Consumed occasionally and in moderate quantities, sweet products are consistent with balanced nutrition!
3.1 Caramel chemistry

Common features of different types of caramel: they are produced by the controlled action of heat on sugars at temperatures generally above 120°C. An illustration of the manufacturing process of a liquid caramel is presented in the appendix 1.

Caramelisation can be done in the presence of acidic or basic catalysts. These catalysts are organic acids, promoters of the hydrolysis of sugars (in the case of aromatic caramels) or other chemical caramelisation promoters (in the case of caramel colours), such as ammonia or sulphites, which permit intensification of the colour. Their use allows better control of the stability and quality of finished products, to correspond to the desired use of the caramel.

The caramelisation process includes a multitude of chemical reactions: first of all the dehydration of sugars, then condensation and combination (or polymerisation) of formed molecules [5]. These reactions are specific to heat treatments and to the sugar raw material used.

From the chemist’s point of view, caramel is a mixture of volatile molecules\(^\text{\textsuperscript{5}}\) (5-10% by weight of caramel), which give the taste and odour of caramel and non-volatile molecules (90-95%) responsible for colour [6]. The non-volatile fraction of caramel is much less known than the volatile fraction, responsible for the characteristic flavour of caramel [7].

\[^{5}\text{Molecules which evaporate easily, also likely to turn into gas, steam.}\]
**Figure 2: Main stages of caramelisation**

**Sucrose**
- Sucrose hydrolysis with acids
- Formation of glucose and fructose

**Glucose-fructose syrup and glucose syrup**
- Evaporation of water

**Mixture at 120°C**

**Caramelisation reaction between 130°C and 190°C:**
recombination of the molecules which break up and recombine, to form large coloured molecules and small volatile molecules

**VOLATILE COMPOUNDS**
- 5 to 10% of volatile compounds: giving the taste and the smell of caramel (approximately 140 molecules identified, such as maltol, cyclotene, furaneol, furfural)

**NON-VOLATILE COMPOUNDS**
- 90 to 95% of non-volatile compounds: residual sugars (5 to 70%), polymers of sugars such as the dianhydrides of fructose and other oligosaccharides, coloured polymers

*Thesis of Laurianne Paravisini, 2013*

*Thesis of Valérie Ratsimba, 2000*

- Maltol
- Hydroxymethylfurfural (HMF)
- Fructose dianhydrides (DFAs)
The smell of caramel: role of volatile compounds

To date, about one hundred volatile compounds have been identified, demonstrating the aromatic richness of caramel [8]. These molecules do not individually smell of caramel but their combination creates the typical aroma of caramel, outcome of a balance between different notes: caramel, fruity, nutty, vegetal, animal, toasted, floral and spicy.

**Figure 3: Volatile compounds of caramel**
More present but less known non-volatile compounds

The analysis of different aromatic caramels and caramel colours indicates the presence of:

- sugars (1 or 2 carbohydrate units) such as fructose, glucose, D-fructose dianhydrides (DFAs) or glucobioses (glucose diosides);
- oligosaccharides (3-9 units) derived from the last two entities [9].

Carbohydrates, sugar, sugars ... What difference?

From a biochemical standpoint, carbohydrates are classified according to their degree of polymerization (DP).\(^6\)

Simple carbohydrates include monosaccharides (a single unit or DP1) and dioses or disaccharides (2 units), such as table sugar or sucrose.

Complex carbohydrates include:
- oligosides (3 to 9 units) with 2 subgroups: maltodextrins and other oligosaccharides, including fructo-oligosaccharides (FOS)
- polysaccharides (DP > 10) grouping the starch and the non-starch polysaccharides.

Polyols or hydrogenated carbohydrates are obtained from mono-, di- or oligosaccharides by fermentation or catalytic hydrogenation at high pressure. More stable than non-hydrogenated carbohydrates, they have a lower energy content than the carbohydrates from which they come and have no (or low) cariogenicity.

Carbohydrate polymers with three or more monomeric units (DP≥3), which are neither digested nor absorbed in the small intestine, are known as fibres. These fibres are present naturally in plant products or obtained by synthesis from raw food.

The term "complex carbohydrates" was introduced to distinguish sugars called "simple carbs" from other carbohydrates including polysaccharides.

The fact that carbohydrates are simple or complex does not prejudge how they will be digested and used by the body, but refers only to the way they are structured. Thus, simple carbohydrates like complex carbohydrates can be completely digested or, on the contrary, entirely escape digestion.

\(^6\)The degree of polymerization is the number of associated units.

The carbohydrate profile of caramels depends mainly on the initial raw material: a fructose caramel contains essentially DFAs, caramel of glucose contains glucobioses and sucrose caramel consists of the two types of dimers.
DFAs, in brief!

Fructose dianhydrides (DFAs) are present in many aromatic caramels and caramel colours.

The DFAs are formed by the condensation of two molecules of fructose with elimination of two water molecules and are characterized by the presence of a spirodioxanic bridge. In 1994, García Fernández and Defaye have published results about the analysis of commercial sucrose caramel (Nigay Ref.1395 SMA6) manufactured at 160°C in the presence of 0.1% acetic acid. They highlighted the presence of 5 isomers of DFAs which constitute 18% of the caramel by weight [10]. Actually, no less than thirteen isomers are currently characterised and structurally defined [11]. The higher the degree of caramelisation of an aromatic caramel, the more the content of DFAs increases [12]. Amounts of DFAs up to 80% by weight have been detected in some caramels.

Fructose dianhydrides, markers of caramelisation

The discovery of DFAs already has applications in the detection of "counterfeit" aromatic caramels. Flavoured syrups made from sugars, colours and flavourings may indeed be used as alternatives to aromatic caramels in some preparations. Not being obtained by the controlled action of heat on sugars, they do not comply with the definition of aromatic caramels according to the AFNOR NF V00-100.

So how to unmask manufacturers who attempt to pass off flavoured syrups for caramel?

A method using gas chromatography, applicable in industrial process routines, was developed in collaboration with the company Nigay S.A.S.. Markers of the heating of sugars, fructose dianhydrides are present in aromatic caramels but are absent from "counterfeit" caramels. As product traceability has become a key parameter for the food industry, these results may constitute a relevant basis to prove the identity and authenticity of caramels.

Brown polymers such as melanoidins, involved in caramel colouring, are present in the non-volatile fraction. The caramelisation process belongs, along with the Maillard reaction, to the reactions known as non-enzymatic browning. These reactions involved in the thermal processing of food, lead to the production of melanoidins, brown pigments responsible for the brown colour of bread crusts as well as that of caramel. By 1936, von Elbe had defined caramel as a mixture of colourless compounds, closely related to the original sucrose, and dark-black "humic" substance (melanoidins) [13]. Darker caramel colours (Class III and IV) are likely to contain the highest amounts of melanoidins.
3.2 Nutritional value

The factors used to calculate the energy content of major nutrients are derived from the definition of metabolisable energy by Atwater. The Atwater factor estimated for carbohydrates in general is 4 kcal/g (17 kJ/g).

In the European Union, the energy value is calculated using the conversion factors (or energy factors) listed in Annex XIV of Regulation (EU) No 1169/2011 [14].

- **Carbohydrates**: 17 kJ/g – 4 kcal/g
- **Proteins**: 17 kJ/g – 4 kcal/g
- **Fats**: 37 kJ/g – 9 kcal/g
- **Organic acids**: 13 kJ/g – 3 kcal/g
- **Fibres**: 8 kJ/g – 2 kcal/g
- **Erythritol**: 0 kJ/g – 0 kcal/g
- **Polyols**: 10 kJ/g – 2.4 kcal/g

A caramel made from polydextrose, a carbohydrate polymer belonging to the class of soluble fibres will therefore display a lower energy value than caramel made from sucrose or glucose because of the lower energy conversion factor applied to fibres (2 kcal/g).

NB: The method of calculating the energy value is not standardized internationally. In the United States, according to the Code of Federal Regulations (CFR) regarding the labeling of foods, the energy value can be calculated by using different methods: on the basis of general or specific Atwater factors, with measures by bomb calorimeter or other appropriate methods.

The energy value of caramel mainly relies on the composition of its carbohydrate fraction. Unlike caramel specialities, whose recipes can include other ingredients than carbohydrates (milk, butter, chocolate, fruit extracts, etc.), aromatic caramels and caramel colours contain no, or only small amounts of, protein or fat.

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Although the caramel is manufactured from carbohydrates whose energy value is 4 kcal/g, these carbohydrates are converted during the caramelisation process to become compounds that would not be fully digested or metabolized (especially fibres).

Given that different molecules are grouped under the term "fibres", the analytical methods for their quantification in foods vary, as do the results in measured fibres. The analyses presented in Table 2 were carried out using the method of the AOAC 2009.01. This method of measuring integrated total fibre enables the determination of soluble and insoluble fibre in a broader spectrum than the AOAC 985.29 method, which underestimates or excludes content estimates for several indigestible carbohydrates (including resistant starch and oligosaccharides). The results show that the energy value of the studied caramels is lower than simple carbohydrates.

The scientific demonstration of the indigestible nature of certain components in caramels, could lead to the recognition of a lower energy value for such caramels. The approach would be like that used for erythritol, a polyol that can be labelled as 0 kcal/g in Europe or "zero-calory" in the United States.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Aromatic caramel Nigay 1395 SMAG</th>
<th>Burnt sugars Nigay SLB 725</th>
<th>Burnt sugar Nigay SLB 16000S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter (g/100g)</td>
<td>80,6</td>
<td>72,5</td>
<td>67,6</td>
</tr>
<tr>
<td>Carbohydrates (g/100g)</td>
<td>80,4</td>
<td>71,9</td>
<td>67,2</td>
</tr>
<tr>
<td>Sugars (g/100g)</td>
<td>54,3</td>
<td>25,6</td>
<td>10,9</td>
</tr>
<tr>
<td>Fructose</td>
<td>20,6</td>
<td>1,7</td>
<td>2,2</td>
</tr>
<tr>
<td>Glucose</td>
<td>28,2</td>
<td>20,8</td>
<td>6,7</td>
</tr>
<tr>
<td>Fibres (g/100g)</td>
<td>4,4</td>
<td>13,0</td>
<td>14,7</td>
</tr>
<tr>
<td>Lipids (g/100g)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Proteins (g/100g)</td>
<td>0,2</td>
<td>0,2</td>
<td>0,2</td>
</tr>
<tr>
<td>Sodium (g/100g)</td>
<td>2,4</td>
<td>8,1</td>
<td>3,3</td>
</tr>
<tr>
<td>Energy value (kcal/100g)</td>
<td>313,6</td>
<td>262,5</td>
<td>240,4</td>
</tr>
<tr>
<td>Energy value of a sugar solution (constant dry matter) (kcal/100g)</td>
<td>322,4</td>
<td>290</td>
<td>270,4</td>
</tr>
</tbody>
</table>

Analyses carried out by the Scientific Institute of Hygiene and Analysis in December 2015
Caramels & Health: Potential risks

Aromatic caramels and caramel specialities are used as ingredients and therefore have not been the subject of specific toxicological studies. This part will be focused on caramel colours which are classified as food additives subject to specific health monitoring.

4.1 Strict monitoring of food additives

Food additives are substances added intentionally to foods to perform specific technological functions, for example to colour (in the case of caramel colours) or contribute to the preservation of food. In general, the additives are the most controlled of all foods, from both technological and toxicological points of view.

All food additives are subject to an exhaustive evaluation of their safety before being included in a positive list enabling their use in Europe. In 2008, legislation was consolidated into several regulations. According to Regulation (EC) No 1333/2008, food additives must be maintained under permanent observation and be reevaluated every time it is necessary, considering the new scientific information available. Regulation (EC) No 1129/2011 establishes a list of all permitted food additives and conditions of use.

Food additives may be associated with:

- an Acceptable Daily Intake (ADI), dose to which it is possible to be repeatedly exposed throughout one’s life without risk to health;
- a maximum level of use in foodstuffs (or in some of them as each additive is only permitted in certain foodstuffs);
- a "quantum satis" (as much as is needed) with regard to the toxicological data, no effect was observed even at the highest doses or because the scientific data beyond current usage levels are insufficient to determine it.
What is the ADI?

The Acceptable Daily Intake (ADI) of a compound is the amount that can be consumed daily throughout the lifetime of a person without health risk. The ADI is expressed in mg per kg of body weight per day. ADIs are established after evaluation of available toxicological data, by first determining the highest dose that doesn’t cause adverse effects in animals. A wide margin of safety is then applied to extrapolate to humans: the safety factor is at least 100. This factor 100 is the product of two components: a factor of 10 for the species difference between humans and animals multiplied by a factor of 10 to account for differences in sensitivity between humans.

This concept is used in many fields and widely used by the authorities in charge of food safety worldwide: EFSA in Europe, JECFA, the World Health Organization (WHO) and national agencies for risk assessment (e.g. ANSES in France, AFSCA in Belgium, etc.).

What is the maximum use in food?

Most of the additives can only be used in certain foodstuffs and in limited quantities. These maximal contents are fixed by the regulations. Food manufacturers are free to use lower quantities.

What does "quantum satis" mean?

The term «quantum satis» means that no maximum level is specified for use in food, but that the manufacturer must use the "right dose to achieve the desired effect".
4.2 Toxicological study of caramel colours

Caramel colours have been used in the manufacture of a wide variety of foods and beverages for over 100 years. In the 1970s and 1980s, toxicological studies led to the subdivision of caramel colours in 4 classes. The standardisation at the international level of the four classes was conducted by the International Technical Caramel Association (ITCA). In 1985, ITCA submitted data on the safety of caramel colours to the JECFA, the European Community, the FDA and other agencies responsible for food safety worldwide. Articles relating to the toxicological evaluation of caramels were the subject of a special issue of the Food and Chemical Toxicology journal published in 1992 [15].

The conclusion of these studies is that caramel consumption – in its globality – presents no danger to humans. As such, no median lethal dose (LD50), quantitative indicator of the toxicity of a substance, could be determined for caramel.

Based on available data, food caramels authorized in the European Union would be neither genotoxic nor carcinogenic. No evidence has been found to demonstrate that they have adverse effects on human reproduction or to fetus development. Caramel colours have an ADI set by the health safety authorities. Moreover, within the industry regulations, caramel colours do not have maximum use limits and are therefore subject to the quantum satis rule.

**TABLE 4: LIST OF THE FOOD COLOURS AUTHORISED IN EUROPE ON THE BASIS OF QUANTUM SATIS**

<table>
<thead>
<tr>
<th>Numéro E</th>
<th>Dénomination</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 101</td>
<td>Riboflavins</td>
</tr>
<tr>
<td>E 140</td>
<td>Chlorophyls, chlorophyllins</td>
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<tr>
<td>E 141</td>
<td>Copper-chlorophyl and copper-chlorophillin combinations</td>
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<td>E 150a</td>
<td>Plain caramel</td>
</tr>
<tr>
<td>E 150b</td>
<td>Caustic sulphite caramel</td>
</tr>
<tr>
<td>E 150c</td>
<td>Ammonia caramel</td>
</tr>
<tr>
<td>E 150d</td>
<td>Ammonia sulphite caramel</td>
</tr>
<tr>
<td>E 153</td>
<td>Vegetable carbon</td>
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<tr>
<td>E 160a</td>
<td>Carotenes</td>
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<tr>
<td>E 160c</td>
<td>Paprika extract (capsanthin/capsorubin)</td>
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<td>E 163</td>
<td>Anthocyanins</td>
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<tr>
<td>E 170</td>
<td>Calcium carbonate</td>
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<tr>
<td>E 171</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>E 172</td>
<td>Iron oxides and hydroxides</td>
</tr>
</tbody>
</table>
ADIs established for caramel colours

In 2011, EFSA published an opinion following a complete re-evaluation of the safety of the 4 classes of caramel colours. ADIs were established for safe use in food:

- A group ADI of 300 milligrams per kilogram of body weight per day (mg/kg bw/day) for the combined exposure to the four classes of caramel colours.
- A more restrictive ADI for the E150c group, with 100 mg/kg bw/day, to take into account uncertainties related to potential effects on the immune system of one of its trace compounds, the 2-acetyl-4 tetrahydroxybutylimidazole (THI).

In 2012, updated data on levels of caramel colour use within several categories of finished products have been made available to EFSA [16] by FoodDrinkEurope, an association representing the food industry at the European level, and EUTECA (European Technical Caramel Association). This information was used to review the consumption level of caramels E150a, E150c and E150d in Europe. The consumption level of the caramel E150b was not included in this last opinion, because the risk of exceeding the acceptable dose is considered low, according to the available data.

According to the EFSA in 2012, the estimated combined exposure to the four caramel colours does not exceed the ADI of 300 mg/kg bw/day for any population group [17].

The only exception is the ADI of E150c, which could be exceeded in at-risk populations (in the Netherlands), and adults with high consumption levels as in Belgium, the Netherlands, Ireland, the UK and Czech Republic [17, Appendix C]. To avoid large consumers of beer exceeding the ADI, Regulation (EU) No 505/2014 has strengthened consumer safety by setting a maximum use of E150c colour in beer and malted beverages [18, 19].

USA

In the United States, foods may only contain substances authorised by the Food and Drug Administration (FDA) and, where applicable, by the U.S. Department of Agriculture (USDA). Some substances, whose employment has been deemed safe in general (substances «GRAS» Generally Recognized As Safe) are immediately allowed.

Caramel has "GRAS" recognition, and is thus recognized as a safe substance, when used in accordance with good manufacturing practices.
4.3 Neoformed compounds in caramel colours

The heat treatment of sugars leads to the formation of many molecules, some of which can be classified as undesirable neoformed compounds.

These compounds could represent a risk to human health in a situation of excess consumption and therefore are subject to special monitoring and recommended thresholds.

It must be stressed that to study their toxicity, these molecules are considered individually. Therefore, the results ignore the potentially synergistic or antagonistic factors observed in their original matrix (e.g. presence of pro- and anti-antioxidant components within the same product).

a) Hydroxymethylfurfural (HMF)

During the caramelisation process and heat treatment in general, dehydration of sugars - including fructose - leads to the formation of compounds called "newly formed" or "neo-formed" products, such as 5-hydroxymethyl-2-furfural (HMF). HMF is the main constituent of the volatile fraction of caramel. It is accompanied by similar, volatile molecules, responsible for the caramel smell.

Figure 5: Hydroxymethylfurfural structure

HMF is present in aromatic caramels and caramel colours but at very different concentrations (a few mg/kg to several g/kg). More generally, this molecule forms in many foods exposed to domestic or industrial heat treatment such as dried fruit, coffee, honey, bread, drinks, vinegar or treated milk. A high content of HMF, responsible for a bitter taste, is for example the indicator of excessive heat treatment of honey.

When the revaluation of caramel colours was conducted by EFSA in 2011, the Scientific Panel on Food Additives (ANS) noted that substantial toxicological data on HMF are available. A study in the "National Toxicology Program" run by the Ministry of Health and Social Services in the United States evaluated the toxicity of 5-HMF during 3 and 13 weeks in B6C3F1 mice and F344/N rats. The carcinogenicity study in mice demonstrated that 5-HMF may induce liver tumours, upon administration of HMF between 188 and 375 mg/kg, but these were considered not to be relevant for human risk assessment, as they are far above any likely human exposure.

Compounds which are non present in raw materials but which appear during treatment such as heating.
Moreover, the biological Ames test to determine the mutagenic potential of a chemical compound was negative for the HMF. Nevertheless, the HMF could be converted in vitro into 5-sulphoxymethyl-2-furaldehyde (SMF) whose mutagenicity was observed. According to EFSA, based on the available toxicological data, there is no relevant carcinogenic reaction in studies in rodents and no genotoxicity or carcinogenicity in humans [21].

No usage limit is currently set for HMF in caramels but EFSA recommends maintaining its rate as low as possible.

Three recent studies have highlighted the positive effects of HMF [22, 23, 24]. HMF appears to decrease the agglomeration of haemoglobin S in patients with sickle cell disease and improve the transport of oxygen by red blood cells [22]. HMF would also play a protective role against oxidative damage induced by cerebral ischemia in rats. The results show that HMF inhibits reduction system APE / Ref-1 involved in DNA repair [23]. It also appears that the HMF is hepato-protective thanks to its antioxidant properties [24].

b) THI

Toxicological studies in the 1970s demonstrated that consumption of caramel colours of class III induces a decrease in the number of lymphocytes, especially for animals consuming a diet deficient in vitamin B6 (tests on mice and rats). This effect, reversible, has been linked to the presence of 2-Acetyl-4-tetrahydroxybutylimidazole (THI), present only in caramel colours of class III.

In contrast, a clinical study in men aged over 65 deficient in vitamin B6 confirmed that absorption of class III caramel colour at 200 mg/kg bw per day for 7 days has no effect on the number of lymphocytes in the blood in humans [25].

**Figure 6: THI structure**

The permitted content of THI in caramels of class III/E 150c is limited to 10 mg/kg in Europe (Directive 2008/128/EC) and 25 mg/kg in the rest of the world, for a 0.1 color intensity. The concentration of neo-formed compounds is linked to a fixed colour intensity as the stronger the colour of the caramel, the less of it is needed in a finished product. The colour intensity is calculated by absorbance at 610 nm of a caramel solution to 1 g/L.
c) 4-MEI

4-MEI has been known since the mid-20th century for its potential convulsive effects. In 2011, 4-MEI has been classified as «Possibly carcinogenic to humans» by the International Agency for Research on Cancer (Volume 101 of the IARC Monographs, 2011), particularly following a long term exposure study of the pure molecule conducted in mice and rats [26].

This molecule may be formed in the caramel colours of classes III and IV, obtained by heat treatment of sugars in the presence of nitrogen in the promoters of caramelisation, and in other food products such as coffee.

**Figure 7: 4-mei structure**

![4-MEI structure](image)

**EUROPE**

In Europe, the maximum levels of 4-MEI in caramel colours E150c and E150d are laid down according to Regulation (EC) No 231/2012 of the Commission. They should not exceed 200 and 250 mg per kg of caramel colours E150c and E 150d, respectively, for a 0.1 colour intensity.

**USA**

In the United States, the Food Chemicals Codex[^9] limits the presence of 4-MEI to 250 mg / kg of caramel colour at a colour intensity of 0.1. The FDA believes that there is no immediate danger in the short term due to the presence of 4-MEI.

However, to ensure that the use of caramel colour in food continues to be safe, the FDA is currently conducting a comprehensive review of data on the safety of 4-MEI and will reassess the potential 4-MEI exposure of consumers related to the use of caramel colours Class III and IV in food products.

[^9]: Sets the pharmacopoeia standards in the US (United States Pharmacopeia).
What about Proposition 65 in California?

The "Proposition 65" is a law, adopted by referendum in 1986, which obliges commercial establishments and workplaces to warn the public of a possible risk of exposure to chemicals that the state of California has identified as potentially carcinogenic and/or with negative effects on reproduction (addition of a cancer risk warning pictogram on their labels if the maximum exposure is not respected).

In 2012, the state of California added 4-MEI, to the list of potential carcinogens. The daily intake of 4-MEI is thus limited to 29 μg per person.

**Calculation of the 4-MEI limit content in caramel colours to meet the daily absorption limit**

Whereas the level of use of a caramel colour at 0.25 colour intensity is around 2 g in a liter of cola and the average cola consumption in the United States is 180 L per year, the 4MEI content can be up to 30 mg/kg in caramel colours. By reducing this value to correspond to a 0.1 colour intensity, the concentration of 4-MEI in caramel must be less than 12 mg/kg.

Following registration by the California authorities of 4-methylimidazole (4-MEI) on the list of probable carcinogens in January 2011, the industrial sector continues its research efforts to develop caramels with low levels of 4-MEI and "clean label" caramels. The caramel manufacturing processes are constantly improved to reduce the presence of undesirable molecules while retaining the characteristics of these products.

Manufacturers have also invested in the development of innovative methods for more accurate analyses to detect the 4-MEI at levels of less than 10 ppm (mg/kg) in caramels and less than 10 ppb (µg/kg) in finished products.

<table>
<thead>
<tr>
<th>Geographical area</th>
<th>Europe</th>
<th>USA</th>
<th>Rest of the world</th>
</tr>
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<tbody>
<tr>
<td><strong>Regulation</strong></td>
<td>Regulation (EC) No 231/2012</td>
<td>Food Chemicals Codex</td>
<td>JECFA</td>
</tr>
<tr>
<td><strong>4-methylimidazole E150c</strong></td>
<td>200 mg/kg*</td>
<td>250 mg/kg*</td>
<td>200 mg/kg*</td>
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<tr>
<td><strong>4-methylimidazole E150d</strong></td>
<td>250 mg/kg*</td>
<td>250 mg/kg*</td>
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</tr>
<tr>
<td><strong>2-acetyl-4-tetrahydroxybutylimidazole - E150c</strong></td>
<td>10 mg/kg*</td>
<td>not defined</td>
<td>25 mg/kg*</td>
</tr>
</tbody>
</table>

*Based on a color intensity of 0.1
Part 5

Caramels & Health: Components of interest

5.1 A lower caloric value related to indigestible carbohydrates

The energy value of carbohydrates is calculated using the conversion factor of 4 kcal/g unless they contain indigestible carbohydrates, such as dietary fibres. Although caramels are made from simple carbohydrates, the caramelisation process results in the formation of carbohydrate compounds which differ from those of the raw materials. Thus, a part of the compounds present in the finished products would be indigestible. This hypothesis is supported by the nutritional analysis results presented in chapter 2.2, which indicate that the caramels are at least a source of fibres (pursuant to Regulation (EC) No 1924/2006). In the samples analysed, the energy value of burnt sugars is 10% lower than that of aromatic caramels because of the presence of up to about 15% of fibres. That other compounds of low molecular weight, such as DFAs, which are not considered as fibres by AOAC 2009.01 (see section 2.2), potentially have an indigestible nature, remains to be demonstrated in humans.

Further analyses are needed to better characterise the indigestible fraction of caramels, probably underestimated due to technical limitations (assay methods specific to caramels need to be developed).

5.2 Fructose dianhydrides (DFAs) and potential beneficial health properties

The DFAs occur naturally in certain plants subjected to heat treatment (food products such as prunes, liquid chicory and dried grapes [27]) and can also be obtained by biosynthesis.

Potential health effects of Fructose Dianhydrides

Several reviews have addressed the issue of the potential benefits of DFAs [28,29]. Some authors have highlighted their prebiotic properties, demonstrated in animals but which remain to be confirmed in humans.

The definition of prebiotics requires the properties of "non-digestible" and "fermentability" but imposes no chemical characteristics. Prebiotics are compounds, usually short chain carbohydrates (2 to 20 monosaccharide or "sugars" units) that promote the development of the intestinal microbiota, particularly bifidobacteria and lactobacilli, thus contributing to health benefits for the host.

NB: There is no regulatory definition of prebiotics. To date, the health applications for allegations related to potential prebiotic effects were rejected by EFSA.
What is the level of evidence in the scientific literature about the potential prebiotic effect of DFAs found in caramel?

By the 90s, some tests have shown that oligosaccharides derived from palatinose, which contain glycosylated-DFAs, **promote the growth of\textit{Bifidobacterium bifidum in vitro}**\[30\]. A study of fermentation of the contents of the caecum of chickens \textit{in vitro}, also indicates that the total concentration of short chain fatty acids, particularly propionate would be increased by the addition of several caramels with a high content in DFAs \[31\]. **The growth of some strains of bacteria (Bifidobacteria, Lactobacilli)** was observed particularly in media containing an aromatic sucrose caramel sold by the Nigay company \[31\].

Regarding animal studies, the results of a Japanese team show an impact of the consumption of 2% of DFA III (β-D-fructofuranose-1,2′:2,3′-dianhydride) or raffinose on the intestinal microflora of rats \[32\]. Ingestion of DFA III for 4 weeks induced an increase in \textit{Clostridia} in the animal faeces; when ingesting raffinose, Bifidobacteria increased. **The bifidogenic effect** of sucrose caramels with a high content of DFAs (> 60%) consumed for 2 weeks was then demonstrated in rats with colonic inflammation \[33\]. In this model, the ingestion of caramels with a high content of DFAs or fructo-oligosaccharides (FOS) increased production of short chain fatty acids in the colon and decreased significantly damage induced by TNBS colitis (model which reproduces Crohn’s disease damages).

Other studies in chickens have shown that sucrose caramel supplementation, characterized by the presence of DFAs (20% of oligosaccharides), **stimulates the growth of bифidobacteria in the caecum** versus the control diet \[34\]. The dry matter content of the caecum was lower in chickens fed with caramel regime compared to chickens fed with the control diet. In chickens, the fructose caramel ingestion with a high content of DFAs for 21 days significantly increased the number of \textit{C. coccoides / E. rectal}, and reduces enterobacteriaceae and \textit{Escherichia Shigella} compared to control \[31\].

In the field of animal nutrition, the use of DFAs as prebiotic has been proposed as an alternative to antibiotics in chickens. Caramels rich in DFAs tested were obtained from D-fructose, D-fructose & sucrose, and D-fructose & β-cyclodextrin. In this model, the caramels with a high content of DFAs resisted in part to the \textit{in vivo} digestion in the small intestine of chickens, were fermented and \textbf{selectively stimulated growth of certain \textit{in vitro} bacteria} \[31\]. The use of products containing DFAs for animal feed could help protect against infections of the digestive system.
A study has also evaluated the modulation of intestinal microbiota in pigs by introducing 30 g per day caramel with a high content of DFAs (18.5% D-fructose, 31.6% DFAs and 48% glycosyl-DFAs) in the diet. Food enriched with caramel leads to a significant increase in the number of lactobacilli and *C. coccoides*/*E. rectal and Bacteroides*, despite a significant decrease in the total number of bacteria as compared to the results of surveys conducted on the same animals after a control diet [35].

### Other beneficial health effects

A clinical study conducted in Japan, has revealed the low indigestible and fermentable property of DFAs in humans [36]. This study was randomized, single blind, cross-over (8 subjects; mean age: 28 years). Three carbohydrates were tested (10g DFAs, lactulose or sucrose in 200 mL water) at 1-week intervals during hydrogen breath tests. No change in glucose, fructose, and insulin in serum were observed after ingestion of DAF III unlike sucrose intake.

Note that in this study in humans, the DFAs were ingested as DAF III (> 97%) of *Lycoris radiata* extract (Red Amaryllis from Japan). DAF III is not among the isomers predominantly present in aromatic caramels. Further isomers may thus have other beneficial actions for humans which are not yet identified.

The beneficial role of DFAs in the intestinal absorption of iron and magnesium in rats has also been suggested [37,38]. The DFAs could notably prevent the inhibitory effect of tannins on iron uptake [38]. In the field of animal nutrition, a study conducted in calves has recently concluded that ingestion of DFA III not only improved mineral absorption, but also had an impact on immunity (increased concentration of IgG) [39]. Preliminary results obtained from young students indicate that DFA III could increase the absorption and retention of iron in humans [40].

Processes to enrich caramels in DFAs are described. The studies of Idri and al. demonstrated the ability to obtain caramels of fructose with 50 % of DFAs [41]. The heating by microwaves allows to obtain these yields with a process time ten times shorter than conventional thermal processes [42].
In brief, DFAs have been the subject of numerous publications, in particular these last 10 years. Promising properties are described:

- Potential prebiotic effect (growth of certain bacteria called "beneficial for the health of the host" such as bifidobacteria or lactobacilli within the intestinal microbiota)
- Decrease of the pathogenic bacteria
- Anti-cariogenic effect
- Improvement of the intestinal transit
- Improvement of mineral absorption (calcium, magnesium, iron)
- Stimulation of immunity
- Lower calorie intake for a caramel with a high content of DFAs vs a classic caramel
- Lower post prandial glycemia after consumption of DAFs III vs sucrose ingestion
5.3 Brown pigments of caramel colours and health benefits

In the early 2000s, an action of the European Cooperation in Science and Technology (COST) was conducted about the link between food melanoidins and health [43]. The main products studied were coffee, beer and bread crust. The main objective of this action was to increase knowledge about the structure and functions of melanoidins and other related molecules in various food matrices. In this context, several methods have been evaluated to estimate the antioxidant capacity of melanoidins as compared to regular foods.

Definition of the character and role of melanoidins (including the possible antioxidant effect) have been the topic of numerous studies on coffee and to a lesser extent on beer, vinegar, honey and cereal products. According to some results from the Nutripan project, some polymers newly formed when baking bread, similar to soluble fibres, could be classified as melanoidins [44].

To date, no specific data on caramel melanoidins have been the subject of a scientific publication.

\textit{In vitro} studies indicate that the activity of melanoidins as \textbf{antihypertensives} might be of interest to develop new functional foods that control blood pressure [45]. If this approach seems promising, more research is obviously necessary to isolate the compounds of interest and study their antihypertensive bioactivity \textit{in vivo}. To go further, a review has identified various potential biological activities of melanoidins [46]. \textit{In vitro} data indicate that some melanoidins could \textbf{inhibit the growth of tumour cells}.

Melanoidins - particularly low molecular weight polymers - would be digestible. Indeed, about 30% of these melanoidins and/or their degradation products could be absorbed by the intestine and \textbf{provide antioxidant activity \textit{in vivo}}. The indigestible melanoidins also represent components of interest regarding their benefits to human health by \textbf{their prebiotic action at the intestinal level}. Thanks to their antioxidant and antimicrobial actions, melanoidins could also play a \textbf{conservation role and help preserving food quality}.
Critical point of the melanoidins characterisation

There is no real standard. Only methodologies such as Nuclear Magnetic Resonance (NMR) could be suitable to assess the structure of these brown polymers.

In brief,

The caramelisation process belongs to reactions called non-enzymatic browning. These reactions result in the production of melanoidins, pigments responsible for the brown colour of different foods (coffee, beer, bread crust, caramel...).

Potential biological activities attributed to melanoidins:

- Antioxydant capacity
- Antihypertensive activity
- Potential prebiotic effect
- Anti-microbial activity, particularly in terms of conservation in food
- Inhibition of the growth of tumor cells

While caramel colours may contain melanoidins, characterisation in this specific matrix has not been released.
CONCLUSION

The "homemade caramel", used especially in desserts, is made by heating white sugar, water and optionally an acid product (vinegar or lemon juice).

The industrial production of aromatic caramels requires the same ingredients but uses larger quantities with better control of temperature and therefore a better reproducibility of the obtained caramels.

Burnt sugars are more brown caramels, obtained only from the heat treatment of sugars. These caramels can be considered as aromatic caramels if they change the flavour of the final product or as caramel colours if they only change its colour.

Caramel colours are produced by heating sugars with promoters of caramelisation, in order to create intense colour and stability in the final product. As additives, they are used in the food industry to bring a brown colour to a variety of foods.

Caramelisation is the heat treatment of simple molecules (sucrose, glucose, fructose) to create thousands of molecules responsible for taste, flavour and colour characteristic of caramel. Among these molecules, some, pure and consumed in high doses by animals (rats, mice, for example), are considered molecules of concern. They are present in certain caramel colours at concentrations of the order of mg/kg.

Many toxicological studies have evaluated the health effects of caramel and only one hazard was identified: the immunosuppressive effect of the THI molecule, present in caramel colour class III. This effect only affects animals with a diet deficient in vitamin B6. However, this effect is reversible.

On the other hand, some molecules of caramel are associated with prospective nutritional benefits. Studies have shown potential prebiotic effects for fructose dianhydrides and some other oligosaccharides (present in the order of several hundred g/kg in some caramels). Melanoidins have also been studied showing interesting benefits to humans, including antioxidant effects. The molecules responsible for the colour of caramel belong to this family of compounds. Although the raw materials are mostly simple carbohydrates, the caramelisation process induces the formation of indigestible compounds in the finished products, resulting in a lower caloric value of caramels with a high content of DFAs compared to other sweet products. Nutritional analyses confirm that the fibre content of caramels, relatively high although potentially underestimated, varies depending on raw materials and manufacturing processes from a few grams to more than 15g/100g.

The demand for functional foods is growing and meets the expectations of consumers aware of the link between food and health. The development of caramels with added nutritional value such as a lower energy content or demonstrated health effects is a promising innovation route.
The fact that the term "caramel" is associated with pleasure and over-eating should not block such developments, as is demonstrated by the approach of the company Barry Callebaut, obtaining a health claim for its ACTICOA® chocolate. Approved in 2013, their health claim was the first to benefit from the recognition of a beneficial effect in the cocoa and chocolate industries. Moreover, the claim "cocoa flavanols help maintain the elasticity of blood vessels, which contributes to normal blood flow." is relatively easily understood by consumers.

Whatever the component of interest studied (melanoidins, DFAs), it must be reasonably possible within a balanced diet and consistent with the current nutritional recommendations, to achieve the quantity of food and pattern of consumption required to obtain the claimed effect.

Caramels are a mixture of compounds, certain of which, at much higher doses than those found in caramel and regulated by the relevant authorities, can have adverse effects on animals and other compounds with potential beneficial health effects and molecules.

**Figure 8: Benefits/risks of caramel scales**

**Components of interest**

- 4-MEI (4-methylimidazole)
- HMF (5-hydroxymethyl-2-furaldehyde)
- THI (2-acetyl-4-(1,2,3,4-tetrahydroxybutyl)imidazole)
- Fibres (lower caloric value)
- Fructose dianhydrides (potential prebiotic effect)
- Melanoidins (antioxidant activity, antihypertensive activity)

**Potential risks**

Heat-formed compounds which are the subject of a strict monitoring to ensure consumer safety.

Caramel has not delivered all of its secrets yet because the complete characterisation of its molecules is far from being achieved. Years of research will be necessary to know the total content of fibres and melanoidins in caramel, and their health effects, mainly in the gut microbiota, as well as other unpublished nutritional benefits.
Appendix 1 - The caramel production process and its supply chain

1. Selection of high quality raw materials: 
   - sugar (beet or cane sugar) 
   - glucose syrup (from wheat, maize...)

2. Reception and check-up of raw materials by laboratory technicians

3. Storage and preparation of ingredients used in the recipe

4. Transfer of raw materials into the cooker - Time and temperature controlled cooking under the monitoring of operators who record each step to ensure traceability

5. Transfer of cooked sugars into an intermediate tank used for cooling. Physicochemical controls: colour, dry matter, density, pH, viscosity...

6. Transfer from the intermediate tank to the storage tank is required to filter the liquid caramel and remove any foreign material

As soon as the control laboratory certifies its quality, caramel is maintained at a constant temperature in storage and will be conditioned according to the desired packaging and labelled.

7. The hot caramel passes through a final safety filter bag before conditioning to the desired packaging and finally labelling.

8. Once the caramel has been conditioned, it is prepared (palletizing, filming, labelling ..) and taken over by the shipping department for editing delivery documents (analysis report, delivery...)

9. The caramels are then delivered by a carrier to the customer so that they can integrate them as ingredients or additives in finished products (drinks, alcohol, dairy products, biscuits, chocolates, soups...)

Different cooking methods: batch process of caramelisation performed in the traditional manner in a cooker or "cauldron", continuous cooking with microwave heating or reactor, extrusion cooking, etc.
Glossary

**Atwater factor:** The Atwater factors represent the metabolisable energy (ME) provided by macronutrients in mixed foods. They are derived from the gross energy (GE) of the macronutrient, from which is subtracted the energy loss due to urine (EU) and faeces (EF).

**Dextrose:** Pure glucose obtained by hydrolysis of starch.

**Dietary fibres:** Non-digestible carbohydrates that come mainly from plant products, fruits, vegetables and whole grain products.

**Glucose syrup:** Sweetening agent produced by hydrolysis of starch. Contains glucose and other carbohydrates of different degrees of polymerization. Can be obtained from wheat, maize, potato, cassava, rice.

**In vitro:** Reactions or experiments, performed in the laboratory, outside of a living organism.

**In vivo:** Biological process observed / studied in a living organism as opposed to in vitro.

**Invert sugar:** Glucose and fructose solution in equal proportions, obtained by hydrolysis of the sucrose.

**Polydextrose:** Complex carbohydrate obtained by condensing at high temperature D-glucose and D-sorbitol in the presence of citric acid.

**Polymerization:** Assembly of several identical molecules to form a more voluminous one.

**Polyol:** Polyols are hydrogenated carbohydrates which have a lower energy content and do not cause dental caries.

**Sucrose:** Commercial powdered sugar and sugar lumps found on our tables. Extracted from cane or sugar beet, it is the pure sucrose, dimer of glucose and fructose.

**Sugars:** "Sugars" grouping all monosaccharides and osides (degree of polymerisation equal to 1 or 2) present in a food, excluding polyols.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADI</td>
<td>Acceptable Daily Intake</td>
</tr>
<tr>
<td>DFAs</td>
<td>Fructose dianhydrides</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerisation</td>
</tr>
<tr>
<td>EFSA</td>
<td>European Food Safety Agency</td>
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<td>EUTECA</td>
<td>European Technical Caramel Association</td>
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<td>FAO</td>
<td>Food and Agriculture Organisation</td>
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<td>FDA</td>
<td>Food and Drug Administration</td>
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<td>FOS</td>
<td>Fructo-Oligosaccharides</td>
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<td>HMF</td>
<td>Hydroxymethylfurfural</td>
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<td>ITCA</td>
<td>International Technical Caramel Association</td>
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<tr>
<td>JECFA</td>
<td>Joint FAO/WHO Expert Committee on Food Additives</td>
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<td>4-MEI</td>
<td>4-Methylimidazole</td>
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<td>THI</td>
<td>2-Acetyl-4-tetrahydroxy-butylimidazole</td>
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<td>WHO</td>
<td>World Health Organisation</td>
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Since 1855, Nigay is unique in its dedication to the art and science of caramelisation which has made its name "The Expert of Caramels" around the world. Discover its comprehensive range of aromatic caramels, caramel colours, burnt sugars and a growing portfolio of caramel specialities. Nigay is constantly innovating and creating caramels with endless possibilities!

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