5. BROADENING THE NET

5.1 Introduction

So far, this book has mainly looked at thermal processing. The concentration of a critical or an important product component or attribute has been linked to processing time, through a reaction rate constant. And because so much of industrial food processing is initiated and controlled by changing the temperature, the effects of temperature on these reaction rate constants have been quite extensively reviewed. Sometimes, effects of time and temperature are sufficient in studying reactions in food processing, but at other times the effects of other processing conditions need to be considered, as illustrated in Fig. 5.1.

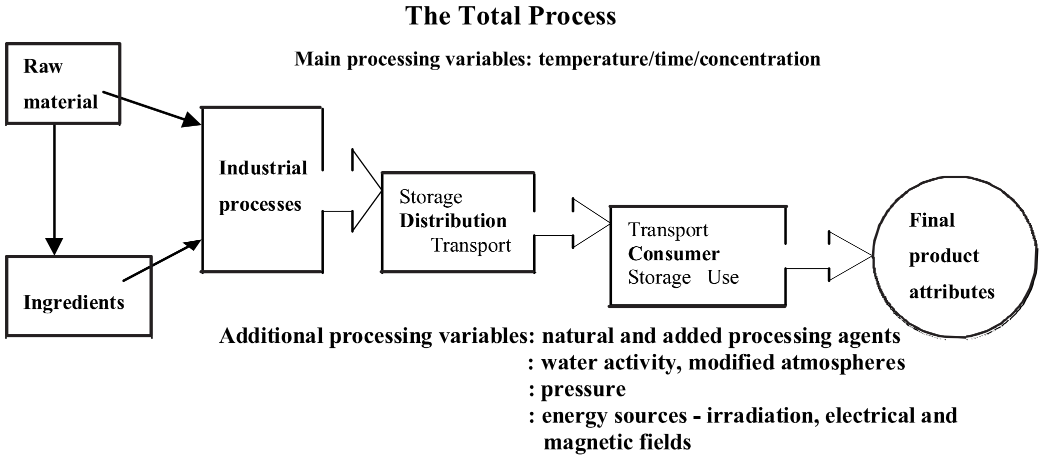


Fig. 5.1. Food processes and the processing variables

Figure 5.1 also emphasises that the "process" is not only the apparent industrial process but also the distribution and the consumer's handling of the food because it is the attributes of the final food as eaten that are important. The reactions and the resulting changes in the food materials during the whole sequence lead to the final product attributes. In foodservice, the control of the whole reaction sequence is technologically possible, but needs knowledge and technical skills. More commonly, food products are manufactured and distributed through complex chains to the final consumer, and it is difficult to have continuous control of the reactions.

Because of the effects on reaction rates of concentrations of the reacting materials and also of natural processing agents in the raw materials, purification and treatment of the raw materials to produce standardised food ingredients have become an important method of controlling the outcomes of the reactions. Processing agents can also be added to the food to increase or decrease the extents of the reactions.

Energy in forms other than temperature can, under suitable conditions, induce, hasten and slow food reactions. Irradiation, increased pressures, and electrical forces have all been suggested and sometimes used in food processing. They need to be taken into account, so that the technology of their use can be considered and their effects predicted. The fit of these into any general food processing pattern needs to be explored.

Water activity affects the rates of many reactions in which water is involved. Choice of the range of water activity limits the types of reaction that can take place; for example, lowering the water activity will firstly stop bacterial growth, then moulds and yeasts; specifying the water activity can be used to control the reaction rate.

Today there is increasing awareness of taking into account several process variables together, and designing the process so that optimum control of the critical and the important product attributes is achieved. Packaging design has greatly aided this, by being able to achieve a controlled atmosphere or vacuum, sterile filling and closing, pasteurising and sterilising of packs. The developments in controlling a number of process variables together have led to improved product attributes, but they also require considerable knowledge of the reactions and the effects of the different process variables when used together. In some cases, otherwise attractive new processes have been unsuccessful because of lack of understanding of the reaction technology.

5.2 Processing Agents

Because of the complex nature of foods, there are often components in the food materials that materially affect the critical and important reactions in the food; also, there may be processing agents that can be added to influence specific reactions. The concentrations of these other components must now be considered more carefully in the processing. Many common food constituents, such as water, acids and enzymes, can be regarded as processing agents as well as ingredients. Obviously, components in the food raw materials cannot just be added or subtracted at will as this may detrimentally affect the product. However, refining and purification to produce food ingredients can remove many of the interfering components; for example, by removing acids from fats by neutralisation, their effect on hydrolysis reactions can be removed. Processing agents can be added to increase or reduce the rate of the reactions – for example, sulfur dioxide to slow down browning and acetic acid to slow microbial growth. Even oxygen, in the atmosphere within which processing generally occurs, enters into many reactions as a significant reacting element.

5.2.1 Additives

Although there could be variations in initial concentration, this could often be only the biological variation in the raw materials, which may be quite minor. Concentration of natural processing agents in the raw materials, and added components from formulations can have a substantial effect on the reactions. So the concentration of added processing agents such as acids and alkalis, salt, sugar, glycerol, antibrowning agents, antioxidants, antistaling agents and essential oils has to be considered (1). There are many instances. An example is the influence of one group of additives, thermal protectants, on the heat denaturing of antibodies and antibacterial components in infant formulas, which has been investigated by Chen *et al.* (2). Table 5.I shows how the activation energies of the heat destruction of immunoglobulin G (IgG) changed with added processing agents, indicating the quite substantial effects of those thermal protective additives on properties that can be very important for processing.

TABLE 5.I
Activation energies of heat denaturation of immunoglobulin G (IgG) with thermal protectants

Sample	Activation energy (kJ/mol)
In phosphate buffer	
IgG in NaCl/phosphate buffer	328.4
IgG + 0.2% glutamic acid	300.5
IgG + 10% whole milk	289.4
IgG + 20% maltose	280.3
IgG + 20% glycerol	265.4
In colostral whey	
Whey	316.1
Whey + 0.2% glutamic acid	292.8
Whey + 20% maltose	273.6
Whey + 20% glycerol	257.3

Bovine milk IgG, in phosphate buffer (pH 7.0) and colostral whey, with added thermoprotectants, at temperatures 70, 72, 74, 78, 82 °C

From Chen, Tu & Chang (2)

These data show how addition of processing agents can change the activation energy of the heat denaturation and therefore both the rates and the relative rates of the reactions. The concentrations cited might not be suitable for some products, but the example shows how addition of thermal protectants can change the effect of temperature on the rates of reactions. Data such as these can be used in the planning of temperature regimes and heating and cooling rates, together with acceptable levels of processing agents, to achieve desirable final levels of the constituents in the final products.

Change of pH, increasing by adding alkalis and decreasing by adding acids, is a common processing strategy, for example in pickled vegetables and sauces to stop microbial growth. Acids affecting pH are often found naturally in food raw materials. Hydrogen ion concentration is normally quoted as the negative logarithm in gram mols per litre, the pH. For the first example of a rate equation in this book, the hydrolysis of sucrose, it was experimentally found that the rate was directly proportional to the concentration of hydrogen ions. This is also true of many other processing situations encountered in the food industry. An account of the effects of pH in different situations and processes is given by Tijskens & Biekman (3). They described simple equilibria and dissociation equations that they found to cover the discoloration in blanched vegetables and the activity of enzymes in different buffered and unbuffered systems.

Experimental results on the kinetic analysis of the breakdown of chlorophyll in green peas by Ryan-Stoneham & Tong (4) are given in Example 5.1. This loss of the bright green colour and development of a final yellowish green colour is common in canning green vegetables (4).

Example 5.1: Effects of pH on degradation of chlorophyll

In experiments on the thermal processing of pea purée, Ryan-Stoneham & Tong (4) examined the kinetics of chlorophyll (a) and (b) degradation as a function of pH. During the sterilisation process, there was a decrease in pH of the peas due to the formation of organic acids.

Rates of colour change and the effects on these of reaction temperature (80, 90, 100 °C) and pH (5.5, 6.2, 6.8, 7.5) were measured. In one set of experiments, the pH values were the starting pH and the pH was allowed to decrease naturally during the processing. They also measured the reaction rate under conditions of controlled pH (by the addition of gaseous ammonia to neutralise the increasing acidity).

Chlorophyll (a) and (b) degradation followed a first order model. With or without pH control, the temperature dependence always followed the Arrhenius relationship. They found their results were a good fit to an equation of the form

$$\ln k = \ln A - E/RT + c_p\, pH$$

where k is the reaction rate constant for the chlorophyll degradation, c_p is the coefficient describing the pH dependence.

Contd..

Example 5.1 (contd)

Using multiple linear regression on their data, the following equations were found to describe the reaction rate constants as a function of temperature and pH for both chlorophyll a and b:

Chlorophyll a $\ln k = 28.38 - 8796.2(1/T) - 1.193\text{pH}$
Chlorophyll b $\ln k = 25.53 - 8475.6(1/T) - 1.014\text{pH}$

The basic reaction was first order in both chlorophyll and hydrogen ion concentrations. That is, at constant temperature,

$$\text{rate } r = k\,(C_{Ch})\,(C_{H+})$$

where (C_{Ch}) is the concentration of the chlorophyll and (C_{H+}) the concentration of hydrogen ions and $-\log(C_{H+})$ is the pH.

Think break

In a company's tomato sauce, acetic acid is always present, and sometimes benzoic acid is added to control microbial growth. Marketing has decided that the acetic acid flavour is too strong, and benzoic acid is now not allowed in the Food Regulations.

- Discuss the microbial growth being controlled by these acids.
- List the other processing variables that could be used to control microbial growth.
- Select possible processing variables and their levels that could be used with acetic acid at lower levels to control the microbial growth.
- Describe the experimental studies you would conduct to find the processing conditions for the optimum product.

5.2.2 Modified atmospheres

Another common reactant in food systems is atmospheric air as the oxygen source for the oxidation of food components. Reducing the oxygen concentration in the ambient atmosphere can directly affect oxidation rates. The oxygen concentration can be controlled by reducing oxygen pressure inside packaging, introducing a nitrogen-enriched or carbon dioxide atmosphere, or conducting processing and packaging under a vacuum. This changes the partial pressure of the oxygen, which is proportional to its concentration. Modified-atmosphere packaging (MAP) has been a significant development in the last 20 years, combining gas atmosphere, temperature and time to ensure product safety as well as sensory attributes. For example, the storage life of fresh meat has been extended by providing much increased levels of carbon dioxide, which inhibits growth of microorganisms. Colour is then restored to the fresh red meat shade either when the package is opened to the air, or by having a packaging film that allows slow passage of atmospheric oxygen so that oxygen levels can slowly rise from, for example, an original 0.1% in the pack. Mathematical modelling has been used to follow such processing, the critical objective being safety. Data on the growth and survival rates of important microorganisms under different storage conditions (time, temperature, atmosphere, and also pH, water activity and meat composition) are the basis of the model. The program predicts the growth characteristics under particular conditions (5).

An early and continuing important use of controlled-atmosphere storage and modified-atmosphere packaging (MAP) is for extending the life of fresh fruit. The atmosphere controls the respiration of the fruit, and therefore first the fruit ripening and then the deterioration. A recent study on sweet cherries by Jaime *et al.* (6) studied the respiration rate for different levels of temperature, oxygen and time. Because respiration involves enzymic reactions, a basic enzymic rate model (Michaelis-Menten equation) was used, relating respiration rate and oxygen level. It was found that there were two different linear relationships, above and below 10±3% oxygen, following the linear relationship:

$$1/\,R_{02} = I/V_m + K_m\,/\,V_m\,[\,O_2\,]$$

where R_{02} is the respiration rate (mL(STP)kg^{-1} h^{-1}), i.e. oxygen consumption rate at Standard Temperature and Pressure (STP), O_2 is the concentration of the oxygen in the atmosphere, and V_m and K_m are equation constants. Values for V_m and K_m obtained by linear regression for the two linear regimes (2-10% and 10-20% oxygen) for showed variation due to temperature and cultivar. Respiration activity increased with temperature following the Arrhenius relationship. The Arrhenius plots at 5%, 13% and 20.8% oxygen were non-linear, which could be related to a change in the limiting enzymic reaction because each enzyme may be affected differently by change in the temperature. This shows how a practical model for designing and testing packaging can be developed from:

- a basic scientific model
- a complex system, which can be divided into linear regimes
- variations in oxygen, temperature and time, which affect reaction rates
- variations in raw materials (in this case cultivars), which affect reaction rate constants.

This work on cherries has been extended by the same authors (7) to examine the dynamics of exchange of modified atmospheres through typical packaging films. Good agreement was found between measured time concentrations of the gases and prediction equations and so these methods could be used in the design of packaging.

Think break

In the sweet cherry study, there were three cultivars – Burlat, Sunburst and Sweetheart. Burlat had the highest respiration rate; Sunburst and Sweetheart were lower and similar. This more active metabolism of the Burlat cherries made them the most perishable of the three cultivars. The differences in respiration rates decreased with the oxygen concentration. The respiration rate was drastically reduced when oxygen concentrations were below 10%.

* List the packing and storage variables you would consider in developing modified-atmosphere storage for sweet cherries.

* If the cherries were to be distributed in large cartons for display in supermarkets, how would you control the variables in storage and distribution?

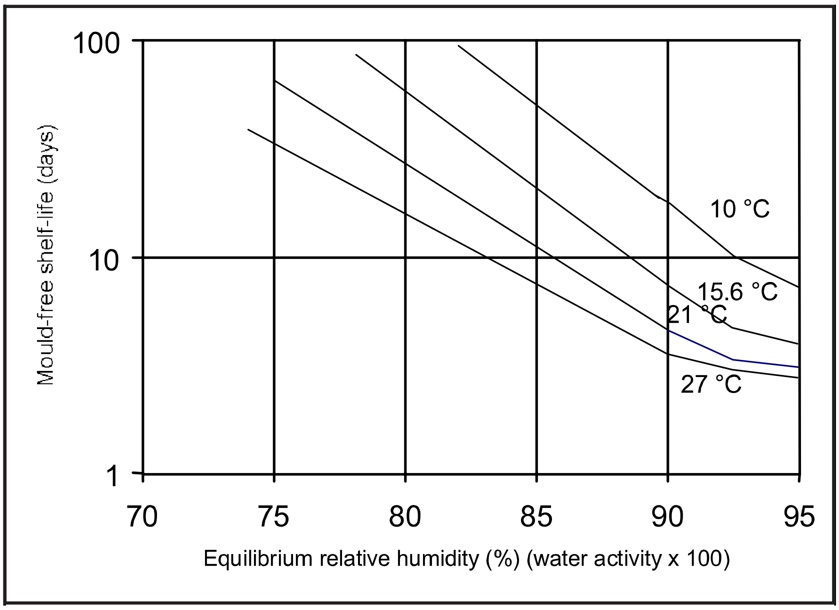
* If the cherries were in individual consumer packs, how would you select the packaging film and the storage atmosphere?

5.2.3 Water activity

Water is one of the reactants in much of food processing, and is also a significant part of all food materials. Often it is present in excess and therefore its effective concentration remains so close to constant that the relatively small changes in water concentrations encountered in food processing make no measurable difference to rates as the reaction progresses. Where water is not in excess, for example as in dried and intermediate-moisture foods, this may not be the case and the actual concentration of the water present needs to be taken into account. Water activity (a_w) is often used as a measure of the water concentration, being numerically equal to the (fractional) equilibrium relative humidity of the water over the product. A familiar example of its importance is with microorganisms, where water activity can have a major influence on growth. An instance of this is shown in Fig. 5.2, showing the effect of temperature (a sensitivity around 12%/°C) and water activity on the mould-free shelf-life of bakery products, from the work of Cauvain & Seiler (8).

Cakes can be considered as intermediate-moisture foods, with water activities between 0.65 and 0.90. At the lower levels, some yeasts can grow, and, as the water activity rises, moulds and other yeasts, and above 0.90 bacteria, also grow.

Moulds grow on the surface of cakes and therefore it is the water vapour in the surrounding atmosphere, equilibrium relative humidity (ERH), that is used as the abscissa in Fig. 5.2. The logarithm of the mould-free shelf-life was found to have a linear relationship with ERH within the range 74-90%, so this graph, or equations derived from it, can be used in shelf-life predictions. As well as controlling the water in the atmosphere surrounding the cake, the water activity can be modified by formulation changes. Such techniques can be used for intermediate-moisture foods, and many stable ambient products have been designed on the basis of understanding the effects of water activity levels on growth of possible spoilage microorganisms.



Adapted from Cauvain & Seiler (7)

Fig. 5.2. Mould-free shelf-life of cakes: effect of temperatures and humidity

Water activity also has a marked effect on chemical reactions such as non-enzymic browning and fat oxidation. In dried foods at low water activity, the fat oxidation and associated bleaching reactions are often predominant in spoilage; then they decrease in importance as the water activity increases. Browning reactions then increase, followed by growth of osmotic yeasts, then other microorganisms (9). The reaction rate effects of such water activity changes can be explored experimentally, optimum water activity ranges identified for different products, and predictive models developed.

Think break

Tomato powder, commonly used in dried soups, mixes and meals, can deteriorate on storage, losing the red colour, turning brown, developing a "hay" odour, and becoming lumpy. These changes are related to the water activity (a_w) of the powder, bleaching of the red colour and associated off-odours occurring at low a_w, and non-enzymic browning occurring at higher a_w. The bleaching is also related to the environmental oxygen.

- Discuss how you would determine the optimum a_w range where the bleaching and the browning were both at a minimum.
- How can this be related to the moisture content achieved during drying, and to the moisture content to be maintained during storage?
- Suggest how a packaging and storage system could be designed for this powder, which is marketed in bulk to manufacturers.

5.3 Alternative Energy Processing Conditions

Another approach to influencing the rates of processing reactions is by the use of higher energy processing conditions, other than thermal energy. Energy can impact on the foods either directly at a molecular level or through their environment. Both are possibilities – placing the food in intense irradiation or electrical fields, or under very high environmental pressures (*ca* 1000 atmospheres). Such systems offer the possibility of inducing and accelerating some of the various possible reactions in the food in differential patterns that are normally not the same as those in thermal reactions. By suitable selection of the energy source and level, desired reactions may be promoted, and undesired ones retarded. These physical processing possibilities all require quite elaborate equipment, more than for the conventional heating and cooling. But, because of the range of opportunities they offer, they have substantial attractions for research, development, and then industrial use.

The product outcomes, the relative qualities of the attributes of the resulting food products, can be quite different from those in heat processing. So opportunities for differentiation are offered. An important example, often the reaction critical to the processing, is that in reducing microorganisms. In particular, safety and storage life in some instances can be enhanced without any or much concomitant loss of other desirable attributes.

Such systems include the use of high-energy irradiation with particle or photon beams; high pressures (steady or intermittent); and high electric/magnetic fields (steady or pulsed). These newer processing methods, because of the new opportunities they offer, are the continuing subject of considerable investigation into their processing potential (1,10). Alternative heating methods for solid foods, where conventionally heating is by conduction, are also possible, such as microwave, radio-frequency, and resistance (ohmic) heating (11).

5.3.1 Irradiation

High-energy irradiation can be emitted from various sources and focused into the food. Sources permitted for use in processing of specified foods include gamma (γ) rays from radioactive isotopes (often Cobalt- 60), machine-generated electron beams from linear accelerators, and X-rays. The major factors determining the impact potential of the irradiation are the energy level and the flux from the source, and the time of exposure. From sources such as radioactive isotopes, the energy level is determined by the nature of the isotope – cobalt 60 has a mean energy level of 1.25 MeV; and the quantity of energy by the source strength – for example, it can be about 50,000 Curies (Ci) for fruit and vegetable disinfection and above 600,00 Ci for meat and poultry pasteurisation depending on the design of the irradiation plant. Electron beam impact is influenced by the flux of electrons and by their kinetic energies (limited by regulation to 10 MeV), and X-ray beams also by quantity and energy levels (limited to 5 MeV). The energy levels available for use are restricted to those below the potential for inducing radioactivity in the target foods, or producing unwanted chemical changes. High-energy electron beams, with their associated charge have limited penetrating power and are suitable only for foods not more than 5-10 cm thick.

The measure of the reaction-creating potential is in energy absorbed in units of Grays. The Gray (Gy) is fundamentally defined by heating capacity and measured in Joules per unit mass. One Gray is 1 Joule per kilogram, which produces very little heating; but, because of the high levels of the energy involved, the reactive impact is very much greater than that of the low-energy-level thermal radiation of the same heating power. There is a limit on the dosage; a maximum currently set by Codex Alimentarius is 10,000 Grays (10 kGy), although there could be changes in the near future.

High-energy-level irradiation in sufficient quantity destroys microorganisms. It inactivates microorganisms by damaging critical elements in the cell, such as in the genetic material. There is a loss of ability to reproduce, preventing multiplication and leading also to random termination of many cell functions (12). The extent of inhibition of growth is related to the absorbed dose in Grays by what amounts to a first order “death”/dosage relationship (“death” in this sense being assessed by absence of potential for growth). The relationship between dosage and bacterial population is not completely linear; there is an initial slower rate, a shoulder, and then a survival portion, or tail, above approximately 6 kGy. But for many practical purposes the irradiation measured in Grays can be related to a decimal reduction dose for organisms.

Therefore, it can be taken that:

$$\log (N_1 / N_0) = D_{10} / D_i$$

where D_i is the applied radiation dose, D_{10} the decimal reduction dose, N_0 the initial bacterial number, and N_1 the expected bacterial number after the irradiation.

The decimal reduction dose can be affected by the types of microorganism – spore forming and non-spore forming. The effect of the state – spores and vegetative cells – are illustrated in Table 5.II adapted from Barbosa-Cánovas *et al.* (1). Bacterial spores are more resistant to radiation than vegetative cells.

TABLE 5.II
Irradiation decimal reduction doses for microorganisms

Pathogenic bacteria	**D_{10} (kGy)**
Bacillus cereus (vegetative)	0.02 – 0.58
(spores)	1.25 – 4.0
Campylobacter	0.24 – 0.31
Clostridium botulinum	1.40 – 2.60
Escherichia coli (non-spore former)	0.23 – 0.45
Salmonella (non-spore former)	0.37 – 0.80
Spoilage bacteria	
Clostridium sporogenes	2.30 – 10.90
Micrococcus radiodurans	12.70 – 14.10
Pseudomonas putida	0.08 – 0.11
Streptococcus faecalis	0.65 – 0.70

Various sources (1,12)

An important point to note in Table 5.II is that some of the spoilage organisms require much higher reduction dosages than the pathogenic bacteria; for example, *Clostridium botulinum* requires 1.4–2.60 kGy, and *Clostridium sporogenes,* 2.30–10.90 kGy. The total range of energy susceptibilities is more compact than for thermal processing, but is still quite substantial. It is related both to the particular organisms and to whether spores can be formed, the spores being roughly one-tenth as sensitive as the vegetative cells.

Perhaps more by association from its success in canning than through any profound logic, a 12D reduction has been adopted as providing "commercial" sterilisation. So, for instance, achieving 12D values for *Clostridium botulinum* in meat systems would require dosages of 38-48 kGy according to Molins (13). Lower levels of reduction can provide pasteurisation to meet various risk-reducing, growth-inhibiting or storage-life criteria. For irradiation, there has been much consideration of the types of food and the composition in setting the standards for treatment. Indeed, in the eyes of many people, irradiation should be considered only where alternative risk-reduction or preservation alternatives are not available; it is to an extent a process of last resort.

A common target level in reduction in the United States has been 5D (5 decimal reduction) cycles (12), but for spices and dried food ingredients a 3D reduction may be adequate (14). The target and corresponding process can also be set by reduction from an initial level of bacteria in the food to an acceptable level, as shown in Example 5.2 for the reduction of *Salmonella* in chicken pieces.

Example 5.2: Irradiation to reduce *Salmonella* in chicken pieces

In a line of packed boned-out chicken pieces, there was thought to be undue risk to consumers from *Salmonella* infection. So it was decided to consider reducing initial levels, some of which had been up to 10^4 cfu/g, down to an acceptable maximum of 1 cfu in 25 g, in a Cobalt-60 irradiation facility.

It is desired to estimate the irradiation time needed, and the expected throughput, from a ^{60}Co source that can deliver 500 Gy/min to the working depth in fifty 1-kg packages, simultaneously.

The required reduction ratio is from 10^4/g to 0.04/g

that is $10^4/10^{-1.4}$

$= 10^{5.4}$ implying 5.4 decimal reductions

From Table 5.II, the decimal reduction dose, D_{10}, for salmonellae is 0.8 kGy = 800 Gy.

Then 5.4 D_{10} will be reached after (5.4 x 800) / 500 = 8.6 min irradiation.

So, the expected plant throughput is around
(60/8.6) x 50 kg /h = 350 kg /h.

A full calculation would be more extensive than this – for example, taking into account particular geometrical factors, radiation, absorbtions, and the plant operation; but this simplified version provides some appreciation of the processing magnitudes involved.

The thickness of food is important because of the reduction of irradiation intensity on passage through a medium. Levels below the surface receive less dosage, generally receiving a logarithmic dosage reduction with distance of penetration. In Example 5.2, the dosage was estimated as being at the mean depth of penetration on a volumetric basis. So the outer layers would have substantially higher levels of reduction than the inner. For example, inactivation of a level of 10^6 cfu/g *Escherichia coli* O.147:H7 in ground beef (D_{10} =0.30 kGy) would theoretically require a minimum radiation dose of (6 x D_{10}) = 1.8 kGy as a critical limit. But if there is a 100-200% difference between the level of radiation absorbed by the food at the points of maximum and minimum exposure under commercial conditions, the ground beef could receive up to 5.4 kGy to ensure that the average dosage (on a volume basis) is adequate (15). The type of food, its composition, and the environmental conditions such as temperature alter the dosage needed for microbial safety. The moisture content, the presence or absence of oxygen, and the addition of processing agents such as nitrites in meat may also affect the dosage needed.

As with heat treatment, on irradiation there are chemical reactions occurring in the food that can cause unwanted sensory changes such as colour change in meat, fat oxidation off-flavours, and texture changes in fruit and vegetables. Sometimes, there are desirable changes such as some tenderising of meat. The reaction rates of these changes with different dosages have to be considered in the search for an optimum process.

Other irradiation possibilities are intense white or ultraviolet (UV) light. Both of these can reduce microbial loads, partly by thermal and partly by photochemical action. A disadvantage is the low penetrating power of visible and UV light, so that the most useful applications are with surface contamination such as on meats, and on thin films as with packaging materials. Systematic treatment of light processing is limited, and essentially particular cases require detailed experimentation and verification of their effects in order to give reliable process operation and outcomes.

The original research on irradiation was carried out about 50 years ago, when it was seen as a major alternative processing agent with great promise. Practical problems, some physical, some psychological, have slowed development of commercial application. The required equipment is substantial in complexity and cost, and there are major precautions needed for safety, both for personnel and for product. But in recent years, greater acceptance and in particular regulatory clearances have led to increased interest, and to commercial as well as research activity (16,17).

Think break

Irradiation is an old process, which had intensive research during the 1950s and 1960s, producing shelf-stable army rations. But it has never become a general preservation method for food products.

* Discuss what factors in food manufacturing and marketing caused this non-acceptance into the food industry.

* What new factors might cause its adoption in the next 5 years?

* Can any lessons be learned for the introduction of other new preservation methods in the future?

5.3.2 Electrical and magnetic fields

It has been observed that high-intensity electrical and magnetic fields can have major impacts on biological materials. The effects are related to the nature of the materials treated, which can include foodstuffs, packaging, and contaminants such as microorganisms. A widely investigated area is the use of pulsed electric fields (PEF), employing high-voltage gradients that have the capacity for disrupting the cellular structure and physiology, so preventing or slowing growth of microorganisms. Very high voltage gradients lead to complete breakdown of structures. But, under less severe conditions, useful reduction in pathogens and spoilage organisms can result and without, or with the minimum of the chemical or physical changes that cause quality loss in thermal processing (10).

The effect on the microorganisms relates to the strength of the electric fields, which are of the order of kilovolts/cm, the number of pulses to which the organisms are subjected, and the shape of the pulses. The sensitivity is also related to the specific organisms and to the phase of growth, being higher for cells in logarithmic growth and substantially lower for spores, as might be anticipated. Some empirical models have been suggested to describe the relation between electric fields and microbial inactivation. The simplest, assuming a first order reaction, was:

$$\ln(N_1/N_o) = -b_E\,(E - E_c)$$

where b_E is the regression coefficient, E is the applied electric field intensity and E_c is the critical electric field, obtained by the extrapolated value of E for 100% survival ($N_1=N_o$) or a survival ratio of one (E_c is related to the resistance of the particular bacteria to radiation), and N_1 and N_0 are the final and initial levels of bacterial counts. Several models have been suggested, some based on the sigmoid form of the survival relationship with strength of electric field instead of a linear relationship, the inclusion of number of pulses as well as the electric field, and a kinetic constant, k, that represents the steepness of the tangent to the sigmoid curve.

Inactivation kinetic models have also been developed that consider the effect of temperature in the first order kinetic relationship:

$$k = k_{E0}\, e^{E/RT}$$

where k is the survival fraction rate constant (μs^{-1}), k_{E0} is an electric-field-dependent variable rate constant (μs^{-1}), E is the activation energy (kJ/mol), R is the Universal Gas Constant and T is the temperature (K). This is only given as an indicative illustration, and more details can be found in Barbosa-Cánovas *et al.* (9). Inactivation kinetics for pathogenic bacteria in various types of food need to be studied, to give the basis for process safety specifications. But the general considerations illustrate how critical factors can be identified (18) and kinetic relationships identified and put to use in the new technologies.

At the present time, PEF applications are largely experimental. Large-scale commercial units would be costly and must be guaranteed safe for the operators, and more research on the treatment of different types of foods is needed to approach optimum outcomes.

Pulsed strong magnetic fields also have useful inhibitory effects on microorganisms and, like the electric fields, they offer real benefits in attacking the biochemistry and life aspects of undesirable microorganisms rather than broader chemical change. So they offer potential for processing, particularly for some classes of foods. The specifics, both of the processing and of the target susceptibilities, limit general treatment at the present state of understanding, but their potential, especially for selective effects on microorganisms, is leading to active interest in their investigation and development.

5.3.3 Very high pressures

In high pressure technology, foods are subjected to high hydrostatic pressure, generally in the range of 100-600 Megapascals (Mpa)/(1000-6000 atmospheres). Usually, this is at or near ambient temperature, although rises in temperature associated with the pressure increase can themselves add significantly to the overall outcome. Foods, in plastic film containers, are surrounded by water and high pressure compresses the water, which compresses the food. Moderately high pressures decrease the rate of growth and reproduction, and very high pressures cause inactivation of the microorganisms; spores are more resistant than vegetative cells. Under the high pressures, spores are encouraged to germinate to vegetative cells and the vegetative cells are then inactivated.

The high-pressure inactivation depends on pH, composition, osmotic pressure and temperature. Lowering the pH reduces the pressure necessary for inactivation. But temperature and pressure have an unusual interaction; generally, at moderate temperatures pressure has a synergistic effect, but at high temperatures increased pressure retards the inactivation. Water activity has a marked effect on inactivation. In one study, inactivation was greatest at 0.96 a_w, and did not occur below 0.91 a_w.

In several microbial studies, high-pressure inactivation with time followed first order kinetics, but in some cases there was a deviation because a small population of bacteria was not inactivated even after long periods of pressurisation (1). Knorr (19) noted that first order inactivation might occur, and in that case logarithmic-survivor curves can be expressed in D-values, but often deviations from this behaviour are obtained. There can be an initial lag phase indicating a certain time-dependent resistance, and also a tailing.

The thermodynamically derived equations relating the pressure to chemical reaction rates is analogous to the Arrhenius equation (18):

$$d\ln(k)/dp = -\Delta V^{++} / RT$$

The characteristic constant ΔV^{++} can take positive or negative values, producing a delayed or accelerated reaction rate with rising pressure.

Enzyme activity can be initially enhanced; and then, with increasing pressure, enzymes can be inactivated, but for some enzymes very high pressures may be necessary. Biochemical reactions are affected; for example, protein denaturation can occur with increasing pressure but it is different from heat denaturation. Because of the low temperatures, the fresh colour, flavour and aroma are retained, but textures can change – for example, softening of fruits and vegetable structures, and tenderisation of pre-rigor beef. There can be increased enzymic browning after pressurisation because of increased activity of polyphenol oxidase. Little loss of vitamin C has been reported in fruit products.

High-pressure technology was introduced as a commercial process in Japan in 1990, and later in Europe. In Japan, fruit products such jams, sauces and juices are marketed. Strawberry jam, for example, retains the fresh fruit flavour. A mixture of fruits, fruit juice and acids is placed in a plastic container and then subjected to high pressures of about 4000 atmospheres for 15 min. Pressurisation allows permeation of sugar solution into the fruits as well as preservation of the jam, which gives a shelf-life of about 17 months (1,20). An interesting development is into the use of high pressures in preparing surimi gels. Research is continuing into high-pressure technology, such as seeking quantitative assessment of the effects on critical organisms, such as on spores of *Clostridium botulinum* (21), and looking at the combined effects of heating (particularly heating which occurs during the pressurising process itself) and high pressures.

High-pressure technology has the advantages of using ambient or lower temperatures, independence of size and geometry of food, flavour, nutritional value and aroma being unaffected, uniform preservation, and reduction of processing times. The disadvantages are: the equipment is expensive and at present there is a limited throughput, often undesirable texture changes, and residual enzymes and sometimes bacteria can cause changes in storage.

Think break

New processing technologies are often expensive and cannot at present be considered as replacement for current heat processes. Therefore, their use could be in developing new products or improving old products, which could carry increased costs.

* Generate ideas for new fruit products aseptically packed, using PEF, that could be accepted in your market.

* Generate ideas for new “gel” products that could be developed using high pressure technology

* Do you think your company would consider adopting these processes – PEF or high pressure. List the reasons for not accepting and for accepting, for both processing technologies.

5.4 Combined Process Technology and the Total Process

When developing new processes and products or improving present ones, it is necessary to firstly consider the total process from the raw materials to the final consumer eating the food, and secondly identify the possible processing variables. The aim is to present to the consumer the optimum product with the product attributes that they need and want. In the past, the emphasis was often on the manufacturing process, with the distribution considered separately; the development effort was concentrated on safety, and the major processing variables, usually time and temperature, were adjusted to ensure this safety. Today, because of the needs of the consumer for “fresh”, nutritionally suitable, and convenient foods, there needs to be a wider, technologically based development process. Not only the critical safety attribute is emphasised but also the important product attributes, which will not cause illness but will cause product failure. All the critical points in the total process need to be identified. Today, the Hazard Analysis and Critical Control Points (HACCP) system focuses the process variables and their effects on the rates of the critical and important reactions.

5.4.1 Hurdle technology

The additive effect of different processing variables on reactions already demonstrated in thermal operations, opens up the possibility of using different levels of several processing variables in parallel or in sequence to reach an overall product outcome. Combining different processing variables can offer significant advantages, both in control of attribute change and also in control of operations, for the efficient utilisation of equipment, production and storage. This approach has been looked at quite extensively in the literature, and given a title, *hurdle technology* (22). Hurdle technology originally emphasised safety and preservation but it can be extended to cover other product attributes.

For example, with acids in foods, pH may not be the only critical factor. The growth of bacteria, and importantly also moulds and yeasts, is influenced not only by pH but also, for many organic acids, by the fraction of the acid that is undissociated, for example with acetic acid. Equations have been derived whereby the incorporation of concentration factors such as undissociated acid as well as pH, salt and specific carbohydrates, can be used to calculate an empirical factor. If this factor exceeds a certain level then microbial spoilage should not be expected. This is substantially arbitrary, but indicates how component concentrations can be added to give a sum that indicates enhanced ability to stop or retard growth of microorganisms (23).

Hurdle technology recognises that most food preservation processes make use of more than one process variable; the levels of these process variables combine to constitute barriers or hurdles to the reactions of deterioration and decay. In most processes, one or two hurdles are applied, and then further minor or additional ones may be added to reach the required outcome (1).

As originally conceived, hurdle technology combined different preservation variables, hurdles, in order to achieve preservation effects using mild processing (24,25). These hurdles are the processing variables described throughout this book: temperature, times, concentrations of food components, natural and added processing agents, water activity, atmosphere (particularly the oxygen concentration), and, where applicable, the less usual variables such as irradiation, high pressure and pulsed electrical fields. Fifty or more different hurdles have been identified in food preservation, which can be grouped as physical, physicochemical, and microbially based (26). These variables are involved in control of raw materials/ingredients, manufacturing controls, distribution, retailing and consumer use. By combining them either at the same time or in sequence, lower levels of these processing variables can be used, and better control of product attributes achieved. It can be thought of as total processing, taking every aspect into account.

Hurdle technology is being considered for improving many current processes. For example, in UHT processing of milk, a conventional continuous flow sterilisation (CFS) process is designed to effect a 9D reduction in the concentration of thermophilic spores of normal heat resistance. However, such a process may be inadequate because of the presence of spores of greater than normal heat resistance. As has been described earlier in the book, the process is constrained at the minimal limit by the need to assure safety, and at the upper limit by the minimal changes in the sensory and nutritional attributes of the product. The milk can be made safe against these higher resistant bacteria, but the increased heat treatment will downgrade the sensory attributes. It is suggested that there is the potential use of sporicidal or sporostatic agents, such as sorbic acid, nisin, lactoferrin, phosphate and even spice and essential oils to reduce the need for such high-temperature conditions (27).

5.4.2 Sous vide

There have been various applications, for example in preserving fruits and vegetables, and in ready-to-use meals. One of the more extensive, and one that has received a good deal of industrial attention, especially in Continental Europe, goes under the French name *sous vide,* meaning literally under vacuum. This is a heat process, with temperature, time and vacuum being the three main process variables; and organic acids, pH, salt, nitrites, spices, and herbs, being secondary variables. In this, the raw materials of a food are either partially cooked, or uncooked, sealed into a plastic bag from which air is excluded so far as practicable, and then given a partial cook sufficient to give target vegetative cells something like a 6 D reduction dose. Although the extent of this cooking varies, a typical specification is for the centre to be brought to 70 °C for some minutes. Some heating specifications, quoted by Creed (28), are shown in Table 5.III.

TABLE 5.III
Some heat treatments for *sous vide* products

Treatment	Chilled life	Target organism
70 °C for 40 min	6 days	*Enterococcus faecalis*
70 °C for 100 min	21 days	
70 °C for 1000 min	42 days	
70 °C for 2 min	5 days	*Listeria monocytogenes*
80 °C for 26 min	8 days	*Clostridium botulinum* (type E)
90 °C for 4.5 min	8 days	

Adapted from Creed (28)

Thereafter, the food is chilled quickly in its package, stored and distributed for periods of up to several weeks before being finally cooked again and consumed. The distribution variables are packaging, modified atmosphere, temperature and water activity. The manufacturing and distribution specification depends on the food and the target organisms. The critical product requirement is to avoid spoilage or any danger from microorganisms. Heating temperatures are lower, and process times are longer than under conventional conditions.

The chilled life of the food depends on the raw material selection and initial preparation, timings, exclusion of air, reduced water activity, and the reduced chill temperature in distribution (below 4 °C), as well as on the partial cooking and its extent. A great deal of fine detail is indicated in the total processing specification, and can be built into computer-integrated design and manufacture. Knowledge of critical and important reactions and the effect of the levels of the processing variables on their reaction rates is essential (29). Although demanding, this detail provides a great deal more constancy of steps, including ingredients, preparations and timings, than is often customary, and so the stage is set for both optimum and very consistent product quality. It does illustrate the potential of fully and tightly organised processing, throughout the total process from raw materials to consumers. The consumers must also use the correct heating and serving conditions to achieve the designed final product quality.

The notable aspect of this form of processing is the claim to preserve, to a very considerable extent, the most desirable attributes of the fresh foods. It can be regarded as a sophisticated cook-chill process. The resulting products are claimed to compete in quality with, and be suitable for, *haute cuisine* (30), although this is not always recognised by the foodservice customers and the final consumers. Chefs would seldom agree that any processed product could reach the same level as their professional preparation and cooking, and consumers would tend to agree with them. So perhaps the most substantial outlet for these *sous vide* products can be as high-quality foodservice products, and these can be marketed for their convenience to the superior foodservice outlet preparing large numbers of quality meals. As "part" meals, they could be sold to chefs who would combine them in their own recipes. The consumer buying chilled meals in the supermarket will not want to meet the greater cost and therefore will not pay a higher price unless they are convinced that the product attributes are outstanding as compared with the more routine cook/chill products.

There have been some rather conspicuous company failures in *sous vide* products by others seeking to follow in the footsteps of the successful French products. Some causes of these failures have been:

- lack of knowledge in controlling the processing of a variety of products
- poor distribution control of temperatures and efficiency of delivery
- lack of adequately low temperatures in retail and foodservice chill cabinets
- poor understanding of consumer needs
- wrong assessment of costs and need for highly technical staff.

5.4.3 Total Process technology

The use of Total Process technology from the raw material producer to the consumer, and taking all steps into account for their effects on the product, offers the process designer considerable scope and flexibility. The whole range of available process steps is carefully assessed and advantage taken of the potential of each step to obtain new and better quality products. The final Total Process is chosen to minimise the adverse reactions but still satisfy the critical criteria taken overall. Hurdle technology and sous vide are examples of the Total Technology approach. Its proper implementation can offer major steps forward for the food industry.

Think break

The use of computer-aided design and integrated manufacturing has played an important part in the development of *sous vide* (29). They have combined several computer-friendly areas such as production planning and control, ingredients and formulation, predictive microbiology, heat transfer in foods, quality management and customer information.

* Identify which of these areas are computer-based in your company.

* For which areas are there data, but they are not in a computer form that is easy to access?

* For which areas does your company not have data?

* What other forms of data would be useful if you were planning hurdle technology in a Total Process?

* Can you see how your company could use computer-based hurdle technology in a Total Process?

5.5 Some Successes of Applied Reaction Technology

Reaction technology has been applied over the years in many aspects of food processing. In the earlier applications, the outcomes have often been reached well before the theory was worked through, only more recently can the explanations be seen more clearly. In recent years, there has been direct application of reaction technology in designing the new and improved processes. Also, the progress of knowledge, when coupled with the demonstrated practicality of the applications, has stimulated research and so led to much increased understanding and therefore improved application.

5.5.1 Canning

An area of conspicuous success, where the theoretical concepts have arguably been indispensable, has been in the broad field of microorganism destruction by the application of heat in canning, pasteurisation, and other thermal processes. The notion of first order bacterial and spore death has proved a most powerful tool, in industry, and in public health. Administered quite strictly, and with continued feedback from measurement and experimentation, its results have given great confidence to the industrial preservation of food. This has been of huge value, establishing the feasibility of safe mass production, with all the low-cost and wide dissemination of products that this brings. The very extended use of canning and the huge numbers of product items consumed each year bear eloquent testimony to the effectiveness of both the practicalities and the knowledge on which they are based. Both techniques and technology are under investigation and improvement all the time, leading to wider product ranges and higher quality. There would still appear to be considerable scope for improvements in product quality, and for extension to as-yet-undeveloped situations, particularly in heterogeneous foods and flexible packs. There have been innumerable publications on the subject, ranging from very practical guides, often put out by manufacturers of food or food equipment, to many scientific papers and books. A recent and quite comprehensive account is that by Holdsworth (31) and includes extensive tables of the kinetic factors that have been considered in this book. Heat transfer theory is used to predict temperatures in the food, and thence the rates of reactions that, integrated with time, predict product outcomes.

5.5.2 Continuous processing

Much of food manufacturing is what is called “batch” processing. This means that the raw materials are assembled, the process is started and all of the elements, subject to considerations such as good mixing, progress uniformly in time to reach the finished product. However, another possible mode is that of continuous processing; the common example is a fluid or a paste flowing through a standard pipe or an extruder. It might be heated, in which case reactions are initiated, and then cooled to terminate them. As the elements of the food move along the pipe, so the reactions occur. The product emerges at the tail of the pipe. In effect, time, sometimes termed space-time, extends along the pipe from zero at entering to total reaction time on emergence, assuming that conditions for reaction occur only in the pipe.

In continuous processing, there can be considerable economies in the space needed for a given production rate; product quality can be more uniform and control easier. But there are rigorous demands on the process understanding and instrumentation; the capital costs are often high.

Continuous processes encountered in food manufacture are largely confined to liquids passing heat exchangers, and pastes and doughs passing through extruders. A notable example is the heat treatment of milk, pasteurisation (31). Pasteurisation has extended over a whole range of liquid products, often followed by aseptic packaging. Continuous extruders are widely used to make snack foods and confectionery, and sometimes bread. Another important continuous process is the freezing of free-flow vegetables such as peas, beans, corn and small fruits.

There are also hybrids, such as continuous sterilisers for cans and pouches, and continuous freezers for fish, meat carcasses and meat in cartons. The units are in a sense batches, in cans, packets, pouches, carcasses, but they are moved through the processing region in a controlled progressing stream. As processing line throughputs increase, so continuous operation becomes more attractive.

Analysis of the process is basically similar to that in batches, if time is thought of as “space time”. There are detailed treatments in reaction engineering books, but considerably simplified in foods by almost always being able to ignore heats of reaction.

Think break

Select a continuous food processing operation with which you are familiar, and a suitable book describing detail of the process (for example canning and Holdsworth (31) or milk pasteurisation and Kessler (32)).

* List the ways in which residence times and temperatures, and residence time distributions, affect both the actual mean extent of processing and also any regulatory standards with which the product must comply.

* How would you proceed to improve quality if spread of residence time distribution was found to be a major quality problem?

5.5.3 Meat freezing

Reaction technology has also provided a powerful tool to the meat industry when examining in detail apparent processing advances, particularly on the mechanical engineering of chilling and handling. With the development of more intensive refrigeration, much quicker chilling techniques became attractive in part from reduced holding times and costs, and in part from improvements in surface quality because speedier lowering of temperatures afforded less opportunity for bacteria to grow. However, feedback from customers indicated increasing dissatisfaction with tenderness of lamb carcasses that had been frozen in this way.

Physical testing of the force required to shear muscle pieces, under various cooling temperature regimes, then substantiated this toughening. The shear force required was related to the rapid lowering of temperatures. Reactions following the death of the animal were substantially slowed, as were manifestations such as slowing of *rigor mortis* and the fall in the pH, and this was found to lead to decreased tenderness. So regimes had to be devised for slower cooling with control of the maximum rate. Although the temperature/time specifications were arrived at by trial, research then quantitatively related them to the kinetics of various reactions in the *rigor mortis* development in the meat. Thus the chilling and freezing process conditions to provide acceptable tenderness in the final meat could be worked out on a systematic basis.

The knowledge base for this application was muscle physiology, and the conversion of muscle into meat. It involved understanding of *rigor mortis*, of muscular contraction, and of the breaking down of the muscle proteins and the consequent impact on the tenderness/toughness of the meat. As metabolic processes wind down, muscle moves towards the new equilibria in “meat”, with changes to pH, colour, and water-holding capacity through many parallel and sequential reactions. Such reaction processes can be modified by changes in the temperatures, which have practical impacts on muscle proteins, on pH, on bacterial growth, and on meat pigmentation, juiciness, and tenderness. Some of these impacts are desirable and some undesirable.

Knowledge of the detail of some of these reactions (33) has promoted quantitative descriptions. For example, once *rigor mortis* is complete (pH has reached the equilibrium level of about 5.9), tenderising of the muscle begins at reaction rates that have an activation energy of about 60 kJ/mol. So there can be an immediate trade-off calculated between holding times before freezing, rates of tenderising and of bacterial growth, and storage temperature regimes. Other significant factors to be taken into account are water-holding capacity, colour and colour stability. As the details are becoming better known and the knowledge gaps filled, it is increasingly practicable to design processing regimes tailored to reach specific goals for meats for target markets.

5.5.4 New ingredients from milk

Milk contains a rich diversity of protein constituents, and these have been found to possess different functional properties that make them attractive, as well as nutritious, ingredients in manufactured foods. Therefore, attention has been directed to the separation of these constituents, especially from whey, which was formerly almost a waste product from cheese manufacture but now is regarded as of major value. Some of the separation can be effected by physical means, such as membrane filtration, but use is also made of the chemical properties of the different proteins, such as substantially different activation energies and rates of denaturation (33). Heating under different thermal regimes has been employed for some time, producing, for example, “high heat” and “low heat” dried milk powders, each with different functional properties and so fitted for different end uses. This has been further developed in the production of whey protein powders of differing properties, more specific in their chemical make-up and tailored more precisely to customers’ requirements (34). Accounts of some of the detail can be found in Kessler (32), in Lewis & Heppell (35), and in publications of the International Dairy Federation.

5.5.5 Fresher fruit for the consumer

From observations on the rates of respiration of fruit after picking, first recorded systematically in the industrial context with apples, ideas have been generated on possibilities for control of ripening, and thus of the keeping time of the fruit. Again, temperature is a major variable, and its combination with atmospheric manipulation has led to quite dramatic extensions of the storage life of fruit. Similar combinations of packaging, atmosphere, and temperature can also be extended to vegetables.

The reaction rates follow the standard processing equations. Practical manipulation is limited by the fundamental rates of the reactions and by the economics of working at the industrial level. As with so many natural raw materials, the rates are related not only to the type of fruit but also to the individual varieties. Quite extensive exploration of the detail has been carried out for example on sweet cherries (6), in order to design processes. Once the parameters have been determined, the desired store or package atmospheres and temperatures can be prescribed. This includes prescription of the permeability of the packing material both to the outside atmosphere and to the gases formed inside the pack, as respiration and deterioration are dynamic and not static processes. Gaseous components can move across the barriers, at rates dependent on the nature of the packaging material, such as permeability and thickness and the partial pressures of the gaseous components on the two sides.

5.5.6 Food ingredients modification

For some major food ingredients, chemical reactions have long been used to modify their properties and make them more adaptable and useful. Fats and starches are major food components; a very wide range of reactions has been investigated to change their characteristics, and many have been applied industrially. The modification processes themselves are generally straightforward chemical reactions, and are described in texts such as Hui (36) for oils and fats, and van Beynum & Roels (37) for starches.

Because these start out by being novel applications in food, and their products have not been through the historical trials (and errors) of historical food selection, a major constraint must be safety in use. This is hard enough to determine for the shorter terms of days and months, let alone the lifetimes and generations that are implied in food consumption. Major problems for food products include demands on purity of ingredients, and on manufacturing practice, which must be specified and known at more demanding levels than for many other industrial processes. However, applications as in modified starches, and hydrogenated and interesterified fats, have found very widespread application because they bring such useful properties. Their manufacture lies somewhere between the chemical and the food industries, just as the technologies, though basically as has been described here, move beyond what has been briefly discussed and towards the more ambitious treatments of the chemical process industries.

Think break

Select a recently introduced novel processed ingredient (it might be a new fat, modified starch, carbohydrate gum, refined protein) and list the raw materials and the reactions required for its production. Try to find out any particular problems that were encountered in its development and introduction. Classify the major difficulties encountered as technical, legal, health, safety, commercial, consumer acceptability.

5.5.7 Storage lives

A successful and widely used food application of reaction technology has been in shelf and storage life prediction and extension. Initially, straightforward zero order, constant rate assumptions, coupled with exponential (Arrhenius or other more or less equivalent) handling of temperature effects, proved very powerful. It is useful for predicting the time that products can be held under particular temperatures and still retain necessary qualities. It is necessary for covering the conditions needed to achieve some mandated storage life, as in product life dating (38).

5.5.8 Packaging

In the context of processing, and assuming that the package is sufficient to prevent access of any organisms such as bacteria, this can be treated as an extension of controlled atmospheres to the extent that the packaging controls and modifies concentrations of potential reactants around the food itself.

The package ranges from the almost totally impermeable and inert can to plastic films of variable permeability, both generally and also to specific constituents such as reactive gases and water vapour. Gases can move in either direction, in or out of the package, increasing or decreasing their concentrations at the food interfaces depending on their partial pressure gradients. Rates of transmission depend on permeabilities and thicknesses of the packaging and on the partial pressure differential. The situation can be complicated by the reactions of the food, which can both absorb and also generate gases. These gases sometimes promote and sometimes inhibit reactions. For example, within the package, lowered oxygen partial pressure can be used to reduce oxidation, and increased carbon dioxide to reduce bacterial growth. The actual access of the gases to the reacting surfaces can be predicted from the physical situation governing concentrations at the gas/solid interfaces using the standard equations of unit operations. From these concentrations, reaction technology has been used in the usual way to predict rates and extents of the reactions. It is also used in combination with package and film selection to design packaging, to predict shelf lives, and to select conditions of storage, in particular temperature, to meet particular needs (39).

Think break

Select a packaged food produced by your organisation or familiar to you (possible choices might be a packet of cheese slices, or of fresh vegetable pieces), and list all the functions of the packaging. From these functions identify the ones that affect the rates of the reactions in the food. Find out as much detail as you can of the relationship between the package (choice of material, thickness, strength and so on) and the rates of the reactions.

Focus any gaps in your knowledge that need to be explored to fully specify an optimum package for that food product.

How might you find the knowledge that you need to achieve optimum storage life?

5.6 Practicalities

Looking across the broader range of processing also exposes some of the practicalities of process measurement and control that arise and which are related to the reactions in the product.

5.6.1 Quantitative product attribute measurement

So far, most of the discussion, in particular the illustrative quantitative examples, has been related to “concentrations” of product attributes, measured in physical terms, in chemical concentrations and in microbial numbers. In fact “scientific” technology is only possible if quantitative measurements can be made, its quality depending on the quality of the measurements; so in part the history of technology is the history of instrumentation. In recent times, this growth in instrumentation and its application in the food industry has been rapid, and even intractable areas such as bacterial concentrations are opening to machine measurement. However, because food is for people, there always remains one ultimate sanction, that of customer approval, and of gradations of this in assessing attributes that can be particularised in taste, such as sweetness, bitterness, and in other aspects of flavour, texture and appearance.

Part of the impetus for the developments in sensory testing arises from practicability and cost. Another aspect is more fundamental in that the sum of personal assessment of sensory attributes adds up to market judgement. Purchase choice is based strongly on personal sensory assessment of the product. So a very significant development has been the "quantification" of sensory attributes and their relation to processing and its dynamics. Sensory attribute measurement by a trained sensory panel has the accuracy needed for use in reaction kinetics (40). The correlation between sensory measurements and physical measurements has been important, which leads to simpler and cheaper quality measurement (41).

But consumer acceptability of the total product can also give quantitative measurement, as shown in Example 5.3 (42).

Example 5.3: Shelf-life of a coleslaw mix

In studying the effects of temperature on the acceptability of coleslaw, Wilkinson (42) had a panel of 20 consumers comparing acceptability of the stored samples against a reference sample, which was freshly made coleslaw. The scores used were, reference = 9, acceptable = 5 and extremely unacceptable = 1. Scores of 5-9 indicated samples that were still acceptable for the market, scores of 1-4 indicated scores that were less than acceptable. The panel tested colour, appearance, aroma, texture, flavour, and overall acceptability. The reference sample was taken as 100% acceptable and the stored sample scores were then expressed as percentages of this, to give % acceptabilities. Internal and cross testing established the consistency and reliability of their assessments so that the scale intervals behaved equally and linearly. So the panel results could be used to make relative judgements on the qualities of a range of products.

This was done with a coleslaw product with the following average results for two replicate tests, after storage at various temperatures.

Contd..

Example 5.3 (contd)

2 °C

Storage time (days)	3	7	10	16
% acceptability	95,91	82,78	71,68	54,50

6 °C

Storage time (days)	3	7	10
% acceptability	86,86	69,64	56,51

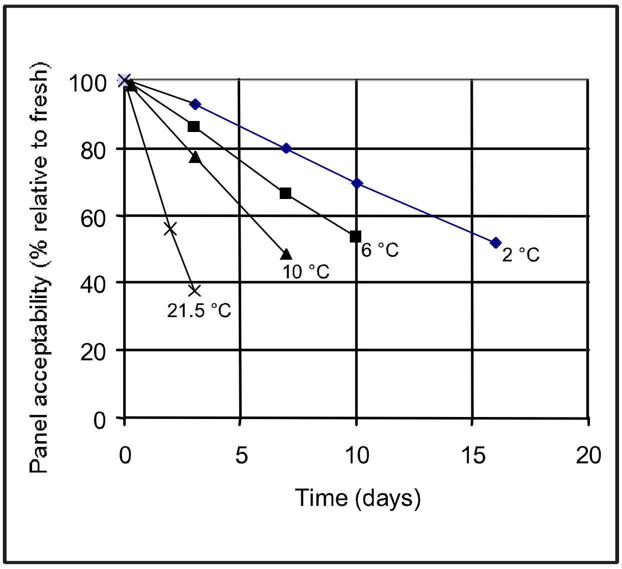
10 °C

Storage time (days)	3	7
% acceptability	80,75	50,47

21.5 °C

Storage time (days)	2	3
% acceptability	60,52	40,35

Plotting these results as shown in Fig. 5.3 displayed consistent zero order behaviour for the acceptability level as judged by the panel. Further, the Arrhenius plot gave a good straight line and a value of the activation energy of 64.7 kJ/mol and a frequency factor of 6.82 x 10 day^{-1}. This knowledge was then used in preparation, marketing and storage of the products.



Adapted from Wilkinson (42)

Fig. 5.3. Acceptability of coleslaw as a function of time, at different temperatures

Example 5.3 demonstrates that acceptability of quality attributes and overall acceptability can be found to behave in a systematic fashion, just as do other measurable attributes such as concentrations of constituents or microorganisms, and physical measurements such as colour. On the basis of such measurements, the shelf-life to some cut-off point on the scale (one judged by the panel as representing the lowest fully acceptable quality), at actual holding temperatures can be predicted with some confidence. Alternatively, a storage programme could be planned to meet a desired storage life within the range of acceptance for this product. Or again, selection and handling of the raw materials, and the various processing steps, could be re-examined to see whether they could be re-set to give longer storage lives if this were thought to be important and feasible. Use-by dates could be supplied to retailers, printed on packets, and incorporated into the planning schedules for this short-life product.

Think break

Your local restaurant trade has asked for a line of high-quality fresh prepared vegetables, which would maintain this quality for at least one week. List the process steps you would need to introduce to set up such products from growers to restaurant. Identify the critical control points and the control procedures associated, to meet this request. What are the important reactions in the process that could affect the quality of the vegetables?

5.6.2 Temperature control

One of the practical outcomes of the reaction technology equations is that, because they show how the outcomes of processing vary with temperature, they also show quantitatively the sensitivity of these outcomes to temperature changes. Conversely, they display how closely temperature has to be controlled to maintain a particular level or band of quality. This in turn indicates the demands on temperature controllers and hence the precision and reproducibility demanded of thermometric elements (thermometers). For instance, if the reaction has a sensitivity of 25%/°C, a thermometer accurate only to 1 °C allows a possible 25% shift in quantitative outcome, and this could well be outside the specifications demanded in many circumstances. Therefore, instruments and controllers need to be considered carefully in regard to the precision of their action, and in turn related to the process technology details and the product quality required.

5.6.3 Measurement of process extent

In quite a number of industrial processing situations, it is difficult, and sometimes impossible, to make measurements on the primary critical attributes as they change during the processing to the degree of precision required for proper control. For example, in canning sterilisation, where there is a nominal 10^{12} ratio between the initial and final bacterial spore counts, and the final count therefore is equivalent to 1 viable measurable spore in perhaps 10^{9} cans, there is no practical way by which this end condition can be directly measured. Imagine conducting spore counts on a thousand cans, let alone a thousand million. The outcome of a sterilising process can be inferred from temperature records through calculations, as has been seen. But it would be very helpful if there were some accessible single measurement that could be taken and which would have direct and unequivocal correspondence to the final bacterial state but without having to take bacteriological measurements or estimates.

As has also been seen, there are chemical changes in the product, which proceed in parallel with the bacterial sterilisation and which may be measurable. But if such inherent reactions are not convenient, then selected cans could be "spiked" with chemicals, which would "piggy-back" with the critical bacterial reaction and would themselves change in a well-behaved manner that can readily be measured. There have been extensive published discussions of these problems, and reviews (43).

The fundamental problem is: what correspondence is there between such a chemical reaction and the bacterial death; indeed, between any two parallel systems of different reactions constrained to follow identical temperature histories?

Reflection on the kinetics (Theory 5.1) shows that there will be direct correspondence if, and only if, the activation energies of the parallel reactions are identical. If they are different, then the degree of correspondence will depend on the temperature path and therefore can only be known if the temperature path itself is also known.

Theory 5.1: Integration of parallel reactions – analogues

Taking two first-order reactions:

$$dC_A / f(C)_A = - k_A \, dt \qquad dC_B / f(C_B) = - k_B \, dt$$

and so, on dividing, $\{dC_A / f(C)_A\}/\{dC_B / f(C)_B\} = - k_A / k_B$

The LHS includes only initial and terminal compositions C_{A0}, C_A, C_{B0}, C_B and is independent of temperature if k_A and k_B are both constant, or if their ratio is constant and independent of temperature.

Since from the Arrhenius equation,

$$k_A/k_B = A_A/A_B \exp\{(E_B-E_A)/RT\},$$

this can only be independent of T,

$$\text{if } (E_B-E_A) = 0,$$

that is, if the activation energies of the two reactions are equal.

In fact, the potential for altering relative process outcomes in different components by manipulation of temperatures during processing depends on such variation. If all temperature paths led to identical relative outcomes for all constituents, then choosing different temperature paths would not affect the outcomes. That this is not true is shown from industry experience, generally, in Theory 5.1, and in specific instances by Example 5.4 and by Fig. 4.7.

These problems can perhaps best be illustrated by a simple example, using a process with two constant temperature steps, in Example 5.4. More complicated processes will compound the problems.

Example 5.4: Parallel reactions: sterilisation and thermal inactivation of trypsin

Thermal inactivation of trypsin, a first order process, has been advocated as a model for first-order, high-temperature, thermal processes for sterilisation (destruction of 10^{12} thermophilic spores), where full experimental measurements covering the thermophilic spores are not possible. A suggestion has been to use the inactivation of the enzyme trypsin as an analogue to be followed, with the idea that this can be related to the sterilisation process.

If the equation for the rate constant of inactivation of trypsin is:

$$k = 8 \times 10^{9} \exp(- 1.01 \times 10^{9}/T) \text{ min}^{-1}$$

and for the sterilisation of typical thermophilic spores is:

$$k = 1.2 \times 10^{42} \exp(-3.73 \times 10^{4} /T) \text{ min}^{-1}$$

Determine the total changes (∇_{spores}, $\nabla_{trypsin}$) for two heat processes, each containing two constant temperature steps in which:

(a) 2.0 min at 116 °C is followed by 1.5 min at 123 °C
(b) 3.6 min at 116 °C is followed by 0.5 min at 123 °C

From the rate constant equations:

for spores, $k_{116} = 2.73 \text{ min}^{-1}$ and $k_{123} = 14.86 \text{ min}^{-1}$
for trypsin, $k_{116} = 0.042 \text{ min}^{-1}$ and $k_{123} = 0.067 \text{ min}^{-1}$

and so for (a) $\nabla_{spores} = (2.0 \times 2.73) + (1.5 \times 14.86) = 27.8$ (= 12.1 D)
$\nabla_{trypsin} = (2.0 \times 0.042) + (1.5 \times 0.067) = 0.185$ (= 0.08 D)
and for (b) $\nabla_{spores} = (3.6 \times 2.73) + (0.5 \times 14.86) = 17.3$ (= 7.5 D)
$\nabla_{trypsin} = (3.6 \times 0.042) + (0.5 \times 0.067) = 0.185$ (= 0.08 D)

Contd..

Example 5.4 (contd)

These results demonstrate clearly the problems of trying to predict from the integrated trypsin inhibition of 0.08D in each case, the integrated results for the spores, 12D in one case and less than 8D in the other. Neither of the processes exemplified was at all extreme. Choosing more extreme cases will lead to more dramatic discrepancies.

Because of the practical importance of being able to conveniently monitor industrial reactions in foods, a great deal of ingenuity and numerous patents for analogue systems have emerged over the years. Chemical, electrical, and physical systems, including enzymic reactions, electrodeposition, and diffusion, with measurements by weighing, densitometers, colour changes, voltages, currents and spectral absorption, have all been advocated. The critical issue, apart from reproducibility and adequate accuracy, remains that of the activation energies, and, if in doubt about any particular application, then it is always wise to conduct your own checks. These are quite simple, although those for product storage may take quite a time.

Think break

Continuous canning presents great difficulties for recording temperatures through the process and therefore predicting the destruction of *Clostridium botulinum* in the cans. Suggest how you could seek an analogue that would enable the prediction of the extent of sterilisation accomplished in continuous canning.

5.7 Opportunities for the Future

Reaction technology applications belong not only to the past and the present, but they also offer prospects for the future growth and development of the food industry as craft skills are increasingly supplemented by systematic application of science and scientific methods, and as understanding of these methods grows.

5.7.1 More uniform product quality

Greater knowledge of the effect of process variables on reaction rates, and more exact measurements and control can lead directly to more precise product outcomes. All parts of the food should receive just that level of processing that is appropriate. This may mean uniformity, but on the other hand it may mean levels that are differentiated for different parts of the food, for instance, the crust on bakery products or on roasted meats.

5.7.2 Nutritional enhancement

Very often, nutritional value decreases on processing, as labile components such as vitamins may be destroyed in chemical reactions whose rates are increased by higher temperatures. Proteins may be denatured or broken down to peptides with diminished nutritional value. On the other hand, access to nutritionally beneficial components may be improved by heating, such as denaturation of trypsin inhibitors in beans or reduction in cyanides in cassava. In any event, knowledge of the basic components and of the reactions they can undergo can be used to design processes that will benefit consumers' nutrition.

5.7.3 Safety

Freedom from the effects of harmful components, and in particular microorganisms that can produce toxins or are pathogenic, can be ensured only by adequate knowledge of their presence and concentrations, and then the application of the necessary and controlled processing needed to reduce these to levels that are safe. To ensure this means continued improvement of processing technology, both to deal with present and known hazards and to be equipped to meet the new ones that will surely emerge, or grow in significance, in the future.

5.7.4 Better and more effective regulation

Greater understanding, and more comprehensive appreciation of the scope, reliability and power of modern simulation and prediction techniques must lead in time to more harmonious and rational conceiving, drafting and implementation of regulatory regimes. It will provide both the regulatory authorities and the industry with a much more substantial base for making decisions that are important and often far-reaching. This is already being seen in many jurisdictions. With the scientific basis and justification of the technology more clearly demonstrable, this should allow for more flexible and adaptable processing to give simultaneously safer, more nutritious, and more desirable foods, making the best use of the ingredients and processing possibilities.

5.7.5 Technological skills

Reaction-based process technology offers a comprehensive and rational basis for understanding the changes that the food industry makes to its products during their manufacture. This can be taught, and will add to staff knowledge, adaptability, confidence, and creativity. It lifts the level of understanding, moving from a craft towards a profession while still retaining and enhancing the skills to produce quality foods. It offers an attractive path to the recruits of the future, smaller in number but more advanced in education, and capable of dealing with the information revolution that the food industry, like all industries, can turn very much to its advantage through superior technology.

5.7.6 Instrumentation and automation

Processing can only be applied under full control if the changes made in product attributes can be measured, and their extent can be determined and ensured. So adequate measuring instruments, with precision and accuracy equal to or at least commensurate with the quality levels demanded by the consumer, must be available. These can be operated manually. But increasingly and desirably, this should be through automatic control equipment, regulating the process, batch by batch, line by line, item by item for today's, tomorrow's, and future production. The better the knowledge of the process, the more completely all of this can be put in place.

5.7.7 Optimisation

Getting the best value for least resource expenditure is always important. So, although trial and error can often provide good solutions, those errors can be costly and time-consuming. Perhaps more importantly, situations are continually shifting and with them the optima, and so the facility to adapt to change is central to good operation. Reaction technology from its very nature can deal with changing numbers, such as concentrations and time, and so, as technology is improved, so attainment of overall optimisation comes closer and closer.

5.7.8 An enhanced basis for food reaction technology

This book has used simplified structures and techniques for the quantitative description of the processing. More elaborate understanding and correlations already exist for parts of food processing – for example, Van Boekel and Tijskens (44) – but they have not been introduced here in part to maintain simplicity, but also because so often neither the available data nor the quality demands of the product justify added complexity. However, in the future, more extensive use of dedicated computer software, increased accumulation of practical data, experience and confidence, and better understanding of the theory will no doubt happen. Also, as the understanding of the underlying chemical changes and their mechanisms extends, this can be used to make predictions of behaviour and so of what might be industrially feasible. So there will be much extended scope for true designer foods and food processes.

5.7.9 New food products

Technology as it opens up possibilities for new, and sometimes unexpected, change can offer access to novel products. This can include both totally new products, such as the whey protein isolates, new products from new processes or new twists on old processes such as the *sous vide* lines, and improvements on old products or ingredients such as the pasteurised liquid whole egg. As both techniques and understanding improve and extend, so new possibilities will appear and new products will reach the market. Increasingly, it will be possible to design these products and production lines systematically, and the technology of the reactions as they are involved in industrial manufacture will be an essential quantitative element in such design.

5.8 References

1. Barbosa-Cánovas G.V., Pothakamury U.R., Palou E., Swanson B.G. *Nonthermal Preservation of Foods.* New York, Marcel Dekker, 1997.

2. Chen C-C., Tu Y.-Y., Chang H.-M. Thermal stability of bovine milk immunoglobulin G(IgG) and the effect of added thermal protectants on the stability. *Journal of Food Science*, 2000, 65 (2), 188-93.

3. Tijskens L.M.M., Biekman E.S.A. pH in action, in *Proceedings of the International Symposium on Applications of Modelling as an Innovative Technology in the Agri-Food-Chain.* Edited by Hertog M.L.A.T.M., Acta Horticulturae, 566, 2001.

4. Ryan-Stoneham T., Tong C.H. Degradation kinetics of chlorophyll in peas as a function of pH. *Journal of Food Science,* 2000, 65 (8), 1296-302.

5. Eburne R.C., Prentice G. Modified-atmosphere-packed ready-to-cook and ready-to eat meat products, in *Shelf Life Evaluation of Foods.* Edited by Man C.M.D., Jones A.A. London, Blackie, 1994.

6. Jaime P., Salvador R.O., Oria R. Respiration rate of sweet cherries: 'Burlat', 'Sunburst', and 'Sweetheart' cultivars. *Journal of Food Science,* 2001, 66 (1), 43-7.

7. Salvador M.L., Jaime P., Oria R. Modeling of O_2 and CO_2 exchange dynamics in modified atmosphere packaging of 'Burlat' cherries. *Journal of Food Science,* 2002, 67 (1), 231-5.

8. Cauvain S.P., Seiler D.A. *Equilibrium Relative Humidity and the Shelf Life of Cakes.* Report 150, Flour Milling and Baking Research Association, Chorleywood, 1992.

9. Jones H.P. Ambient packaged cakes, in *Shelf Life Evaluation of Foods, 2nd Edn.* Edited by Man C.M.D., Jones A.A. Gaithersburg, MD, Aspen, 2000.

10. Barbosa-Cánovas G.V., Góngor-Nieto M.M., Pothakamury U.R., Swanson B.G. *Preservation of Foods with Pulsed Electric Fields.* San Diego CA, Academic Press, 1999.

11. Ohlsson T. Minimal processing of foods with electric heating methods, in *Processing Foods: Quality Optimisation and Process Assessment.* Edited by Oliveira F.A.R., Oliveira J.C. Boca Raton, CRC Press, 1999.

12. Dickson J.S. Radiation inactivation of microorganisms, in *Food Irradiation: Principles and Applications.* Edited by Molins R.A. New York, John Wiley & Sons, 2001.

13. Molins R.A. Irradiation of meats and poultry, in *Food Irradiation: Principles and Applications.* Edited by Molins R.A. New York, John Wiley & Sons, 2001.

14. Farkas J. Radiation decontamination of spices, herbs, condiments and other ingredients, in *Food Irradiation: Principles and Applications.* Edited by Molins R.A. New York, John Wiley & Sons, 2001.

15. Molins R.A., Motarjemi Y., Kaferstein F.K. Irradiation: a critical control point in ensuring the microbiological safety of raw foods, in *Irradiation for Food Safety and Quality*. Edited by Loaharanu P., Thomas P. Lancaster, PA, Technomic, 2001.

16. Molins R.A. (Ed) *Food Irradiation: Principles and Applications.* New York, John Wiley & Sons, 2001.

17. Loaharanau P., Thomas P. *Irradiation and Food Safety and Quality*. Lancaster, PA, Technomic, 2001.

18. Wouters P.C., Alvarez I., Raso J. Critical factors determining inactivation kinetics by pulsed electric field food processing. *Trends in Food Science and Technology,* 2001, 12, 112-21.

19. Knorr D. Process assessment of high-pressure processing of foods: an overview, in *Processing Foods: Quality Optimisation and Process Assessment.* Edited by Oliveira F.A.R., Oliveira J.C. Boca Raton, CRC Press, 1999.

20. Wan X., Melton L.D. High-pressure preservation of food. *New Zealand Food Journal*, 1999, 29 (6), 220-2.

21. Sizer C.E., Balasubramaniam V.M., Ting E. Validating high-pressure processes for low-acid foods. *Food Technology,* 2002, 56 (2), 36-42.

22. Leistner S., Rödel W. The stability of intermediate moisture foods with respect to microorganisms, in *Intermediate Moisture Foods.* Edited by Davies R., Bench G.G., Parker K J. London, Applied Science, 1976.

23. Jones A.A. Ambient-stable sauces and pickles, in *Shelf-Life Evaluation of Foods, 2nd Edn.* Edited by Man C.M.D., Jones A.A. Gaithersburg, MD, Aspen, 2000.

24. Gorris L.G.M., Tauscher B. Quality and safety aspects of minimal processing technologies, in *Processing Foods: Quality Optimisation and Process Assessment.* Edited by Oliveira F.A.R., Oliveira J.C. Boca Raton, FL, CRC Press, 1999.

25. Leistner L. Minimally processed, ready-to-eat and ambient-stable meat products, in *Shelf-Life Evaluation of Foods.* Edited by Man C.M.D., Jones A.A. Gaithersburg, MD, Aspen, 2000.

26. Ghazala S., Trenholm R. Hurdle and HACCP concepts in *sous vide* and cook-chill products, in *Sous Vide and Cook-Chill Processing for the Food Industry.* Edited by Ghazala S. Gaithersburg, MD, Aspen, 1998.

27. Reid D.H., McCarthy, O.J. Development in the aseptic processing of milk and other foods: a critical review. *NZ Food Journal,* 2000, 30 (3), 98-107.

28. Creed P.G. Sensory and nutritional aspects of *sous vide* processed foods, in *Sous Vide and Cook-Chill Processing for the Food Industry.* Edited by Ghazala S. Gaithersberg, MD, Aspen, 1998.

29. Martens T., Nicolaï B. Computer-integrated manufacture of *sous vide* products: the ALMA case study, in *Sous Vide and Cook-Chill Processing for the Food Industry.* Edited by Ghazala S. Gaithersburg, MD, Aspen, 1998.

30. Ghazala S. *Sous Vide and Cook-Chill Processing for the Food Industry.* Edited by Ghazala S. Gaithersburg, MD, Aspen, 1998.

31. Holdsworth S.D. *Thermal Processing of Packaged Foods.* London, Blackie Academic, 1997.

32. Kessler H.G. *Food Engineering and Dairy Technology.* Freising, Verlag A. Kessler, 1981.

33. Young O.A., Lovatt S.J., Simmons N.J. Carcass processing: quality controls, in *Meat Science and Applications*. Edited by Hui Y.H., Nip W-K., Rogers R.W., Young O.A. New York, Marcel Dekker, 2001.

34. Huffman L.M. Processing whey protein for use as a food ingredient. *Food Technology*, 50 (2), 49-53, 1996.

35. Lewis M.J., Heppell N.J. *Continuous Thermal Processing of Foods*. Gaithersberg, MD, Aspen, 2000.

36. Hui Y.H. (Ed.) *Bailey's Industrial Oil and Fat Products. 5thEd.* New York, Wiley, Interscience, 1996.

37. van Beynum G.M.A., Roels J.A. (Eds) *Starch Conversion Technology.* New York, Dekker, 1985.

38. Man C.M.D., Jones A.A. (Eds) *Shelf-Life Evaluation of Foods. 2nd Edn.* Gaithersburg, MD, Aspen, 2000.

39. Brody A.L. Intelligent packaging improves chilled food distribution. *Food Technology*, 2001, 55 (10), 85-6.

40. Meilgaard M., Civille B.S., Carr B.T. *Sensory Evaluation Techniques.* 3rd Edition. Boca Raton, FL, CRC Press, 1999.

41. Munoz A.M. *Relating Consumer Acceptance and Laboratory Data.* (*PCN28-030097-36*). West Conshohocken, PA, American Society for Testing Materials, 1997.

42. Wilkinson B.H.P. *Extended Shelf Life of Vacuum Packed Chilled Coleslaw and Salad Products*. Internal Report, Food Technology Research Centre, Massey University, 1982.

43. Hendrickx M., Maesmans G., De Cordt S., Noronha J., Van Loey A., Tobback P. Evaluation of the integrated time-temperature effect in thermal processing of foods. *Critical Reviews of Food Science and Nutrition*, 1995, 35 (3), 231-62.

44. Van Boekel, M.A.J.S., Tijskens L.M.M. Kinetic modelling, in *Food Process Modelling.* Edited by Tijskens L.M.M., Hertog M.L.A.T.M., Nicolai B. Cambridge, Woodhead, 2001.