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Symposium on 'Food technology: can it alter the functionality of nutrients'

Functionality of nutrients and thermal treatments of food

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Since discovering fire man has used heat to modify the sensory properties and to preserve foodstuffs. Nutrients are involved in a number of reactions induced by this form of treatment. Some of these reactions are desirable, e.g. the improvement in the digestibility and the attractiveness of a food. Some reactions are undesirable because they lead to considerable nutritional loss or may result in the formation of mutagenic and carcinogenic molecules. The present paper reviews recent studies in which most of the modifications generated by thermal treatments at both the industrial and domestic level are demonstrated. We focus on the processes and the importance of thermal treatments used currently, as well as the necessity for optimization to minimize undesirable effects.

Résumé

L'homme a toujours recherché les moyens de développer ou modifier les propriétés sensorielles des aliments. Certaines sont souhaitées (amélioration de l'attractivité de l'aliment, meilleure digestibilité), d'autres sont proscrites en raison de la perte de qualité nutritionnelle ou de l'apparition de substances mutagènes et carcinogènes, par exemple. Cet article est une compilation des plus récents travaux sur les modifications générées par les traitements thermiques des aliments, tant au niveau industriel que domestique. Il insiste particulièrement sur les process. En conclusion, l'importance des traitements thermiques est aujourd'hui confirmée, mais il convient de poursuivre l'optimisation des procédés afin de réduire les effets indésirables.

Thermal treatment of foods: Sensory properties of foods: Nutritional status: Maillard reaction

The main objective of the food industry today is to preserve the quality of nutrients through optimized processes, together with the safety now asked for by the consumer.

The quality of a food (its nutritional, hygienic and sensory aspects) depends on a large series of variables, related to the production at agronomic level, the packaging, the distribution and, finally, the cooking (Potter & Hotchkiss, 1995). Among these variables, thermal treatments have been used universally, since the discovery of fire (about 700 000 years ago), to modify and to preserve the organoleptic properties as well as the nutritional value of foodstuffs.

Down the millennia man has developed his 'know-how' in cooking with increasing scientific knowledge; from firewood cooking (itself derived from drying), the necessary production of heat has passed through the use of various combustibles and fuels, steam and irradiation treatments, to the use of microwaves. The need for seasonal preservation has led to the development of methods which have become available as the result of technological and scientific advances. Among these advances the discovery of canning by Appert, the destruction of micro-organisms by Pasteur, and modern sterilization techniques (e.g. ultra heat-treatment) have proved to be particularly important.

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In addition, heat has been used for traditional transformation processes other than cooking, i.e. toasting and coffee-roasting, and also as part of other processes such as drying and smoking, or more recently to develop new products and textures, as in the case of extrusion cooking. These thermal treatments induce several biological, physical and chemical modifications in foodstuffs and, consequently, sensory and nutritional changes. This set of very complex reactions obeys kinetic laws, some of which are now well established. These laws give a scientific background to the phenomena observed and applied. It is common knowledge that the kinetics of micro-organism destruction are more rapid than those of foodstuff degradation (Table 1).

Basically, this knowledge was applied in ‘high-temperature short-time’ processes which led to modern ultra heat-treatments.

When focusing on thermal treatment processes, it is important to consider the time–temperature combination and to take into account the production and transfer of heat. Other variables must also be considered, e.g. pressure, product shape and size (Fig. 1), and other physical and chemical properties of the medium (pH, water activity etc.). In fact, the action of heat on the functionality of foodstuffs should be described in terms of positive and negative effects.

These treatments affect the nutritional value of foods by chemically altering the nutrients, and by the synthesis or the destruction of various exogenous or endogenous biologically-active molecules.

Table 1. Some important values for thermal kinetic variables associated with the destruction of micro-organisms, thermal inactivation of nutrients and changes in food quality

	$D_{T°}$	Z (°)	Q_{10}
Clostridium botulinum, buffer pH 7	D_{121} 12 s	10	10
Escherichia coli 3127:H7 homburger	D_{60} 24–48 s	5–8	< 30
Ascorbic acid (in peas)	D_{121} 250 min	50	1·6
Thiamin	D_{121} 150 min	31	2
Milk browning	D_{121} 12 min	26	2·4
Texture of potatoes (cooking)	D_{121} 12 min	20	3·2

D_{TO}, decimal reduction time required to reduce a population of micro-organisms by a factor of 10 at a given temperature T (60° and 121°); Z, temperature change (°) required to change decimal reduction time by a factor of 10; Q_{10}, temperature coefficient, the kinetics of the reaction multiplied by a constant factor when the temperature is increased by 10°.

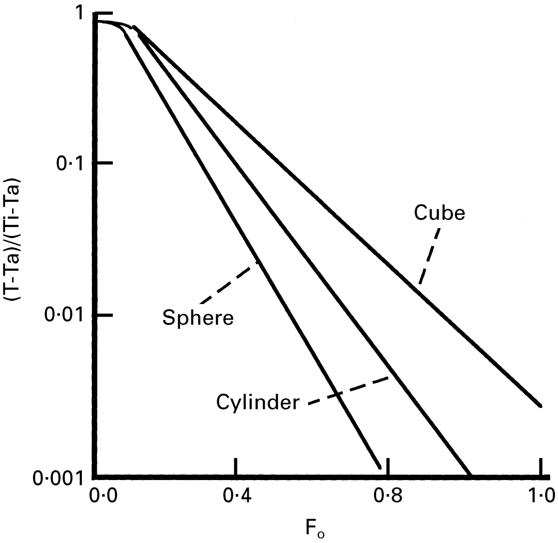

Fig. 1. Temperature at the centre of a solid as a function of its shape. (From Schneider, 1955.) F_o, Fourier no., derived as $F_o = KQ\delta/X$, where $Q\delta$ is temperature, K is thermal diffusivity and X is the distance from the surface to the centre of the solid; T, surface temperature, Ta, ambient temperature; Ti, initial temperature.

Modification of the nutritional value

Effect on proteins

Heat leads to protein denaturation. This effect, defined as a modification of the quaternary, tertiary and secondary structures of the macromolecules, is linked to important physical, chemical and functional properties, i.e. lowering of solubility and wetting. Coagulation and aggregation may also occur, and nutritional properties are affected to a greater or lesser extent depending on the intensity of the thermal treatment. It has been shown that digestibility can be lowered as well as essential amino acid content. For example, Castrillon *et al.* (1996) demonstrated that heating at 115° for 90 min had little effect on the composition of a tuna fish product, but the availability of lysine was significantly lower (about 25 %) due to the condensation reactions with reducing sugars (Table 2). On the other hand, when thermal treatments are moderate and applied in humid conditions digestibility is enhanced, due to partial protein unfolding, and also to destruction of trypsin inhibitors. The latter observation is particularly relevant in the case of vegetable proteins. The availability of legume proteins can be greatly improved by the use of appropriate thermal treatments (Cheftel, 1986).

Chau *et al.* (1997) studied the effects of domestic ‘boiling-water’ cooking on the amino acid content and anti-nutritional factors of three leguminous seed varieties. They observed a reduction in all anti-nutritional factors (phytates, tannins and trypsin (*EC* 3.4.21.4) inhibitor) by between 30 and 80 %. The availability of amino acids remained at about 10 % (Table 3).

Wu *et al.* (1996) measured the nutritional quality of red kidney beans (*Phaseolus vulgaris*) *in vivo* and *in vitro*, and showed that a sterilizing thermal treatment reduced weight gain in rats in proportion to the severity of the treatment, while the overall protein intake was unchanged (Table 4).

Obviously, heat treatment affects digestibility. Qin *et al.* (1998) studied several varieties of soyabean and found that digestibility was related to thermal treatment, with the

Table 2. Effects of sterilization time on available lysine during canning of tuna fish (From Castrillon *et al.* 1996)

(Mean values and standard deviations for four replicates per treatment)

	Available lysine (g/kg protein)	
Sample	Mean	SD
Raw	83	3
Steam cooked	59	1
Canned: 55 min	69	4
90 min	59	4

Table 3. Recovery (%) of amino acids *v.* raw product (100 %) during 'boiling-water' cooking of beans (*Dolichos lablab*) (From Chau *et al.* 1997)
(Mean values and standard deviations for four replicates)

	Content of raw product (mg/g protein)		Recovery (%) after cooking for:	
Amino acid	Mean	SD	60 min	120 min
Aspartic acid	115	1·74	94	94
Threonine	38·3	0·35	95	93
Serine	59·3	0·45	95	92
Glutamic acid	159	0·89	93	93
Proline	42	0·4	91	93
Glycine	40·6	0·74	100	94
Alanine	43·4	0·05	94	91
Valine	53·5	0·11	94	91
Methionine	12·5	0·23	81	71
Cysteine	13·0	0·13	84	80
Isoleucine	41·4	0·30	94	93
Leucine	77·2	0·48	95	92
Phenylalanine	51·5	0·39	91	87
Tyrosine	36·6	0·36	96	92
Histidine	28·2	0·04	96	94
Lysine	63·1	0·30	96	92
Arginine	55·9	0·13	98	92
Total amino acids	415		94	90

Table 4. Effect of thermal treatment of red kidney beans on the protein intake, weight gain of rats and net protein ratio (From Wu *et al.* 1996) (Values are means for four rats per diet group)

Diet	Protein content (g)	W gain (g)	NPR
Raw bean	5·1	–22	–0·79
Boiled bean	7·8	6	1·32
Canned bean (ind)	7·4	6	1·34
Autoclaved bean			
121° for 10 min	7·8	5	1·22
121° for 40 min	6·6	1	1·17
121° for 90 min	6·6	–1	0·98
128° for 20 min	7·1	–1	0·86

NPR, (weight gain of rats fed on the test diet + weight loss of rats fed on protein-free diets)/protein intake.

specific relationship depending on the variety. Fig. 2 shows the variation in protein dispersibility index and trypsin (*EC* 3.4.21.4) inhibitor activity for a Chinese soyabean heated at two temperatures.

Animal proteins are unfolded by heat (e.g. milk) or coagulated (e.g. meat). Unfolding of soluble proteins in milk has been widely studied. It is often described in terms of Arrhenius's law, but Oldfield *et al.* (1996) demonstrated that the results did not fit this law exactly, which suggests more complex mechanisms and an order of reaction of > 1. Immunoglobulins are also affected, according to Mainer *et al.* (1996), who obtained a value of 1·5 for the order of reaction and found that activation energy depended on the substrate. Essentially, the proteins can withstand 'high-temperature short-time' pasteurization treatment (72° for 15 s) without any structural damage. This property of soluble proteins is well known by processors of dairy products who use this treatment to increase the hardness of fermented gels and to improve yields in cheese making.

The digestibility of muscle proteins is already very high in the raw state and does not change with heat treatment, while the digestibility of connective tissue proteins is clearly improved. At 100°, no amino acid deterioration is observed, while S amino acid loss is clearly apparent above 120° (Wirth, 1977).

Effect on carbohydrates

After water content, carbohydrates represent the second main component of foodstuffs. Apart from their participation in specific interactions induced by heat (e.g. Maillard reaction and various condensation reactions), the nutritional properties of mono- and disaccharides are little affected by heat, as long as the treatment remains moderate.

Most sugars have a digestibility of 98 %, but the digestibility of starch varies from 85 % to 98 % according to its origin, its structure and degree of gelatinization. Gelatinization begins with wetting, followed by swelling through a range of temperatures depending on the source; potato starch gelatinizes between 56 and 67°, while rice and sorghum starches change between 68 and 78°. This property is used in extrusion cooking processes and has been widely studied. The most important effect of thermal treatment on

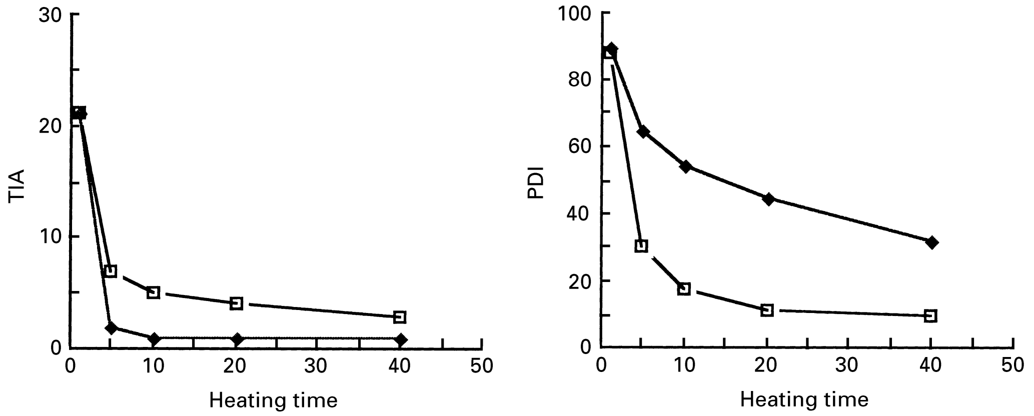

Fig. 2. Variation in protein dispersibility index (PDI) and of the trypsin (*EC* 3.4.21.4) inhibitor activity (TIA) of a Chinese soyabean heated at 100° (□) and 118° (◆). (From Qin *et al.* 1998.)

starch is due to gelatinization and to the improvement of solubility which leads to better absorption in the intestinal tract.

Effect on lipids

The nutritional value of lipids is affected by chemical transformations such as lipolysis, oxidation, polymerization and degradation. These reactions induce modifications in the physical properties and nutritional availability of lipids and lipid-containing foods. Also affected are digestibility and energy value, which may lead to growth problems with, in extreme cases, toxic and carcinogenic effects (Pomeranz, 1985).

These molecular changes involve modification of the unsaturated bonds, fatty acid position on the glycerol skeleton, isomerization and polymerization, which result in modification of organoleptic properties of the lipids. Among these chemical reactions, oxidative rancidity seems to predominate. In addition, the hydroperoxides formed are able to destroy carotenes, vitamin A and tocopherols, contributing to the lowering of nutritional value.

In some processes (e.g. toasting and coffee-roasting), when high temperatures are reached, other forms of degradation occur. Berna *et al.* (1997) showed that roasting produced up to 30–40 % loss of isobutyric acid in coarsely-ground carob (*Ceratonia siliqua*) (Table 5). In this particular case the effect is considered favourable because of the unpleasant odour associated with this fatty acid.

Table 5. Effect of roasting time on the concentration of isobutyric acid of coarsely-ground carob (*Ceratonia siliqua*) (From Berna *et al.* 1997)

	Isobutyric acid concentration (g/kg DM)		
Roasting temperature (°) . . .	120	140	160
Heating time (min)			
0	6·3	6·2	6·3
10	5·3	5·8	4·3
20	5·2	5·2	3·5
30	5·0	4·7	3·1
60	4·4	3·9	2·2

Effect on micronutrients

Vitamins are the micronutrients most sensitive to thermal treatments. This thermolability has been known for a long time. Nevertheless, the extent of thermolability is dependent on the nature of the vitamin (Harris & Kamas, 1975). Vitamin A and carotenes are almost completely stable to moderate treatments, but oxidation occurs rapidly at high temperatures in the presence of O_2. Vitamin D is also stable. However, vitamin C is the most sensitive vitamin to oxidation at high temperature, and is easily destroyed during processing (Table 6). Thiamin remains stable during heating of acid foodstuffs, but it is destroyed in all other cases. For example, Ilo & Berghofer (1998) have investigated thiamin loss during extrusion cooking of low-water-containing maize grits. The kinetics of loss depend on temperature (according to Arrhenius's law), water content and shear-stress generated by the extruder.

Synthesis or destruction of chemicals

Thermal treatments induce a series of complex chemical reactions in foodstuffs, not only in proteins, lipids and carbohydrates, but also in various other substances such as enzymes or some allergens and pesticides which could have been introduced from the cultivation process or during processing by the food industry.

In the reactions involving proteins, lipids and carbohydrate the Maillard reaction (discovered 1912) is particularly important in food science. Some recent studies have also suggested a role in the ageing process (de Bry, 1993).

The Maillard reaction

Also known as the ‘non-enzymic browning reaction’, the Maillard reaction is a complex series of chemical reactions which take place during the preparation or the preservation of foods. More precisely, sugars, amino acids and proteins react with each other to facilitate the formation of a large variety of compounds with differing volatilities and solubilities. Several variables are involved, e.g. structure and concentration of the components, pH, temperature, pressure, water activity and the presence of catalysts or inhibitors (e.g. sulphites), as well as light and time (Namiki, 1988). The final products of the reaction are mainly melanoidins with a pyrrole nucleus or indole-containing compounds, volatile aromatic components and high-molecular-weight coloured compounds, with differing solubilities, whose structure is not well established (Rizzi, 1993).

The Maillard reaction is dramatically increased by temperature (20 000-fold between 0° and 70°), and hydration plays an important role. Labuza *et al.* (1970) have shown that the kinetics of browning reach maximal intensity in the 0·60–0·80 Aw range (Fig. 3).

Table 6. Stability of vitamins during various degradation processes (From Harris & Kamas, 1975)

Vitamin	pH 7	pH < 7	pH > 7	Air or O_2	Light	Heat	Cooking loss (%)
Vitamin A	st	unst	st	unst	unst	unst	0–40
Ascorbic acid	unst	st	unst	unst	unst	unst	0–100
Biotin	st	st	st	st	st	unst	0–60
Carotenes	st	unst	st	unst	unst	unst	0–30
Vitamin B_{12}	st	st	st	unst	unst	st	0–10
Vitamin D	st		unst	unst	unst	unst	0–40
Folic acid	unst	unst	st	unst	unst	unst	0–100
Inositol	st	st	st	st	st	unst	0–95
Vitamin K	st	unst	unst	st	unst	st	0–5
Pantothenic acid	st	unst	unst	st	st	unst	0–50
P-aminobenzoic acid	st	st	st	unst	st	st	0–5
Vitamin B_6	st	st	st	st	unst	unst	0–40
Riboflavin	st	st	unst	st	unst	unst	0–75
Thiamin	unst	st	unst	unst	st	unst	0–80
Tocopherols	st	st	st	unst	unst	unst	0–55

st, stable; unst, unstable.

These reactions lead to undesirable effects, particularly on nutritional properties, by lowering the availability of some amino acids (e.g. lysine) and some vitamins. However, the reactions also exhibit favourable organoleptic aspects since they improve visual and aromatic attractiveness, e.g. bread crust, potato chips, coffee and roasted meat.

Thus, the non-enzymic browning reaction can be both undesirable and advantageous; it may pose problems in some processes, such as the production of intermediate-moisture foods, or may need to be enhanced by the addition of artificial brown pigments when the process is unable to induce the 'natural' reaction, which is the case with microwave cooking.

Endogenous and exogenous biologically-active molecules

Among the allergenic or mutagenic molecules which may occur in foods, many are generated during storage, cooking and other treatments. For example, the first evidence of mutagenic molecules produced during cooking was found in meat by Commoner *et al.* (1978). Some substances responsible for mutagenic activity on the surface of cooked meat and fish come from Maillard reaction products (Eichner & Schirmann, 1993).

Mutagenic substances may be produced by amino acid pyrolysis in the presence of sugars (Bailey & Williams, 1993). The barbecue is a popular method of cooking which can generate some mutagenic compounds; the fat contained in meat falls through the grid, decomposes by pyrolysis, and some polycyclic hydrocarbons (up to 200 pg/g) may be incorporated into the smoke and deposited on the surface of the meat (Lijinsky, 1991). On the other hand, it has been recently shown that heat may help to diminish the allergenic activity of celery (Jankiewicz *et al.* 1997; Fig. 4).

Moreover, thermal treatments may induce thermolysis of certain undesirable exogenous substances. Zabik & Zabik (1996) were able to demonstrate the role of various cooking processes in lowering the levels of polychlorinated biphenyl compounds in several varieties of Great Lakes fish (Fig. 5).

Enzyme inactivation

The role of thermal treatments in the preservation of foods via enzyme inactivation is well known. For example, blanching of vegetables before freezing is of great interest. Yemenicioglu *et al.* (1997) investigated the inactivation kinetics of polyphenol oxidase (*EC* 1.10.3.1) in six varieties of apple. They observed that the inactivating Z variable (i.e. the temperature change (°) required to change the thermal inactivation time by a factor of 10) was equal to 7·1 at 10°, thus showing that apple polyphenol oxidases were more stable than those found in other fruits. In milk the inactivation of plasmin (*EC* 3.4.21.7) is one of the targets now taken into account for optimization of ultra heat treatment, because the consequences of insufficient inactivation lead to preservation problems. On the other hand, pasteurization of milk is sufficient to inhibit most natural and microbial lipases, as well as alkaline phosphatase (*EC* 3.1.3.1), a classic indicator of the efficiency of pasteurization.

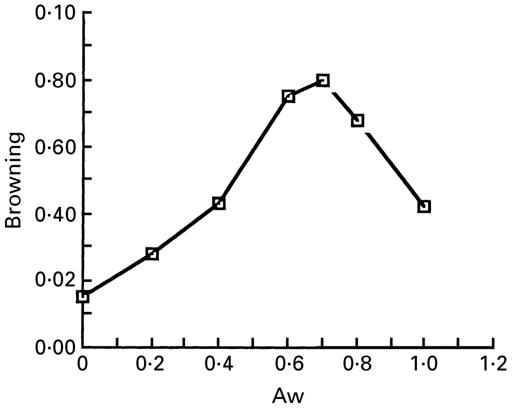

Fig. 3. Effect of water activity (Aw) on the browning of a pea soup at 54°. Browning is expressed in arbitrary units based on optical density measurements. (From Labuza *et al.* 1970.)

Modification of food attractiveness

Thermal treatments are sometimes carried out to improve the organoleptic properties of foods. It should be remembered that whatever the 'health value' might be, unless there is severe malnutrition, foods are eaten for pleasure.

All organoleptic properties are affected by heating; most colour and flavour changes are due to the Maillard reaction, while texture depends more on the unfolding and

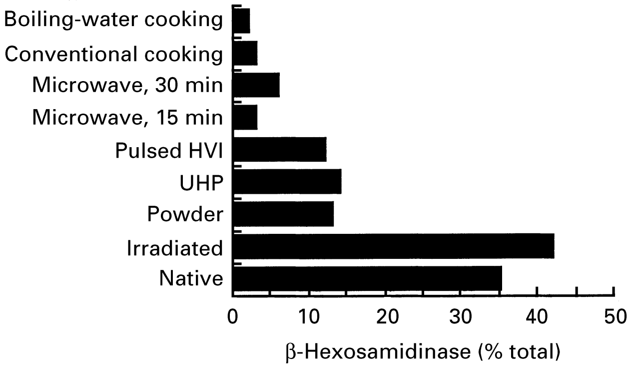

Fig. 4. β-Hexosaminidase (*EC* 3.2.1.52) liberated (% of total liberated after subtraction of spontaneous liberation) by rat cells sensitized with an antiserum reacting with murine antibodies raised against variously treated celery root extracts. HVI, high voltage impulse treatment; UHP, ultra high-pressure treatment. Protein concentration 1 μg/ml. (From Jankiewicz *et al.* 1997.)

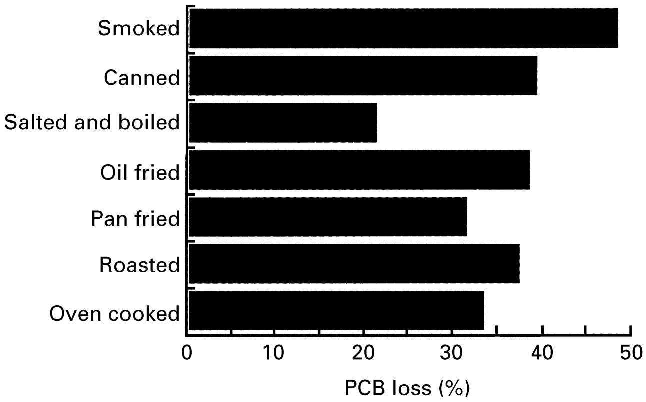

Fig. 5. The effect of various cooking methods in reducing polychlorinated biphenyl compounds (PCB) in Great Lakes fish. (From Zabik & Zabik, 1996.)

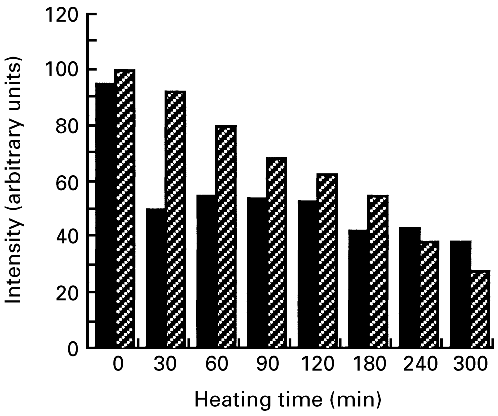

Fig. 6. Changes the perception of colour (■) and texture (▨) of carrots subjected to different blanching times. (From Schamaila *et al.* 1996.)

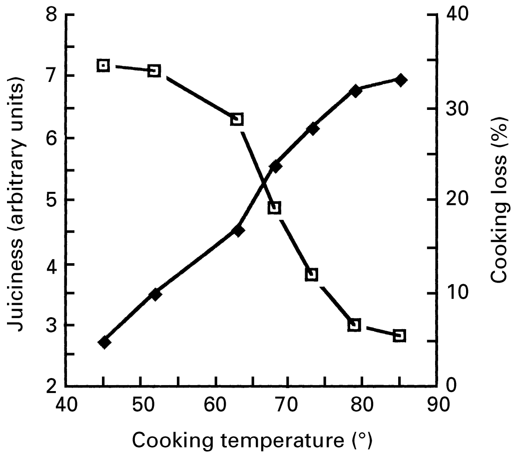

Fig. 7. Variation in juiciness (▣) and cooking loss (◆; based on ml liquid expressed from 100 g meat sample) of *Muscularis semimembranosus* as a function of thermal pretreatment. (From Martens *et al.* 1982.)

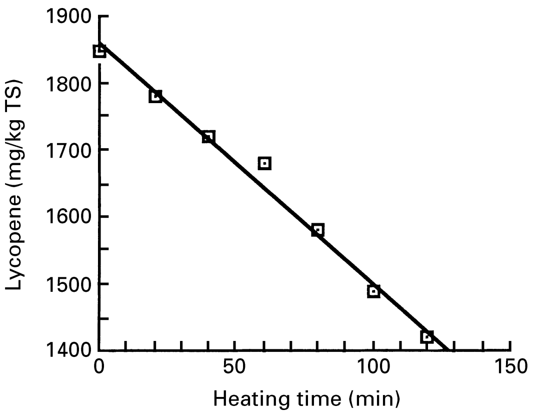

Fig. 8. Degradation kinetics of lycopene in tomato pulp heated at 100°. TS, tomato pulp solids. (From Sharma & Le Maguer, 1996.)

denaturation of proteins and carbohydrates, or changes in the hydration of foodstuffs.

For example, Schamaila *et al.* (1996) studied the blanching of carrots and showed that the contents of volatile compounds, e.g. terpenoids, were modified by up to 50 % in 60 s. This process results in a lowering of quality characteristics: colour, aroma and texture (Fig. 6).

Gandemer & Meynier (1994) studied the oxidation of meat phospholipids during cooking, and demonstrated that a positive effect on flavour was due to the production of ketone compounds and condensation of lipid-oxidation products with Maillard reaction compounds. Furthermore, in meat, heating not only plays a positive role in aromatization, but also in its perceived juiciness (Fig. 7) and colour, which are the main factors involved in visual attractiveness of roasted meat (Martens *et al.* 1982).

Another example is the tomato pulp concentration process. Sharma & Le Maguer (1996) studied the kinetics of lycopene degradation and calculated a temperature coefficient Q_{10} of 1·4 for its loss during cooking at approximately 100° (Fig. 8).

In all cases, these sensory modifications mainly depend on heating conditions, heat production and heat transfer. Califano *et al.* (1997) evaluated the effect of the cooking medium, temperature, heat transfer coefficient and size of the meat sample on the tenderness of cooked beef. These authors devised models of the conditions, so that texture gradients could be derived from the meat samples.

Conclusion

Most industrial concerns about foods are generated by the requirements of the consumer, e.g. food safety and palatability. On this basis, thermal treatments are now necessary, and facilitate the elimination of toxic substances and antinutritional factors, the destruction of pathogenic microorganisms and of enzymes responsible for various forms of degradation. Moreover, their role in accelerating reactions and interactions leading to organoleptically favourable substances has been clearly demonstrated. Thus, these processes are safe and necessary in food technology.

It has also been established that while thermal treatments could result in the formation of some potentially toxic substances, the use of heat is still the most effective industrial process, because the positive effects on organoleptic and sensory properties mainly predominate. The question is only of optimization and this should be the way chosen by researchers in food science and by food manufacturers.

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