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The manufacture and applications of pasta as a food and as a food ingredient: a review

C. ANTOGNELLI

Introduction

It was probably during the Neolithic era, about 8000 BC, that man first began to consume cereals, or rather, products made from cereals, since it was about this time that he abandoned the nomadic way of life and settled to cultivate the land. Throughout the centuries, and today still, wheat is the most widely used cereal on account of its nutritional properties, discovered and appreciated by man during thousands of years of experience. The origin of wheat is still uncertain, but it has been mentioned in some of the earliest written documents. Wheat kernels have been found in prehistoric settlements particularly near the Swiss lakes. It seems that in 4000 BC wheat was grown in China, and it is mentioned also in the Bible (Genesis, 30, 14). It appears, therefore, that wheat is the oldest known foodstuff.

Presumably, prehistoric man consumed wheat and other cereals not as whole grains but after crushing and milling them between stones, as some primitive peoples are still doing now. By stages he learned to mix the resulting coarse flour with water and, after fire had been discovered, to cook the flour on hot stones or in water, first in 'natural' vessels and, later, in terracotta vessels. These thick gruels were eaten also in ancient Rome, where they were called 'pultes', from which is derived the Italian 'polenta' (cornflour and water). These mashes made by crushing wheat and boiling in water may be considered the forerunners of pasta, but it is not known where, when and how these primitive foods have been transformed into pasta. Traditionally this is ascribed to the Chinese, but Marco Polo on his return from Katai reported on a kind of pasta made from breadfruit flour he had seen in Java, not in China. Undoubtedly, pasta was known many centuries before, among Arabs and other people of the Mediterranean area. Stucco reliefs (a pasta roller, a small wheel to cut pasta, *etc.*) on Etruscan graves in Cerveteri indicate clearly that Etruscan people knew the technique of preparing noodles or lasagne (Greek 'laganon' or 'lasanon',

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Roman 'lagana'). Many documents full of details and anecdotes on pasta have been found through the centuries from the Graeco-Roman times to the last century, and manufacture developed mainly in the South of Italy. It was here that the climatic conditions were especially favourable for the growing of durum wheat and for the drying of pasta. The combination of moist south-east winds and dry north winds, resulting from the particular conformation of the Italian peninsula, was ideal for drying pasta. And it is the drying stage which is the most difficult operation in pasta manufacture. Today the availability of modern drying plant has made pasta manufacture independent of the environment, so that it is now effectively a worldwide activity.

Raw materials

Durum Wheat

The best quality pasta is made from semolina obtained from the variety of hard wheat known as durum. Traditionally, durum wheat would grow satisfactorily only under warm and relatively dry climatic conditions, but efforts are being made to increase the production of durum wheat and extend its cultivation to regions where it could not be grown previously, through the improvement of agronomic techniques and the genetic breeding of special cultivars. Already more than 50% of increase in production is ascribed to the genotype.

On the basis of extensive research carried out on polyploidy, on heterosis, on spontaneous and induced mutations, and on the chromosome number and structure, many researchers have obtained high yielding durum wheat varieties or hybrids, characterized by being resistant to cold climate. Since 1968 the IBP Industrie Buitoni Perugina Research Centre has selected and studied twenty-one varieties of durum wheat. So far two new cultivars, 'San Sisto' and 'Perla', have been recorded at the National Register Institute of Seed-Product Varieties, and there are plans to record some other new ones.

Characteristics peculiar to these new durum wheat varieties are resistance to cold climate, high average yield (36 cwt/acre, with peaks of 45 cwt/acre) resistance to flattening, resistance to cryptogams and good pasta-making quality. The Italian Nuclear Energy National Centre has also recorded a high-yielding durum wheat variety designated 'Creso', which has properties suitable for a cold climate. Among other cultivars should be mentioned the new variety 'Modoc' (Puri *et al.*, 1976), a hybrid D7069 × Leeds, developed by the Department of Agronomic and Range Science, California, USA, and new varieties developed in Canada (Matsuo, 1974).

Besides yield and tolerance to climatic conditions, research has also been directed towards maintaining and/or improving the particular properties of durum wheat that are required for obtaining a good semolina, suitable for pasta manufacture.

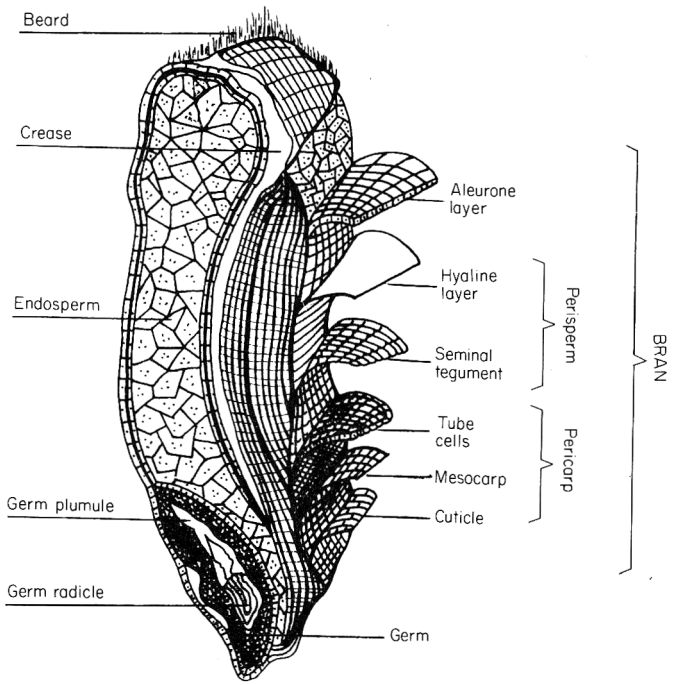

Figure 1. Endosperm related to other component parts and layers of the wheat grain.

Durum wheat is usually classified according to the following characteristics (Moldoveanu, 1974; Feillet & Abecassis, 1976; Mauze & Scotti, 1974); vitreousness (glassiness) and colour; gluten content and quality; blanching propensity; density and moisture content; endosperm/involucre ratio *; endosperm friability; ease of involucre separation.

By using special laboratory mills such as the Bühler Mahlautomat (MLU–202) or the Brabender Quadrumat Senior, in which it is possible to adjust the distances between roll surfaces, the number of passages, and the characteristics of the roll surfaces, the wheat quality can be tested and, also, the optimum processing conditions needed to obtain a high quality semolina in high yield can be determined.

Endosperm related to other component parts and layers of the wheat grain (IBP 'San Sisto' variety) is shown in Fig. 1.

Semolina

Semolina may be defined as the product originating from the wheat grain endosperm. Durum semolina is a granular product of dark yellow colour and having a vitreous (glassy) structure. It is resistant to compression, unlike soft

*involucre = outer layers of the grain.

wheat semolina which tends to crumble if pressed between the fingers. For best results the particle size should be within the fairly narrow range of 200–300 μm with less than 10% outside this range. Excess fines in the semolina lead to thermal stresses during pasta manufacture, which may cause protein denaturation. Coarse particles over 500 μm do not absorb water adequately during the kneading stage, and so may cause blotchiness in the dried pasta.

The chemical composition of semolina is similar to that of the endosperm, and may be considered under five headings: (1) Non-nitrogen compounds (starch), (2)nitrogen compounds, including gluten, (3) lipids, (4) mineral matter and (5) biodynamic elements.

1. Non-nitrogen compounds. Starch constitutes about 60–70% of semolina; it consists of granules, the structure of which. when examined microscopically, is seen to be stratified around a linear, inner nucleus known as the hilum. The diameter of these granules lies between 20 μm and 50 μm.

Starch plays a most important part in the exchanges of water taking place during the manufacturing process between semolina and its environment. Because of its high hygroscopicity starch absorbs about 36% of water at 21°C and in the presence of high relative humidity. (Katz, 1928). Gelation of starch (starch-water slurry) begins at tempeatures between 65° and 75°C. During the manufacture of pasta, starch undergoes partial hydrolysis due to α- and β-amylases which are present in the wheat grain and hence in semolina. The hydrolysis ratio increases with the number of damaged granule walls (Kent-Jones & Amos, 1967a). While starch depolymerization has a good influence on the 'sweet' taste of pasta, too high a hydrolysis ratio impairs the cooking quality. It is necessary, therefore, to control the diastatic power of semolina. Non-nitrogen compounds other than starch are present in semolina in relatively small quantities, comprising sucrose (0.2%), glucose (0.1%), fructose (0.6%), dextrins (0.2%) (Geoffrey, 1950).

2. Nitrogen compounds, gluten. Gluten was discovered by the Italian, Jacopo Bartolomeo Beccari (1682–1766), Professor of Medicine, Anatomy and Chemistry at the University of Bologna. It was he who detected the presence in flour of this substance, which he called 'Gluten', after the Latin Gluten = glue. In 1818 another Italian, Gioacchino Taddei (1792–1860), a chemist and pharmacologist in Florence, showed that gluten consisted of two components: one, soluble in ethanol, he called 'Gloiodina' (gliadin); the other, insoluble in ethanol, he called 'Zimoma' (glutenin).

Bungenberg de Jong & Klaar (1929, 1930a, b, 1931, 1932) studied the physical properties of gliadin-glutenin mixtures at different pH levels. They ascertained that these colloidal mixtures followed an additive law, except within the range of pH bounded by the isoelectric points of the two proteins. Within this pH range, gliadin is positively charged and glutenin negatively charged; this difference in electric charge causes the interaction between the two proteins. Osborne and Voorheer (cited by Kent-Jones & Amos, 1967b) detected, by a solubility method, five component proteins: glutelin, prolamin, globulin, albumin and proteose.

The last three constituents are present only in insignificant quantities (globulin 0.6–0.7%, albumin 0.3%, proteose 0.3%), and hence the protein content of semolina consists essentially of glutelin (glutenin) and prolamin (gliadin) (Kent-Jones & Amos, 1967b).

By a fractional precipitation technique, Sandstedt & Blish isolated three fractions: gliadin 40%, glutenin 25% and mesonin 25%. According to these authors, mesonin is an intermediate fraction between gliadin and glutenin (Portesi, 1957a). Pence & Elder (1953) found that wheat albumin consisted of at least six individual components which differed in their electrophoretic behaviour.

Electrophoretic and chromatographic investigations have revealed the heterogeneity of wheat nitrogen compounds: albumin, globulin, prolamin and glutenin. They are proteins which differ in their amino acid composition, in their molecular weight and in their electrophoretic mobility (Woychik, Boundy & Dimler, 1961; Wall, 1967). Particularly in glutenin and, also, in gliadin, the kind and number of these sub-units were found to be fundamental for pasta-making quality (Wasik & Bushuk, 1975).

It is known that the shape, dimensions and solubility of wheat proteins are influenced by the co-valent bonds, that is, by the total and reactive sulphydril groups, by the disulphide groups and by physical-electrostatic bonds such as the hydrogen bond and the hydrophobic bond. Researches carried out on total and reactive sulphydril groups and on disulphide groups have shown a strict correlation between the oxidation and the reduction of these groups and the rheology of the dough (De Deken & De Deken-Grenson, 1955; Bushuk, 1963; Mecham, 1964; Mecham, Knapp & Cheryl, 1966; Jankiewiez & Pomeranz, 1965; Tsen & Bushuk, 1968).

Disulphide-sulphydril interchange causes the transfer of the attachment of disulphide bonds from one protein chain to another (Goldstein, 1957) in this way:

$$P_1S\text{–}SP_2 + P_3SH \rightarrow P_1S\text{–}SP_3 + P_2SH$$

This interchange strengthens the protein network by elongation or relaxation of the chain of a structure which otherwise would be too rigid (Krull & Wall, 1969). Dalek-Zawistowska, Bartoszewicz, & Kaczkowski (1975) found a mutual interconversion between high- and low-molecular weight fractions of glutenin and gliadin, which seems to be correlated more with the conditions of dispersion than to the differences in the protein sub-units constituting the fractions. This is confirmed by studies carried out by Prishchep *et al.* (1974), who found that gluten quality is not correlated with its gliadin and glutenin content. The so-called gluten is not present as such in semolina, but is formed by the combination of gliadin with glutenin during hydration of the semolina to form a dough. Complete formation of gluten takes 25–30 min. Thus it has been shown, by Borasio & De Rege (cited by Portesi, 1957b) that after 30 min the cohesive strength of a semolina-water dough is three times greater than after 15 min.

Factors influencing the formation of gluten are (a) nature and concentration of the ions (i.e. Na^+, Ca^{2+}) in the dough water, (b) activity of the semolina enzymes, and (c) pH of the dough.

It is well known that water having a low salt content is not suitable for pasta manufacture. The mineral content of water helps gluten to agglomerate, but excessive salt content will cause the pasta to become fragile. Proteases increase gluten formation, with 'glutase' being particularly active (Issoglio, 1948).

The pH value also plays an important role in the gliadin-glutenin interaction, within the range of pH 6.6, the isoelectric point of gliadin, and pH 5.3, the isoelectric point of glutenin. Extreme agglomeration values are observed at pH 5.35.

Dough gluten has a characteristic structure, consisting of particles and filaments plaited together in a close network which envelopes lenticular particles of the hydrated starch. The elastic and plastic properties of the dough and of the cooked product are wholly dependent on the constitution of this gluten network.

3. Lipids. The lipid content of semolina is quantitatively irrelevant, and depends on the germ content of the semolina because germ is richer in lipids than other parts of the wheat grain. Semolina contains about 1.0–1.5% lipids (Sullivan & Howe, 1938). According to these authors the lipids consist mainly of unsaturated fats (oleic acid approx. 20%, linoleic acid approx. 56%)

4. Mineral matter. Durum wheat semolina may contain different minerals in varying amounts. Always present are potassium, sodium, calcium, magnesium, iron, manganese and aluminium combined as carbonates, sulphates, phosphates, silicates and chlorides. Many trace-elements may be found such as zinc, copper, iodine, vanadium, cobalt etc. The total mineral content in durum semolina lies generally between 0.9 and 1.0%.

5. Biodynamic elements. (a) *Vitamins.* The nutritionally important vitamins in durum wheat semolina are thiamine (approx. 1 mg/100 g) and riboflavin (approx. 0.1 mg/100 g). (b) *Enzymes.* Proteases, amylases, lipase the lipoxygenase are all directly concerned with pasta manufacture, and for this reason their activity must be controlled. Semolina having no enzymatic activity would be ideal for pasta manufacture.

Water

Water, like durum wheat semolina, is a 'direct' pasta raw material. It is necessary to pay as much attention to the choice of water as to the quality of semolina, since unsuitable water may cause problems during manufacture and also impair the quality of the finished product. For best results, water for pasta manufacture should have the following characteristics: (Portesi, 1957c): about 30° hardness; low levels of sodium, magnesium and chloride ions; lowest possible concentration of iron salts; residue after evaporation not exceeding 400–500 mg/litre, and

of composition Ca and Mg carbonates 180–200 mg, sulphates 70–90 mg, silicates 25–30 mg, chlorides 5–10 mg.

Optional direct raw materials

Other ingredients besides semolina and water may be used, with two aims in mind: a gastronomic one, and a dietetic one. Eggs and vegetables are the most frequently used ingredients to achieve flavour effects. These are added either as a puree or as frozen or freeze-dried products. If a puree is used, the dough water content must be reduced accordingly. When vegetables are added it is necessary to add egg as well, in order that the binding power of the egg protein will compensate for the decrease in the gluten content.

For dietetic pasta, various ingredients may be added, depending on the dietetic objective:

(a) For protein enrichment, ingredients used are milk powder, milk proteins or whey proteins; whole egg, egg white or egg yolk (either fresh, or frozen, or dried); animal proteins from meat or fish; flours or proteins from legumes, soya, peanuts or potatoes; yeast and yeast hydrolysates; whole or defatted wheat germ, or wheat gluten.

(b) For carbohydrate reduction, it is possible to add extra protein, as above, and also to include such ingredients as cellulose derivatives and processed bran.

(c) For reduction of protein, or perhaps elimination of protein, pasta can be made from starch together with non-nitrogenous binding agents such as alginates, sodium, carboxymethylcellulose and other vegetable gums.

When the rather critical balance between semolina and water is disturbed by the inclusion of other ingredients, it may be necessary to make adjustments to such parameters as particle size, temperature, pressure, proportion of water etc. Inclusion of some ingredients will reduce the binding power of the gluten, which means that extra binding agents must be added. In contrast, when high binding proteins are used, such as egg and gluten, it may be necessary to reduce the extra resistance to softening during cooking by increasing the proteolytic enzyme activity of the semolina and so effecting partial protein hydrolysis.

Manufacture of pasta

A scheme for the continuous manufacture of pasta is outlined in Fig. 2.

Mixing

When semolina and water are mixed together the two fundamental reactions taking place are starch hydration and protein hydration. In calculating the exact proportion of water to semolina there must be taken into account the natural

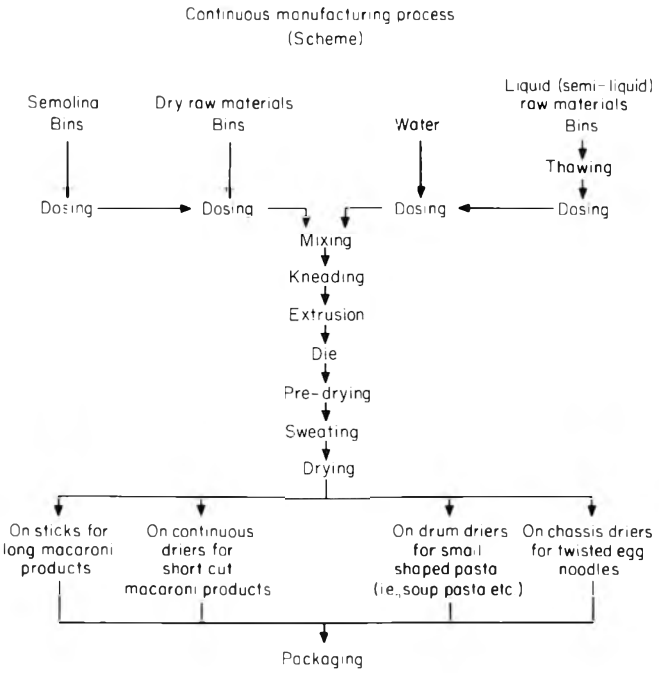

Figure 2. Continuous manufacturing process.

water content of the starch incorporated in its molecular structure and the amount of water retained in the particle surfaces by weak forces. Factors determining the optimum proportions of water to semolina are: the variety of durum wheat from which the semolina was obtained; gluten quality; protein content; initial moisture content of the semolina; particle size.

Commonly, durum semolina of 14–16% moisture content is mixed with 22–25% of water. Optimum water temperature is 35–40°C, depending on the speed of the mixer, and on the temperature of the semolina and of any other ingredients. This slightly elevated water temperature speeds up the mixing process and also reduced the time required for kneading the dough. In the mixing step, dry and liquid raw materials are metered in small amounts and in rapid succession into a rapid mixer comprising a shaft fitted with bevelled blades. Here the ingredients are mixed intimately until a deep, reciprocal penetration is obtained. The mixing must be carried out quickly in order to minimize oxidation of pigments, which is most rapid during the early stages of mixing and which stops almost completely as soon as the liquid suspension is emulsified (Radley, 1950).

The mixing process is an important stage in the manufacture of pasta;

incomplete or uneven hydration of the semolina would impair the superficial quality of the finished product (loss of opacity, tendency to crack, formation of white spots).

Kneading

Kneading of the semolina-water dough involves driving the mixture through a cylinder by means of bevelled helical blades, which have blunt edges in order to prevent the formation of discontinuous phases and disturbances to the forming process of the gluten.

These days dough kneading is usually carried out under vacuum. This is a fairly recent development and the first attempts, described by Bondi (1953), were not entirely successful. The idea of vacuum kneading was derived from the vacuum manipulation of clay pastes in the brick manufacturing process, in which the objective was deaeration in order to obtain a product of more compact structure and consequently greater resistance. In the pasta manufacturing process, absence of air bubbles imparts brightness and transparency to the product and, additionally, causes a more intimate contact between the semolina granules and so favours osmosis between the more hydrated granules and the less hydrated granules (Portesi, 1957d). Finally, deaeration reduces the tendency of pasta to crack, especially during cooking.

In the early stages, opinions on the value of processing under vacuum differed, and its adoption was delayed by the initial lack of success. It was not until it was appreciated that semolina doughs were different from clay doughs, with complex starch/water and protein/water reactions taking place within the dough, that suitable modifications were made to the vacuum process and successful results obtained.

During kneading, there is a considerable increase in the volume of the proteins present, since the proteins absorb about 200 times their weight of water (Portesi, 1957e), and interact to form the gluten network which constitutes the backbone of pasta. There is also appreciable absorption of water by the starch fractions in semolina.

Minerals present both in the semolina and in the dough water contribute to the coagulation of the proteins and to osmosis at cell level. Finally, lipids tend to emulsify as a result of mechanical stress (Secchi, 1954). Actually, a real colloidal system is formed, by suspensions of starch, solutions of sugars, dextrins, minerals and soluble proteins, colloidal solutions of protein and, partially, of starch and lipids, and emulsions of lipids (Chindemi, 1949).

In comparison with the old kneading process, carried out in open equipment under atmospheric pressure, the vacuum process may give rise to a greater enzymatic activity, due to the more compact dough. Therefore it is advisable to operate the kneading stage at a dough temperature either above or below the temperature at which the enzyme system is most active. Practical experience

indicates that the dough should be either below 30°C or above 42°C, with 30°C being the temperature most often selected.

The time taken for premixing and kneading is usually about 15 min.

Extrusion

Here the kneaded, compact mass of semolina and water is handled so as to complete and stabilize all the physicochemical reactions such as gluten formation, gluten network stabilization, and increase in the plasticity of the mass.

Modern extrusion presses comprise a worm fitted inside a water-jacketed steel cylinder. The pitch: diameter ratio is designed to cause high pressures to be generated within the mass. Depending on the particular shape of pasta, the pressure may vary from 1100 to 1850 lb/in^2 (80–130 kg/cm^2). Cold water is circulated through the cylinder jacket to keep the dough temperature down to around 45–50°C.

The dough is forced by the extrusion worm into a cylinder head and is delivered through narrowing feed lines to the die, thus causing a further increase in pressure. The die system itself must be carefully designed to ensure that there is a uniform distribution of pressure throughout the dough. This is to prevent the pasta 'slipping' on itself, since the inner core tends to be more mobile than the outer core, which is subject to friction in contact with the walls of the feeding lines. Manufacturers of extrusion presses have therefore developed different die systems, all of which ensure a uniform flow of the dough through the die orifices. When a very smooth pasta surface is wanted the orifices are lined with Teflon.

The extruded pasta is cut by rotating knives to whatever length is required and is subjected to a hot air jet. This causes a slight temporary hardening of the pasta surface which helps to prevent the pasta from becoming deformed and from sticking. This is only a temporary effect, since if the pasta were to be left to stand for a few minutes it would soften again completely.

Drying

The moisture content of the pasta as it emerges from the die is about 29–30%. The object of drying is to reduce the moisture content to below 12.5% in such a way that there are no undue stresses set up within the complex protein and starch structure, which could cause cracking and other physical defects.

Drying of pasta takes place in three stages, conveniently designated pre-drying, sweating, and drying. Pre-drying involves subjecting the extruded pasta to circulating air at temperatures between 55° and 90°C depending on the shape of the pasta. Within 1 hr the moisture content falls to 17–18%.

Pre-drying is carried out for five main reasons: to minimize undesirable microbiological or enzymatic activity; to stabilize the peripheral gluten network and so prevent it from migrating towards the inner core of the pasta; to

strengthen the structure of the pasta shape, so that it can be handled without distortion; to inhibit superficial enzymatic browning; to reduce the total drying period.

Pre-drying is carried out in insulated tunnels with a current of air at pre-determined, automatically controlled temperature and humidity.

After the initial pre-drying stage the air circulation is switched off, and the pasta is allowed to rest. The purpose of this is to achieve moisture equilibrium between the inner core of the pasta and its surface. This step, known as 'sweating', is carried out alternatively with periods of hot air circulation.

At the beginning of the pre-drying stage moisture will migrate from the inner core of the pasta through the capillary channels at the same rate as moisture evaporates from the surface. But soon this internal migration rate decreases and the moisture becomes concentrated around the inner core. It is therefore necessary to allow the moisture to achieve an equilibrium between the interior and exterior.

This alternation of diminishing periods of hot air circulation and of longer periods of sweating constitutes the actual drying process. The main difficulty is the reduction of the moisture content from 17–18% to 12.5% maximum. About half of the water is believed to be absorbed by the starch component of the pasta. The other half is absorbed by the protein, and this absorbed water is much more difficult to remove. Hence the long sweating periods.

The rate of migration of water from the inner core to the outer surface depends on several factors: the diameter of the capillaries which is dependent on the pressure used during extrusion through the die; the surface to weight ratio of the pasta; temperature of the pasta; and water content – as the product gets drier the migration decreases, due to the product shrinking and the capillary diameters decreasing.

It follows that each of the many different pasta shapes will require its own special drying regime. Mathematical models have been applied to establish optimum temperature, moisture, and air volume parameters for each shape.

Temperatures usually vary from 45 to 70°C, and total drying time from 6 to 28 hr. Efforts have been made to reduce drying time by use of infra-red and microwave techniques but so far have not led to any commercial development.

Mention should be made, though, of the 'ATR' drier developed by Braibanti & Company in Italy. This operates at a higher temperature than conventional driers, that is 75–80°C, with total drying time cut to 8–12 hr. It is claimed that pasta dried in this equipment has improved cooking firmness on account of the partially agglomerated gluten network which is formed in the raw pasta. With commercial, that is, conventional raw pasta, there is no such agglomeration until the pasta is cooked. Resimini, De Bernardi & Mazzolini (1976) and G. Dalbou (1978, private communication) have studied specimens of pasta manufactured in the 'ATR' drier, and have kindly given permission to publish results of their electron microscope investigations. Samples were prepared by freeze-fracturing and platinum-carbonium metallization techniques, and were soaked in 30% aqueous glycerol solution. To comprehend fully the results, it is

necessary to observe and compare the microscopic appearance of different samples, shown in Figs 3–8:* (1) commercial durum wheat semolina, (2) washed starch, (3) commercial raw pasta, (4) commercial cooked pasta.

Figures 3–8. Scale bar = 1 μm.

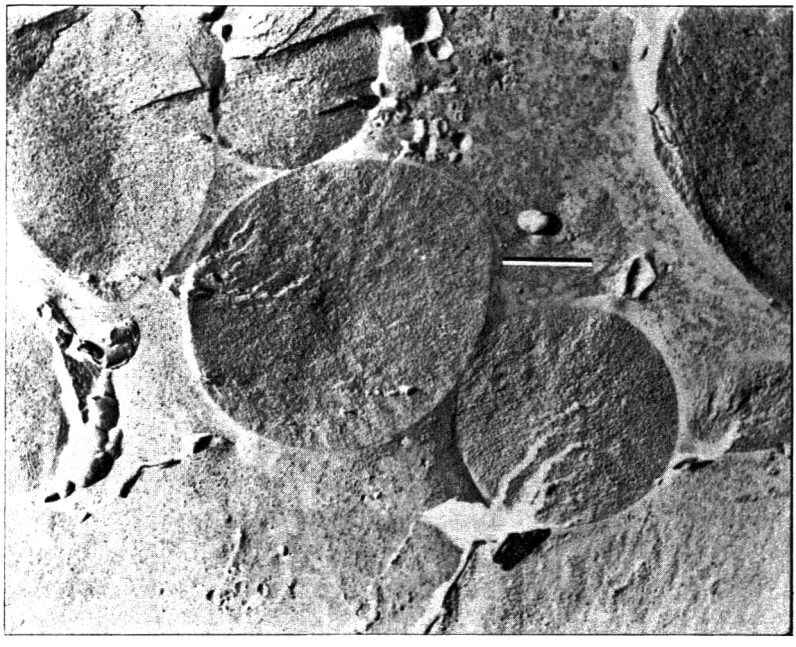

Figure 3. Durum wheat semolina.

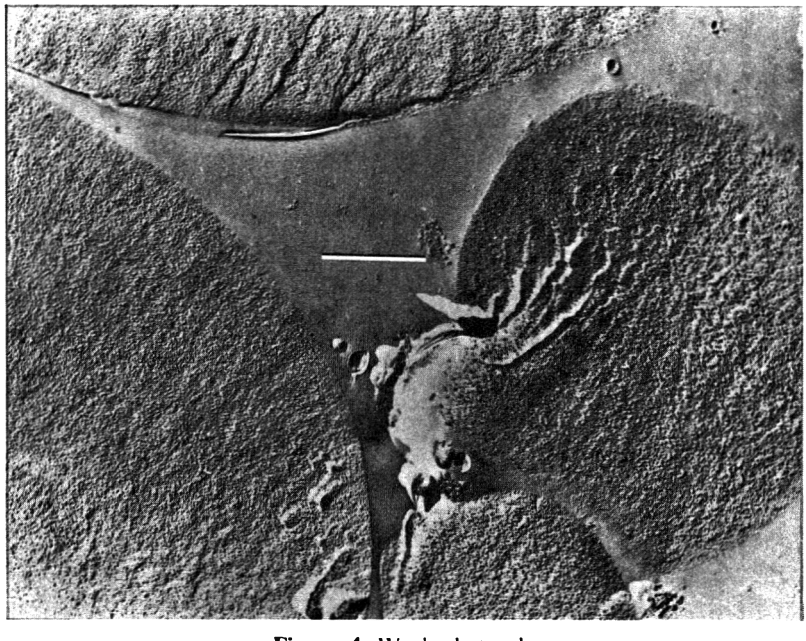

Figure 4. Washed starch.

*Figs 3–8 are published by kind permission of Messrs. Dott. M., G. Braibanti, Milan, Italy.

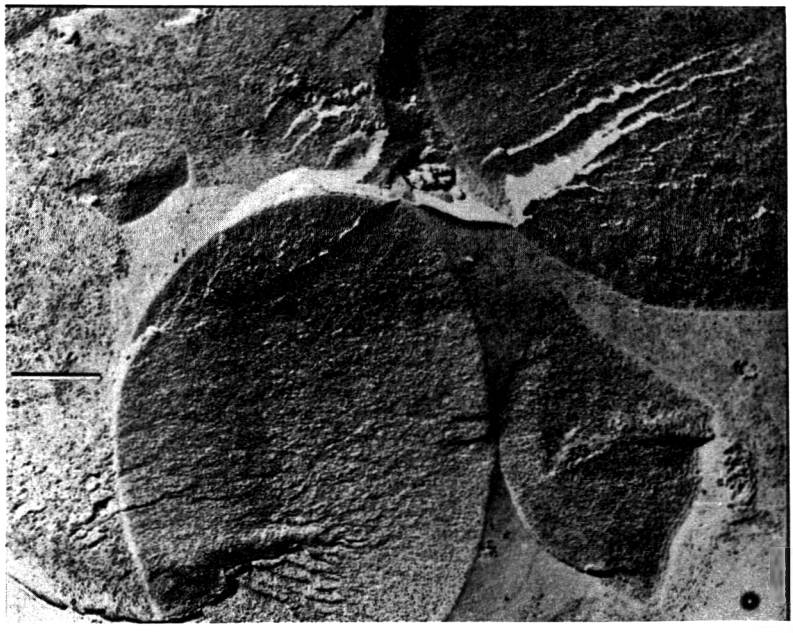

Figure 5. Commercial raw pasta.

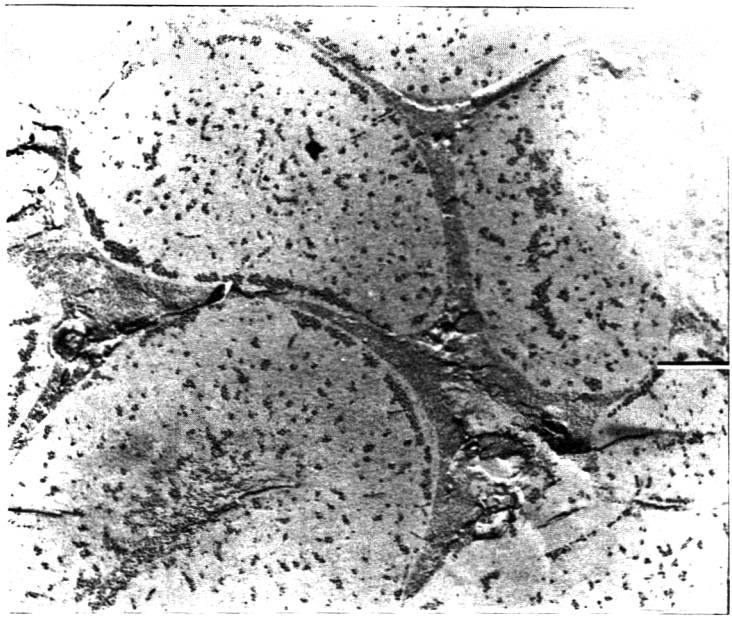

Figure 6. Commercial cooked pasta.

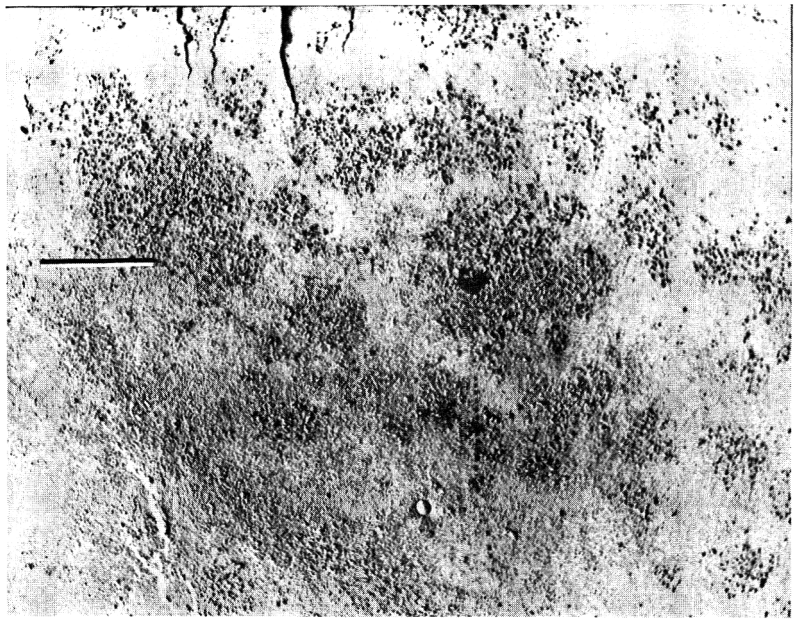

Figure 7. Gelatinized starch.

Figure 8. ATR pasta.

Figure 3, Durum wheat semolina, shows the perfectly intact starch granules and the protein matrix (gliadin, glutenin, soluble proteins) finely dispersed among the starch granules. After enzymatic solubilization of proteins and washing the starch granules (Fig. 4) are still intact and the interstitial proteins have disappeared almost completely. In commercial raw pasta (Fig. 5) the starch granules are almost completely intact and the proteins are finely distributed. In commercial cooked pasta (Fig. 6) the starch granules have swollen and partially gelatinized and a protein network has been formed by protein agglomeration which envelops the starch granules. Completely gelatinized starch after high temperature treatment is shown in Fig. 7. It is possible to see how the native starch granules are completely disintegrated, and finely distributed particles and small agglomerates are evident. 'ATR' pasta, dried for 8–12 hours at 80°C in an ATR drier is shown in Fig. 8. The protein network has formed already in the raw pasta, while in traditional dried products this occurs only after cooking.

When the moisture content of the pasta has fallen to below 12.5%, the pasta is conveyed from the dryer into a cooling chamber in which the air humidity is controlled. After cooling it is packaged.

Characteristics of pasta

The physical and organoleptic properties of pasta cannot be defined solely on the basis of fixed parameters, because opinions as to the optimal qualitative characteristics depend largely on subjective concepts. According to their own food habits, consumers expect physical and physico-chemical properties not on the basis of scientific knowledge, but simply on the basis of their prejudices, traditions, personal preferences etc. Irrespective of subjective judgment, however, it is generally accepted that pasta, made from good quality raw materials and according to good manufacturing practice, should have the following characteristics: smooth surface; a bright yellowish colour, more or less intense, which improves after cooking; firmness, i.e. resistance to cooking without sticking or mashing; a good 'bite' resistance in the mouth, without being either too elastic or too soft; an appreciable increase in volume in cooking.

Classification of pasta products

There are many possible variants, in which other food components are combined with durum semolina in one way or another. Of greatest practical significance are the following: regular dry pasta, made from durum semolina; egg pasta, made from durum semolina and eggs; 'pasta verde', made from durum semolina, eggs and spinach; high protein pasta, made from durum semolina supplemented with egg, wheat gluten, milk protein, soya protein; whole wheat pasta ('pasta integrale'); composite products, such as ravioli, canelloni, lasagne etc., in which pasta is combined with meat and vegetables in a tomato-based

sauce (such products are usually delivered as canned or deep frozen items); canned spaghetti or other pasta shapes in tomato or cheese sauce; dry mix products, including pasta-based soup mixes.

Pasta as a food and food ingredient

Compositional and nutritional data for regular dry pasta are shown in tables 1 and 2.

Pasta made from wheat alone is a nutritionally unbalanced food. It has a very low fat content, and the protein has a rather low biological value on account of its lysine deficiency. However, it should be remembered that pasta, like other cereal products and derivatives, is almost always consumed in combination with other foods. As a food ingredient it is perhaps uniquely versatile, because it can be combined with most other foods in several ways to yield a wide variety of appetising and nutritionally satisfactory dishes. Thus the combination of pasta with legumes, the proteins of which are rich in lysine, was known many centuries ago. For example, 'puls fabata', a mix made with flour, water and broad beans, was considered a holy food by the Romans. Horace, in his Satires, described how pleasant it was to return home to eat lagani (macaroni) with chick peas.

In many traditional pasta dishes the different protein components complement each other, resulting in amino acid pools of high biological value. Moreover, the incorporation of fats (butter or margarine) makes it possible for dishes based on pasta to be complete dietetic meals. To illustrate this, one may consider a simple and common pasta dish widely served in Italy consisting of 70 g (dry basis) pasta, 70 g tomato sauce and 10 g cheese. Nutrients and energy provided by a traditional pasta meal are shown in Table 3.

Table 1. Composition and energy content of dry pasta

		Energy/100 g	
	g/100 g	Kcal	%
Moisture	12.5	—	—
Protein (NX 5.7)	10.5–11.5	46	13
Lipid	0.8– 1.0	11	3
Carbohydrate	74–75	293	84
Ash	0.60–0.85	—	—
Total		350	100

Table 2. Amino acid composition: dry pasta *vs* FAO model composition, 1973

Amino acids	g/16 g.N	
	Pasta	model composition/FAO 1973
Isoleucine	4.0	4.0
Leucine	7.16	7.0
Lysine	2.57	5.5
Methionine	1.66	—
Cystine	2.08	—
Sulphur Amino Acid Total	3.76	3.5
Phenylalanine	4.45	—
Tyrosine	2.90	—
Total Aromatic Amino Acids	7.35	6.0
Threonine	3.10	4.0
Tryptophane	1.45	1.0
Valine	4.90	5.0

The lysine deficiency of wheat protein is well known; the other limiting amino acid is threonine. All the other amino acids correspond closely to the model composition proposed by the Joint FAO/WHO Expert Group for the determination of the Chemical Score (FAO, 1973).

Table 3. Nutrients and energy provided by simple pasta meal.

Food	Weight (g)	Protein	Lipid	Carbohydrate	Kcal
Dry Pasta	70	8.05	0.60	53.0	250
Cheese	10	3.60	2.80	0.5	42
Tomato sauce *	70	1.0	11.70	8.5	143
Total		12.65	15.10	62.0	435
Kcal.		51	136	248	435
Calories percentage		12%	31%	57%	—

*Tomato sauce: 100 g tomato; 11.5 g olive oil; 5.5 g sugar; basil.

Table. 4. Amino acid composition: Simple pasta meal. *vs* FAO model composition (1973)

Amino acid	Weight in 70g pasta (8.05g protein)	Weight in 10g cheese (3.60g protein)	Total amino acids in 11.65g protein	Total amino acids g/16gN	FAO (1973) model Composition g/16N
Isoleucine	0.32	0.19	0.51	4.38	4.0
Leucine	0.58	0.37	0.95	8.15	7.0
Lysine	0.21	0.29	0.50	4.29	5.5
Methionine	0.14				
Cystine	0.17				
Total Sulphur Amino Acids	0.31	0.12	0.43	3.69	3.5
Phenylalanine	0.36				
Tyrosine	0.23				
Total aromatic Amino Acids	0.59	0.36	0.95	8.15	6.0
Threonine	0.25	0.12	0.37	3.18	4.0
Tryptophane	0.12	0.04	0.16	1.37	1.0
Valine	0.39	0.26	0.65	5.58	5.0

The A/E Chemical Score related to the limiting amino acid. lysine. is 49 in pasta alone. compared with 72 in pasta seasoned with cheese.

Table 5. A/E Chemical Score. Lysine

Amino Acid	Pasta g/16g N	Pasta + Cheese g/16g N	FAO (1973) model composition g/16g N
Lysine A/E	2.57/34.29 = 7.49%	4.29/38.78 = 11.05%	5.5/36 = 15.28%
Chemical Score A/E	49 Lys	72 Lys	

Table 6. Nutrient and energy data for a complete and balanced pasta meal

Food	Weight (g)	Protein (g)	Lipid (g)	Carbohydrate (g)	Kcal
Pasta	130.0	14.30	1.3	97.5	459
Butter (or Margarine)	18.6	—	15.0	—	135
Cheese (Parmesan)	18.6	6.70	5.2	9.3	111
Tomato	150.0	1.50	0.3	5.3	30
Total	317.2	22.50	21.08	112.1	735
Kcal		90	196	449	735
Calories percentage		12%	27%	61%	—

The percentage distribution of calories between protein, fat, and carbohydrates is in accordance with recommended dietary allowances, Furthermore, the protein has a higher biological value than pasta above, and is nutritionally complete.

From a nutritional standpoint, therefore, a garnished or seasoned pasta dish can contain a good balance of nutrients of high dietetic value: These protein have a chemical score similar to that of chicken meat (A/E = 79) (FAO 1970). Lipids can be chosen from a wide range, so offering the opportunity of a high polyunsaturated/saturated fatty acid ratio. The carbohydrates are easily digestible (dextrins, malto-dextrins and gelled starch).

If the quantity of pasta in a simple dish of pasta, butter, cheese and tomato is increased from 70 g to 130 g, and the quantity of cheese, butter and tomatoes increased in proportion, we obtain a very good substitute for a main meal. This would provide 735 Kcal, which is about one quarter of a standard adult male's daily requirement, and about one-third of a standard adult female's daily requirement. It is considered that it would not be easy to devise, at this cost, any other palatable food combination having the same nutrient balance and the same high biological value protein, which yield 735 Kcal and contains 22.5 g protein.

Apart from the relatively low cost of a complete pasta meal, all the many variations and alternatives offered by combination of pasta with other foods make pasta a very important food item not only from the nutritional point of view but also from a gastronomic one.

Future prospects for pasta

Worldwide, the demand for cereals is increasing. The development of this demand is under continuous review by those scientists and economists who are

involved with the problems of world nutrition, especially in the United Nations Organisation.

At the 1974 UNO World Food Conference held in Rome many proposals were put forward to promote action at both national and international levels. The importance of cereals, and particularly wheat, in contributing to improvements in present and future nutrition emerged very strongly at this conference.

It is clear that pasta as a food represents perhaps one of the cheapest means of achieving the improved dietary regime in the developed countries as indicated by the American National Nutrition Programme, and also of helping to mitigate the problem of hunger in developing countries. The unique combination of properties of pasta–cheapness, ease of preparation, palatability, versatility, nutritive value, and long shelf life – will ensure that pasta and products made with pasta will continue to play a role of primary importance as world demand for cereal derivatives increases.

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Purification of crude glucose solution from the enzymatic hydrolysis of potato waste, by solvent precipitation, ultrafiltration and ion exchange

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Summary

A crude, dilute glucose solution produced by the enzymatic hydrolysis of waste from a dehydrated potato plant, contained high concentrations of non-carbohydrate and coloured materials. Purification using solvent precipitation, ultrafiltration and ion exchange, reduced the concentration of non-carbohydrate materials from 27% to 3%, and increased the glucose concentration from 53% to 96% of the total dissolved solids. The purified material was suitable for use in some food applications or as a fermentation substrate.

Introduction

During the factory processing of whole fresh potatoes into dehydrated potato powder, 15–20% by weight of the ingoing raw material emerges as solid waste. These waste materials are usually used for land-fill or incorporated into animal feeds, neither of which are economically satisfactory outlets.

In an attempt to upgrade this material Moreton (1978) described a process in which the wastes were hydrolysed with α-amylase and amyloglucosidase enzymes, and the yeast, *Candida utilis*, cultivated on the liquid phase of the hydrolysate. As an alternative to the propagation of yeast on the hydrolysate, it was decided to treat the crude hydrolysate in order to prepare a purer glucose solution, which might find wider applications.

During the commercial production of glucose syrups from starch, the main purification processes take place prior to the hydrolysis, ensuring that the starting material is relatively pure starch, thus minimizing subsequent purification after hydrolysis. Such post-process purification as is necessary is usually accomplished using activated carbon for decolourization and ion exchange for

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de-ashing. Such processes have been described by Petersen (1975) and Khaleeluddin, Sutthof & Nelson (1974). It was not known whether the conventional methods could produce a material of low colour and high purity from this crude material, or whether the end product would be suitable for commercial use.

Among the non-carbohydrate materials present, the hydrolysate contained high concentrations of Na^+ residual from the caustic peeling process, and Cl^- from the HCl used to neutralize this alkalinity. The coloured materials present could include many of those formed in impure carbohydrate solutions by enzymic and non-enzymic mechanisms particularly after prolonged heating as in the hydrolysis process, (Hervé, 1974a,b; Greenshields & Macgillivray, 1972).

Of the toxic materials known to be found in potatoes, the steroid alkaloid, solanine, has been shown to cause abnormalities in rats, humans and chick embryos (Kirk & Mittwoch, 1975, Mun *et al.*, 1975.) This compound would be particularly likely to be present in potato waste material, since this includes the skin and peridermal layers, together with those parts removed by trimming because of mechanical damage or mould infection.

Ion exchange, activated carbon decolourization, solvent precipitation and ultrafiltration were used in various combinations to remove these impurities.

Materials and methods

Potato waste

This material was supplied by Cadbury-Schweppes Ltd., Tea and Foods Division, Bournville, Birmingham. The composition of the wastes was as described by Moreton (1978).

Potato waste hydrolysate

The potato waste was enzymatically hydrolysed using a two stage process (Moreton, 1978), with a thermostable α-amylase (Termamyl) and an amyloglucosidase (Amyloglucosidase 150), both supplied by Novo Industri A/S, Enzymes Division UK, Windsor, Berks.

Activated carbon

Gluconoblend 2 and Actibon G4, both recommended for the decolourization of carbohydrate solutions, were purchased from Norit-Clydesdale, Glasgow. Decolourization tests with potato waste hydrolysate and activated carbon were carried out by continuously agitating 10 ml of hydrolysate and a known quantity of activated carbon, for 10 min at 60°C, the temperature at which the hydroly-

sate would leave the second stage of the hydrolysis. Samples were filtered through Millipore 0.45 μm HAWP filters (Millipore, Wembley, Middx) to remove particulate material before estimating the colour.

Ion exchange resins

'Amberlite' IRA-401, 402, 410, 904, 93 and 47, IRC-50, CG-120, XAD-2 and 'Dowex' 50W-X8 were purchased from B.D.H. Poole, Dorset. 'Amberlite' 252 was obtained directly from Rohm and Haas, Newcastle upon Tyne.

Each resin was regenerated before use, the acid and base exchangers with 5 bed volumes of 5% (v/v) HCl or 5% (w/v) NaOH respectively, followed by 6 bed volumes of deionized water. The non-functional resin XAD-2 was regenerated with 2 × 2 bed volumes of 1% (v/v) HCl in methanol, 2 × 2 bed volumes acetone/methanol/water (10 : 45 : 45 v/v) and 5 × 2 bed volumes deionized water.

Ultrafiltration equipment

Amicon ultrafiltration equipment and membranes were purchased from Amicon, High Wycombe, Bucks, and ultrafiltration cells from Camlab, Cambridge. Paterson-Candy ultrafiltration equipment was used on the manufacturer's premises (Paterson-Candy International Ltd., Laverstoke Mill, Whitchurch, Hants).

Analytical methods

Total dissolved solids (TDS). Determined by drying aliquots of solution to constant weight at 105°C.

Glucose. Determined by the glucose oxidase method (Sigma Chemical Co., Poole, Dorset).

Total carbohydrate. Determined by the phenol-sulphuric acid method (Dubois *et al.*, 1956).

Trace elements. Determined by flame photometry.

Pectin. Determined by the carbazole method of Rouse & Atkins (1955).

Conductivity. Measured using a Radiometer CM3 Conductivity meter (Radiometer, Copenhagen).

Colour. The extinction at 420 nm of solutions in 1 cm cuvettes in a Unicam SP1800 spectrophotometer (Unicam, Cambridge) was used as a measure of colour.

Alkaloid detection. Steroid potato alkaloids were determined qualitatively by a combination of the extraction method of Wang, Bedford & Thompson (1972) and the TLC chromatographic detection method of Shih & Kuc (1974). Aliquots (200 ml) of potato waste hydrolysate were blended with 1 litre of methanol/chloroform (2 : 1 v/v) for 5 min, 600 ml of 0.8% Na_2SO_4 added, and the mixture shaken vigorously. After separation into two layers, the lower chloroform layer was discarded, and the upper methanol layer re-extracted with 100 ml of 0.8% Na_2SO_4 and the lower layer again discarded after separation. The methanolic extract was evaporated nearly to dryness at 45°C under reduced pressure using a rotary evaporator (Buchi, Switzerland), and the residue made up to 5 ml with methanol. Samples of from 2–10 µl were applied to Silica Gel 60 TLC plates (Merck Art. No. 5553, Anderman & Co., London) and the plates run for 5 h using the solvent system Butan-1-ol, acetic acid, water (4 : 1 : 1 v/v). After drying at 105°C for 10 min, the plates were sprayed with anisaldehyde reagent containing anisaldehyde, ethanol, conc. H_2SO_4 and acetic acid (5 : 90 : 5 : 1 v/v). After development at 105°C for 2–3 min, solanine appeared as blue/green spots and solanidine as blue spots. Authentic purified samples of solanine and solanidine were obtained from the Medical Research Council Steroid Reference Collection.

Results

Analyses of waste hydrolysates

Due to the inherent variability of the waste, the hydrolysates showed wide variations in composition. Analytical results for two batches of hydrolysate are shown in Table 1. Glucose represented 54 and 65%, and total carbohydrate 73

Table 1. Composition of crude waste hydrolysate (g/litre)

		Hydrolysate 1	Hydrolysate 2
1.	Total carbohydrate	81.00	109.1
2.	Reducing sugars	67.50	—
3.	Glucose	59.85	95.65
4.	Nitrogen	1.80	6.25
5.	Protein	5.25	4.97
6.	Na^+	6.15	11.24
7.	K^+	2.72	4.30
8.	Mg^+	0.13	0.20
9.	SO_4^{--}	0.20	0.16
10.	PO_4^{--}	1.00	0.43
11.	Total dissolved solids	111.15	147.00
	1 + 6–10 as percentage of 11	85.57%	88.70%
	3 as percentage of 11	53.84%	65.06%
	1 as percentage of 11	72.87%	74.21%

and 74%, of the TDS in these two examples. Addition of the values for total carbohydrate, protein plus trace elements, leaves 11 and 14% of the total dissolved solids unidentified. A purification process must therefore remove 26% in hydrolysate 1 and 27% in hydrolysate 2, of the total solids to leave the carbohydrate fraction, and 35 or 46% to leave pure glucose.

Decolourization of crude hydrolysate by activated carbon

Decolourization characteristics with increasing concentrations of activated carbon are shown in Fig. 1. The hydrolysate required similar quantities of Gluconoblend 2 and Actibon G4 to achieve the same colour reduction, although Actibon G4 required a shorter contact time for the same colour reduction.

Selection of ion exchange resins for decolourization and dissolved solids removal

In the absence of information on the chemical composition of the coloured and non-carbohydrate materials present in the hydrolysate, resin selection was empirical. A wide variety of resins which have been used in carbohydrate purification processes, were screened using crude waste hydrolysate in simple batch absorption tests. The strong and weak acid cation exchangers had little effect on colour, whereas the weak base exchangers were more effective, and the strong base exchangers even more effective. However, the weak base

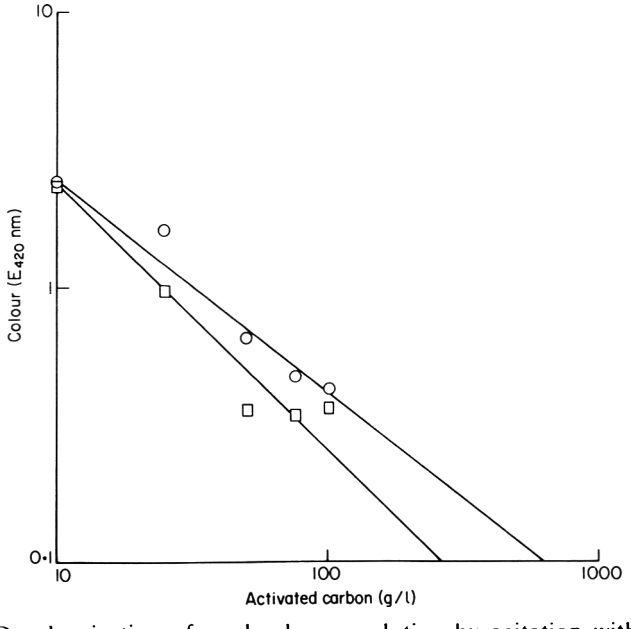

Figure 1. Decolourization of crude glucose solution by agitation with activated carbon for 10 min at 60°C, Gluconoblend 2 (○) and Actibon G4 (□).

exchangers showed higher total solids reduction than the other types. The non-functional resin XAD-2 showed excellent colour removal properties with intermediate solids removal.

Similar tests were carried out with various combinations of cation and anion exchangers in series. Of the combinations, Dowex 50W – X8 or Amberlite IR-120, followed by Amberlite IRA-93 or IRA-904 were the most effective, reducing T.D.S. by 26–28%. Treatment with XAD-2 between the cation and anion resins enhanced colour reduction and prolonged the life of the anion resin.

Pre-treatment by ultrafiltration

Decolourization of the hydrolysate with activated carbon had shown that very high addition rates would be required to reduce the colour to an acceptable level. For example, to reduce the colour of one tonne of glucose in solution from an initial value (E_{420} nm) of about 6.0, to 0.08, would require 0.5 tonnes of activated carbon. Since activated carbon costs over three times as much as glucose, this approach was obviously not going to be successful. Pre-treatment of the hydrolysate was therefore necessary to reduce this high requirement for activated carbon.

Ultrafiltration appeared to be suitable for this purpose and trials were carried out with Amicon membranes and one Amicon hollow fibre unit. Each membrane, 7.6 cm in diameter, was tested in a 500 ml Camlab ultrafiltration cell, pressurized to 30 p.s.i. with N_2. Flux rates across the membranes were measured with deionized water, 10% (w/v) glucose solution, and untreated hydrolysate. The three membranes and their nominal molecular weight cut-offs were UM 05(500), UM 2 (1000) and UM 10 (10,000). The H1P5 hollow fibre unit had a nominal cut-off of 5,000. This unit has an integral peristaltic pump which was used to pump material along the fibres. The UM 05 membrane has the lowest cut off in the Amicon range, and is nearest to the molecular weight of glucose (180).

The ultrafiltered permeates were analysed for total dissolved solids, colour and glucose concentration. Glucose concentration was unaffected by ultrafiltration. Decolourization tests with activated carbon (Actibon G4) were carried out as before with each ultrafiltrate. Results are shown in Fig. 2. The ultrafiltered permeates showed greatly reduced colour and a much lower requirement for activated carbon to further reduce the colour, than the original hydrolysate. To produce a colour of E_{420} 0.26 would require 170 g/l of activated carbon with the original hydrolysate, 39 g/l for the H1P5 permeate, 22 g/l for the UM 10 permeate, 5.2 g/l for the UM2 permeate or 1.5 g/l for the UM05 permeate. The performance of the H1P5 hollow fibre unit was inferior to that of the UM 10 membrane. Despite the excellent performance of the UM 05 membrane, flux rates were extremely low, 0.01 l/m²/h with hydrolysate. The UM 2 membrane, which also showed good decolourization characteristics, had a water flux rate of 5.9 l/m²/h, with 10% (w/v) glucose, 1.0 l/m²/h and with hydrolysate 0.13 l/m²/h.

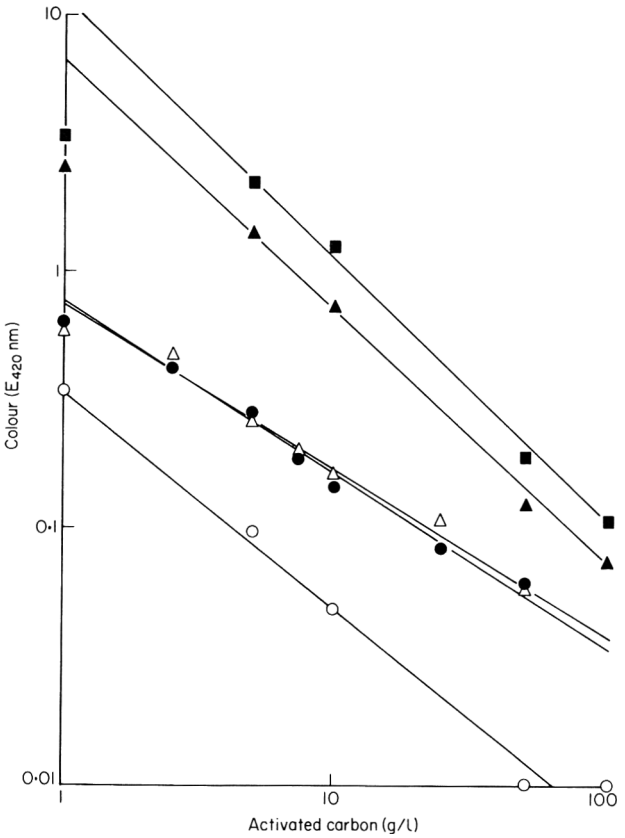

Figure 2. Decolourization of crude glucose solution with Gluconoblend 2 after ultrafiltration with HIP5 hollow fibre unit (■), UM10 (▲), UM2 (●), T5/A (△), or UM05 (○) membranes.

Hydrolysate for these trials had been filtered through sixteen 20 × 20 cm EKS asbestos filter sheets in a Carlson-Ford filter press to remove particulate material. These ultrafiltration membranes are known to bind steroids (and presumably steroid alkaloids) and also divalent cations, which could reduce the flux rate. The hydrolysate also contained 3.62 g/l of pectin derived from the skin and cell walls of the potato. Since it was thought that this material could be responsible for the low flux rate, samples were treated with 0.1 g/l 'Novo' Pectozyme, a pectinolytic enzyme, at 45°C for 6 h, which reduced the pectin content to 112.5 mg/l; no increase in ultrafiltration rate was observed after this treatment.

Further trials were carried out with membranes from another manufacturer, Paterson-Candy. The most suitable membranes appeared to be types T 2/40 or T2/A and these were used in the first experiment together with the next highest cut-off membrane, T4/A. The membranes were arranged in a test rig in three pairs, each membrane being a hollow tube 2.44 m long and 12.5 mm internal

Table 2. Ultrafiltration of waste hydrolysate with Paterson–Candy membranes

Membrane type	Flux rate (l/m²/hr) at different pressures			
	200 p.s.i.	400 p.s.i.	500 p.s.i.	600 p.s.i.
T 2/40	—	6.50	10.00	12.75
T 2/A	8.62	13.00	11.90	13.60
T 4/A	13.70	13.70	14.60	13.65

diameter. Flux rates at pressures up to 600 p.s.i. are shown in Table 2, they are approximately 100 × higher than those with the Amicon membranes. Flux rate was not measured with the T2/40 membrane at 200 p.s.i., however, flux rate increased from 400 to 600 p.s.i. The T2/A showed an increased flux from 200 to 400 p.s.i., then little change at 600 p.s.i., whereas the T4/A membrane showed similar flux rates at all values from 200 to 600 p.s.i.

Analyses of the three permeates at 600 p.s.i. are shown in Table 3. The T2/40 membrane (specification: passes 20–40% of 150 mg/l sucrose at 150°C and 210 p.s.i.) passed 8% of the glucose and 83% of the Na^+. The T2/A (rejects 97% of a 6,000 mol. wt 300 mg/ml polyethylene glycol (PEG) solution at 140 p.s.i. and 15°C) membrane passed 12% of the glucose and retained 66% of the Na^+ ions, whereas the T4/A membrane (rejects 50% of a 300 mg/ml, 5,000 mol. wt PEG solution at 140 p.s.i. and 15°C) passed 30% of the glucose and retained 35% of the Na^+.

The flux rate results showed, particularly with the T2/A and T4/A membranes, that increasing pressure increased the concentration polarization effect (aggregation of solute molecules at the membrane surface) negating the pres-

Table 3. Analysis of permeates (600 p.s.i.) after ultrafiltration of crude waste hydrolysate (g/litre)

	Original Hydrolysate	Membrane type		
		T4/A	T2/A	T2/40
Total carbohydrate	92.55	21.00	10.50	4.05
Reducing sugars	67.50	20.60	—	—
Glucose	59.85	18.35	7.45	2.80
Nitrogen	2.89	0.60	0.49	0.38
Protein	14.00	2.00	1.79	1.36
Na^+	6.15	4.02	2.05	1.04
K^+	2.72	1.82	1.23	0.84
Mg^{++}	0.132	0.042	0.006	0.001
SO_4^{--}	0.70	0.01	—	—
PO_4^{---}	1.00	0.12	0.03	0.005
Total dissolved solids	111.75	29.51	15.98	4.89

Table 4. Analysis of permeates (84 & 112 p.s.i.) after ultrafiltration of crude waste hydrolysate (g/litre)

	84 p.s.i.		112 p.s.i.	
	T5/A	T4/A	T5/A	T4/A
Total carbohydrate	65.70	65.45	65.70	56.70
Glucose	63.10	60.75	59.30	52.75
Nitrogen	0.896	0.938	0.840	0.770
Protein	4.07	3.325	3.15	2.45
Colour E_{420} nm	0.965	0.575	0.662	0.400
Total dissolved solids	70.35	69.18	70.27	59.02

Original hydrolysate as for Table 3.

sure increase. This effect reduces the effective pore size of the membrane leading to rejection of solutes below the nominal cut-off range.

With the T4/A membrane again, and the higher cut-off membrane T5/A (rejects 90% of a solution of 20,000 mol. wt PEG) at 84 and 112 p.s.i. pressure (Table 4), flux rates were higher than before using the same hydrolysate as in Table 3. The glucose concentration in all cases is above the original level due to concentration during ultrafiltration. The T5/A membrane showed slightly higher glucose passage than the other membranes, although these showed lower colour and higher retention of extraneous materials. There was little difference between the performance of the T5/A membrane at 84 and 112 p.s.i. The T4/A membrane, however, showed a higher retention at 112 than at 84 p.s.i. In the original hydrolysate, glucose comprised 53.55% of the TDS, whereas in the T5/A permeate at 84 p.s.i., it comprised 89.69% of the TDS.

A larger quantity of ultrafiltered permeate was produced using six T5/A membranes in parallel at 84 p.s.i., which gave a flux rate of 22.32 l/m²/hr, (Table 5). With this batch of hydrolysate, glucose originally comprised 76.36% of the TDS, which increased to 84% after ultrafiltration. The TDS was reduced by 19.15%. Decolourization characteristics of this batch of ultrafiltered hydrolysate have been included in Fig. 2.

Table 5. Analysis of permeate from T5/A membranes at 84 p.s.i. after ultrafiltration of crude waste hydrolysate (g/litre)

	Hydrolysate	Permeate
Total carbohydrate	61.40	64.96
Glucose	60.00	54.60
Nitrogen	1.26	0.84
Protein	8.13	4.20
Colour E_{420} nm	6.01	0.86
Total dissolved solids	80.40	70.12

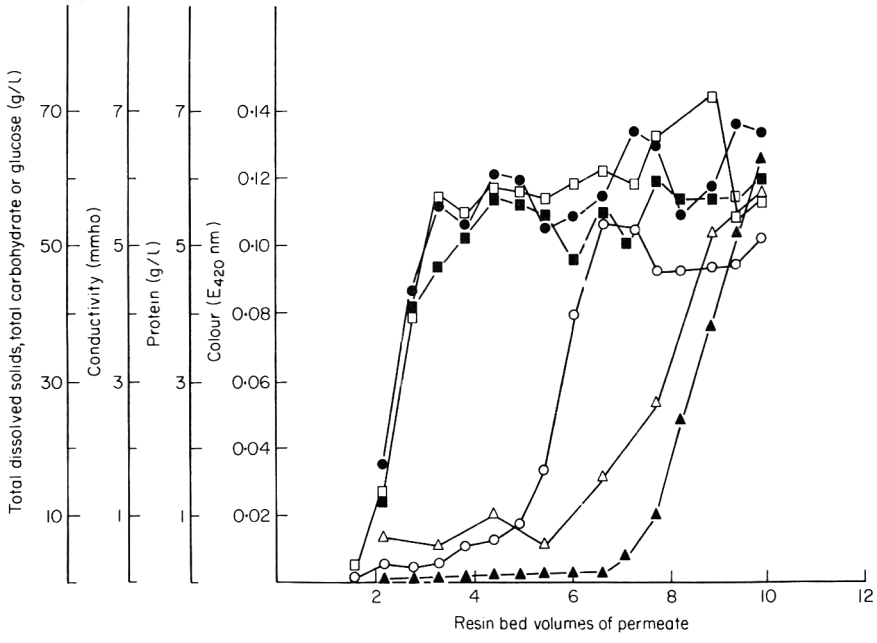

Figure 3. Ion exchange chromatography of glucose solution after T5/A ultrafiltration, with IR-120, XAD-2 and IRA-93 resins. Symbols, total dissolved solids (□), total carbohydrate (●), glucose (■), conductivity (▲), protein (△) and colour (○).

Ion exchange treatment of ultrafiltered hydrolysate

Ultrafiltered T5/A permeate was further purified by column chromatography using Amberlite IR-120, XAD-2 and IRA-93 resins. Each column contained 900 ml of wet, regenerated resin, the column dimensions were 55 × 390 mm (IR 120) and 65 × 330 mm (XAD-2 and IRA-93), the flow rate was 50 ml/min. Fractions (500 ml) were collected and analysed for TDS, glucose, total carbohydrate, protein, conductivity and colour. Results are shown in Fig. 3. Up to 3 bed volumes (1 BV = 900 ml) the column was still being loaded with hydrolysate, from 3 to 5 bed volumes the fractions were virtually colourless, had no odour and a sweet taste with no unpleasant taints. Between 5 and 6 bed volumes, the colour gradually increased and a slight taste became apparent. By 8–9 bed volumes, when protein and Na^+ had returned almost to their original levels, the taste became strong and objectionable, a combination of bitter/salt flavours completely masking the sweet taste.

Solvent precipitation

The ultrafiltration/ion exchange process produced a satisfactory material but with a very short resin life before regeneration would be required. Whilst screening organic solvents for their ability to extract coloured materials from

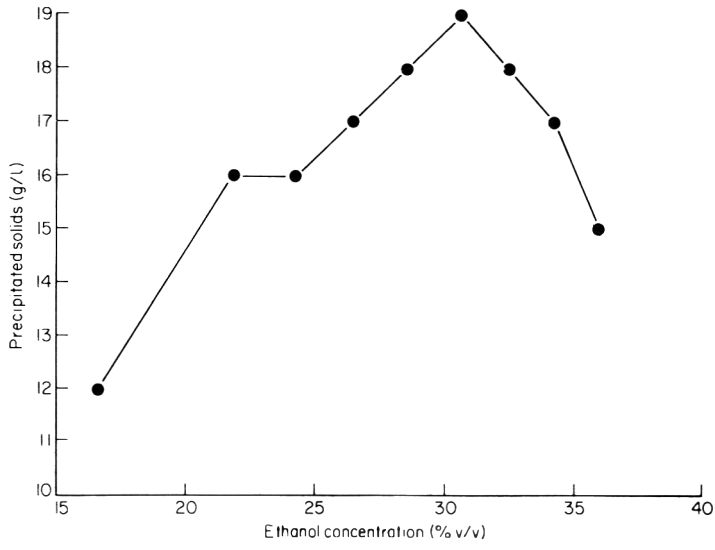

Figure 4. Solvent precipitation of crude glucose solution with ethanol.

the hydrolysate, it was noticed that both ethanol and acetone produced a heavy precipitate (up to 19 g/l). The effect of increasing ethanol concentrations on the quantity of precipitate can be seen in Fig. 4, the optimum concentration being 30% (v/v) ethanol.

Crude hydrolysate, after precipitation with 30% (v/v) ethanol and removal of the precipate by centrifugation (11,000 *g*/20 min), was treated in a rotary evaporator under vacuum at 60°C to remove ethanol and ultrafiltered in a 2 l Camlab cell at 30 p.s.i. using an Amicon PM 10 membrane, 15.2 cm in diameter. This membrane has the same nominal cut-off (10,000) as the UM 10, but is made from a different material. A flux rate of 4.411 l/m²/hr was obtained at 4°C. The PM 10 membrane was used since there was insufficient material available to use the pilot scale T5/A test rig which required > 50 l of hydrolysate. The PM10 permeate showed a lower colour but higher protein content than the T5/A permeate. The ethanol precipitated, PM10 ultrafiltered permeate was treated with three ion exchangers in 5 ml bed volume columns. Results are shown in Fig. 5. The permeate showed greatly extended resin life for all measured values. At 22 bed volumes (1BV = 5ml), the colour had only reached 60% of its original value. Most of the components had returned to their original values by 22 bed volumes. The fractions were visually and organoleptically acceptable up to 16 bed volumes.

Figure 6 shows the results after ion exchange using the same 5 ml bed volume system with IR 120, XAD 2 and IRA 93 resins, after two stage ultrafiltration of ethanol precipitated hydrolysate, using 15.2 cm Amicon membranes, permeate from a PM 10 membrane (flux rate 1.74 l/m²/hr) being again ultrafiltered using a UM2 membrane (0.2 l/m²/hr). Colour and protein remained stable at E_{420}

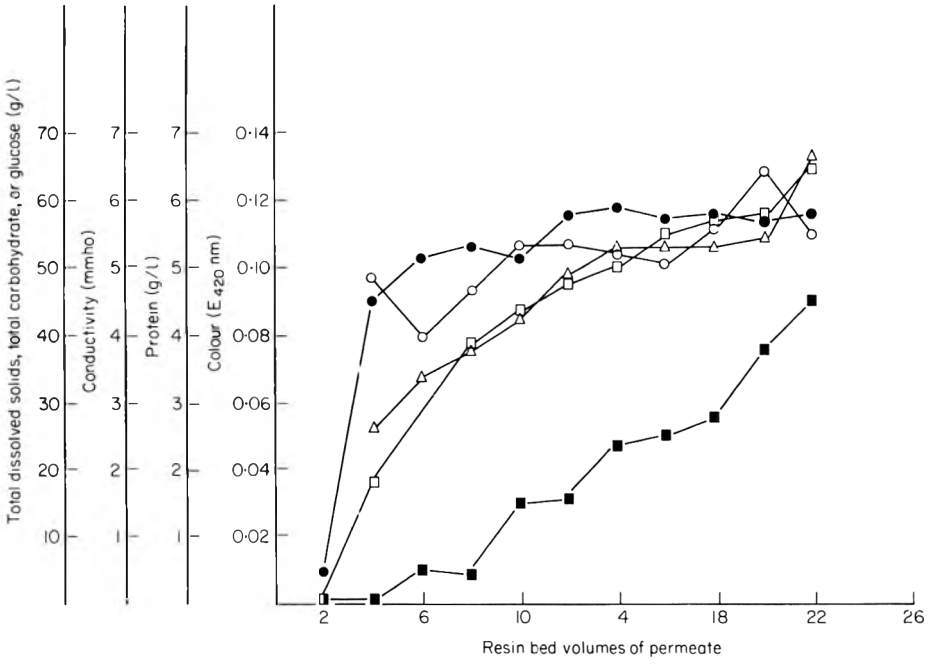

Figure 5. Ion exchange chromatography of ethanol precipitated, PM 10 ultrafiltered glucose solution, using IR-120, XAD-2 and IRA-93 resins. Symbols as for Fig. 3.

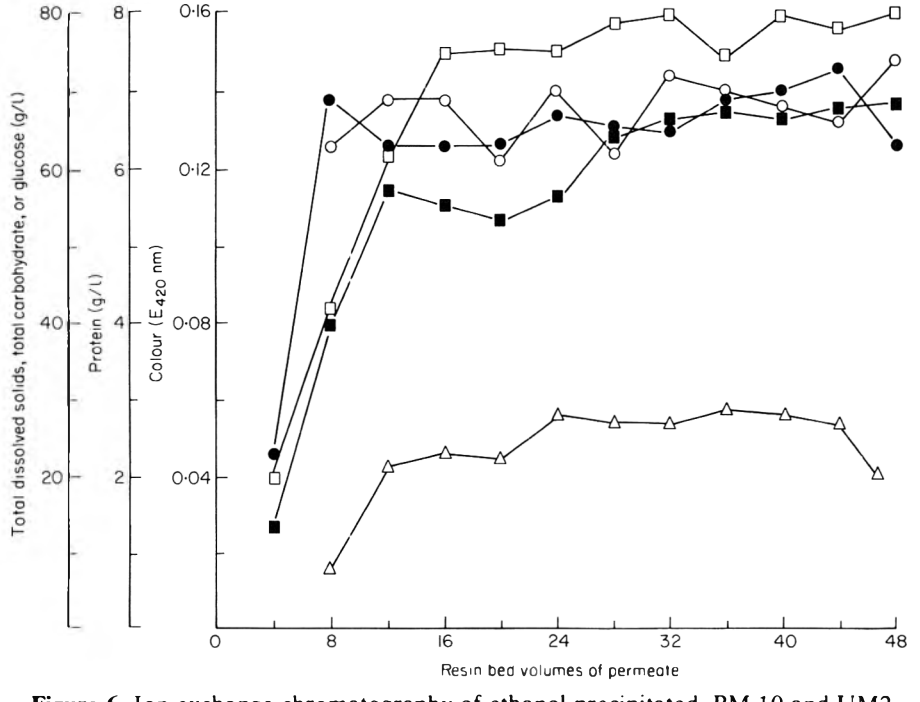

Figure 6. Ion exchange chromatography of ethanol precipitated, PM 10 and UM2 ultrafiltered glucose solution using IR-120, XAD-2 and IRA-93 resins. Symbols as for Fig. 3.

0.135 ± 0.02 and 2.0–2.85 mg/l respectively from 12 to 48 bed volumes, indicating that the resins were not exhausted at this stage. No measurements were made after 48 bed volumes. Comparative analyses for hydrolysates purified by ion exchange after T5/A ultrafiltration, PM 10 ultrafiltration following ethanol precipitation and PM 10 and UM 2 ultrafiltration following ethanol precipation are shown in Table 6. Although there were variations in composition between different batches of hydrolysate, overall purification was similar with each treatment method, only the effective resin life was changed.

Detection and elimination of steroid alkaloids from potato waste hydrolysate

The steroid alkaloids found in potatoes are hexacyclic bases with a fused indolizidine moiety, considered to be derivatives of solanindane. The two commonly occurring members of this group are solanine and chaconine, differing only in the structure of the sugar side chain.

Estimations of the concentrations of these compounds in the wastes were made using TLC of concentrated chloroform/methanol extracts. Although not truly quantitative, this method can be made partially so by chromatographing dilutions of standards and extracts and comparing the concentrations at which no detectable spots are seen. The method proved to be reproducible and very sensitive, capable of detecting < 0.1 μg of each alkaloid. R_F values for solanine and its aglycone solanidine were found to be 0.30 and 0.76 respectively, with another major spot at 0.39, which was probably chaconine, although in the absence of a purified standard this could not be confirmed. Concentrations of these compounds in the various waste fractions were from 250–1000 mg/kg dry weight. The alkaloids are unchanged by the enzymatic hydrolysis process, and can be found in both the liquid hydrolysate and the unhydrolysed solid residue. After ultrafiltration of the hydrolysate, however, they were not found in the

Table 6. Analysis of purified waste hydrolysate after T5/A ultrafiltration, ethanol precipitation and ultrafiltration with PM 10 or PM 10 + UM2 ultrafilters, followed by ion exchange with IR-120, XAD-2 and IRA-93 resins (g/litre)

	T5/A	PM 10 (ethanol precipitated)	PM 10+UM2 (ethanol precipitated)
Total dissolved solids	56.02	58.0	75.30
Total carbohydrate	54.00	56.00	70.00
Glucose	52.00	56.00	67.00
Protein	0.015	0.005	0.002
Colour E_{420} nm	0.012	0.077	0.113
Glucose as percentage of TDS	92.82	96.38	88.97
Glucose as percentage of total carbohydrate	96.29	100.00	95.71
Total carbohydrate as percentage of TDS	96.39	96.38	92.46

permeate. The ability of the ion exchange resins to remove these alkaloids was also tested by adding 5 mg of purified solanine or solanidine to 10 ml of potato waste hydrolysate plus 1 g of regenerated IR-120, XAD-2 or IRA-93 resin. After shaking for 10 min, samples were removed and chromatographed. No alkaloids were found after treatment with IR-120 and XAD-2, but appeared unaltered with IRA-93. The concentration of alkaloid added was chosen to be fifty times greater than the detection limit in the volume applied to the TLC plate.

Discussion

The purification process was required to produce a tasteless, odourless, clear glucose solution. This was achieved by a variety of methods. Decolourization using activated carbon proved effective, but required very high addition rates to produce an acceptable colour. Other materials not removed by activated carbon were removed by three ion exchange resins in sequence. Working life of the resins, however, was very short before regeneration was required.

Ultrafiltration reduced the colour of the hydrolysate to a level, which after ion exchange treatment, was acceptable without activated carbon treatment, as well as removing some of the dissolved solids and extending the resin life. Protein, which seemed to be associated with the strong bitter flavour of the original hydrolysate, was reduced to very low levels, whilst the carbohydrate fraction of the hydrolysate originally approximately 72%, was increased to approximately 95% of the dissolved solids. Resin life was further prolonged by ethanol precipitation and a two stage ultrafiltration process. Useful resin life with these processes was 2 bed volumes for ultrafiltered, ion exchanged hydrolysate, 16 bed volumes for ethanol precipitated, ultrafiltered hydrolysate and >40 bed volumes for the ethanol precipitated, two stage ultrafiltered hydrolysate.

The applicability of this process to potato and other hydrolysable carbohydrate wastes, will depend upon a variety of factors, including the quantity of waste available, the carbohydrate concentration and the concentration and nature of the contaminating materials. The most obvious use for a dilute glucose solution, such as that produced by this process, would be as a make up medium for products where solid glucose or sucrose are added during the process. The degree of purification required may also vary with the nature of the desired product; for example, if the product is strongly flavoured or coloured, extreme purification would not be necessary. Ultrafiltration could also be used to concentrate the solution to a higher solids content, which would increase its range of applications and be more economical than a thermal concentration process. The location of the waste relative to the point of ultilization of the purified material will also be relevant, as transport of either waste or hydrolysate would probably be uneconomical. A partial purification process could also increase the range of the original application of the material as a fermentation

feedstock to processes where the original crude hydrolysate could not be used. As raw material costs increase, the economics of recovery processes such as this, will become more attractive as manufacturers take a more integrated approach to their raw materials rather than regarding them as 'useful' fractions and waste. The costs associated with disposal of the wastes, whether transportation or drying for animal feed, can also be off-set against the operating costs of the purification process.

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Hydrolysis products from glucosinolates in rutabaga (*Brassica napobrassica*, Mill.)*

W. J. MULLIN

Summary

Samples of rutabaga were subjected to two different treatments, one sample was allowed to autolyse and in the other autolysis was kept to a minimum. Both samples were freeze dried. Glucosinolate hydrolysis products from the freeze dried solids were analysed and quantified. The isothiocyanates and nitriles, derived from glucosinolates, were extracted from the freeze dryer condensate and analysed qualitatively. Autolysis reduced the concentration of glucosinolate hydrolysis products and was particularly effective in reducing goitrin content.

Introduction

Of all the cruciferous vegetables consumed, rutabaga (Swede turnip) is second to cabbage in terms of per capita consumption in Canada (Benns, Hall & Beare-Rogers, 1978). In the United States and Europe it is also a staple vegetable being eaten the year round. Its relative ease of cultivation and storage are factors in the popularity of rutabaga. Cruciferous vegetables contain glucosinolates (Kjaer, 1960) which hydrolyze to give isothiocyanates, nitriles and oxazolidinethiones (OZT) (Cole, 1976) that contribute to the aroma and flavour of the vegetable, some of these compounds are also goitrogenic (Van Etten, 1969).

Rutabaga has been identified as the main contributor of glucosinolates to the diet (Mullin & Sahasrabudhe, 1978). The glucosinolate hydrolysis products can be influenced by the pH and endogenous enzyme systems of the vegetable (Daxenbichler, Van Etten & Spenser, 1977). This paper reports the isothiocyanates, nitriles, ionic thiocyanate and OZT which are formed by the hydrolysis of glucosinolates in rutabaga.

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Material and methods

Sample preparation

A 20 kg bag of washed rutabaga roots (*cv* Laurentian) was purchased at a local market. The roots were stored for one week at 4°C before processing. They were divided into two lots and subjected to different treatments. Lot 1 (10.6 kg) was diced into 1–2 cm cubes, immediately frozen by immersion in liquid nitrogen, and stored in closed polyethylene bags at −5°C. Lot 2 (4.4 kg) was diced then mascerated in a Comitrol 3600 (Urschel Labs, Valparaiso, Indiana) which was fitted with a cutting head (2–K–030–120D) having ⅛″ openings. The finely ground product was placed in glass dishes, covered with aluminium foil and left at room temperature (25°C) for 24 h, allowing autolysis of glucosinolates to take place, then frozen to −5°C. The samples were freeze dried separately (F.J. Stokes Model 902–003–1), the solids were ground to a fine powder and stored at −5°C before analysis.

The freeze dryer condensate from each sample was collected and thawed. From the total condensate, measured amounts were placed in five separating funnels (total volume of condensate used = 2.8 l). Methylene chloride was added to each separating funnel, the mixtures were shaken, allowed to separate and the methylene chloride layer removed. The extraction was repeated and the combined extracts (525 ml) dried overnight with anhydrous sodium sulphate. The dried extract was concentrated to 0.5–0.7 ml under a slow steam of dry nitrogen while being kept at 0°C in an ice bath. The concentrate was analysed by gas chromatography (GC). It was only possible to obtain qualitative data from the concentrate. Incomplete trapping of volatiles in the freeze dryer, losses of volatile constituents during the extraction and concentration of such large samples were unavoidable.

The freeze dried solids were analysed for glucosinolates hydrolysis products by the method of Wetter & Youngs (1976) with minor modifications. To inactivate endogenous myrosinase a portion of the powdered sample was heated to 95°C in a water bath. Boiling buffer (pH 7.0) was added and the sample kept at 95°C for 30 min. After cooling a solution of myrosinase (extracted from *Brassica hirta*, Moench) and methylene chloride was added then the mixture was shaken for 2 hr. The tubes were centrifuged and the methylene chloride layer was used for OZT and GC analysis. For GC analysis 5 ml of the methylene chloride layer was concentrated to 1.0 ml. Concentration of this quantity of extract did not result in the loss of glucosinolate hydrolysis products and reliable quantitative data were obtained. OZT was measured according to the method of Wetter & Youngs (1976) without concentrating the methylene chloride extract.

Thiocyanate concentration, a measure of the indolyl glucosinolates, was measured according to the method of Josefsson (1968).

Analysis

The GC was a Perkin Elmer 3920 fitted with dual flame ionization detectors and 2 m × 2 m i.d. glass columns packed with 80/100 mesh Chromosorb W HP coated with 1.5% OV 17 liquid phase. After an initial isothermal period of 8 min at 50°C, the column oven temperature was increased 8°C/min to 210°C remaining at this temperature for 16 min. The carrier gas was helium. The injectors and detectors were maintained at 230°C and 250°C respectively. An internal standard, methyl palmitate, was added to each sample immediately before commencing GC analysis. The sample volume injected was 4 μl. Response factors, relating to the internal standard, were calculated independently using standard compounds or homologues. No suitable standards for the s-methyl compounds could be obtained, the response factor was arbitrarily assigned as 1.0 with respect to methyl palmitate.

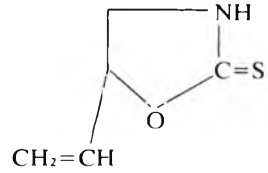
The gas chromatography–mass spectrometry (GC–MS) analysis of methylene chloride extracts was carried out on a Finnigan Model 3100D interfaced with a Finnigan 6100 data aquisition system. The GC columns and temperature programme were the same as already described. The MS separator and transfer lines were maintained at 250°C. A mass range of 35–500 was scanned.

Results and discussion

The major glucosinolate hydrolysis products which were found in this study are listed in Table 1. In the following text these compounds are referred to by the Reference Number assigned to them (Table 1). The data processing system of the GC–MS was used to subtract the spectrum of the preceeding valley or shoulder from the spectrum scanned at maximum total ion current. In this way the mass spectrum was effectively cleaned of background interference spectra. The mass spectra of I and III showed fragments at m/e 61 (CH_3–SCH_2+) and M–47 (M–CH_3–S+). The molecular ion of m/e 129 indicated compound I as being 4-s-methyl-1-cyanobutane; the molecular ion of m/e 143 indicated compound III as being 5-s-methyl-1-cyanopentane. Further confirmation of the identities of compounds I, III and IV was gained by comparing their mass spectra with the data of higher homologues published by MacLeod & Islam (1976). The major ion fragments of compound II were identical to those of the mass spectrum of 3-phenylpropionitrile published by MacLeod & Islam (1975, 1976). Compound IV gave fragments of m/e 61 and 72 indicating CH_3–S–CH_2+ and CH_2NCS + ions respectively. Other ion fragments together with the molecular ion of m/e 161 were consistent with the presence of 4-s-methyl-1-butylisothiocyanate.

Compound IV has been previously described by Kjaer & Gmelin (1955) where it was found to occur in seeds of *Eruca sativa*, Mill., and was noted as having a radish-like smell and flavour. The related nitrile (I) was not described.

Table 1. Glucosinolate hydrolysis products from rutabaga

Reference number	Compound	Formula	Retention time (min)	Glucosinolate hydrolysis products (μg/g fresh weight)	
				Lot 1 freeze dried diced solids	Lot 2 freeze dried ground solids
I	4-s-methyl-1-cyanobutane	$CH_3S(CH_2)_4CN$	17.6	10.80	8.47
II	3-phenylpropio-nitrile	$C_6H_5C_2H_4CN$	18.4	4.34	1.92
III	5-s-methyl-1-cyanopentane	$CH_3S(CH_2)_5CN$	18.9	0.00	0.02
IV	4-s-methyl-1-butylisothiocyanate	$CH_3S(CH_2)_4NCS$	21.6	29.90	7.11
V	2-phenyethy-1-isothiocyanate	$C_6H_5C_2H_4NCS$	22.3	20.31	3.73
VI	5-vinyloxazolidine-2-thione		25.7	161.40	17.00
	Methyl palmitate (internal standard)		27.4		
	Ionic thiocyanate SCN		—	15.27	15.36

Compounds I–VI identified by GC–MS

Two compounds, V and VI were identified by reference to standards of known purity (phenylethylisothiocyanate, Eastman Kodak Co., Rochester, New York; goitrin was a gift from C.H. van Etten, U.S.D.A. Peoria, Illinois). They gave identical GC retention times and GC–MS data when compared to their respective standards. Goitrin, compound VI, was not quantitated by GC due to its non linear response factor. No 5-s-methypentyl isothiocyanate was detected in this study, although it has been found in some other rutabaga cultivars during our current work on intercultivar variations of glucosinolates in rutabaga. The precursor of compound III is likely to be 5-s-methylpentylisothiocyanate.

Ionic thiocyanate (Table 1) content of the two samples of freeze dried solids was constant. SCN^- is the result of the hydrolysis of indolyl glucosinolates; p-hydroxybenzyl glucosinolate also gives SCN^- on hydrolysis but has not been reported to be present in rutabaga. Indolyl glucosinolate hydrolysis products are not known to affect the flavour or odour of plant materials but SCN^- does contribute to the goitrogenic effects.

The autolysis of glucosinolates in cruciferous plants is difficult to control and may lead to the formation of nitriles. Friis & Kjaer (1966) described the difficulties in extracting intact glucosinolates from radish roots. Elaborate precautions taken to prevent hydrolysis were only partially effective. Autolysis of glucosinolates in cruciferous plants resulting in nitrile formation have been described by Daxenbichler *et al.* (1977) and Cole (1976). In the analysis of glucosinolates from the freeze dried solids by the method of Wetter & Youngs (1976), endogenous myrosinase is destroyed by heat treatment. The subsequent addition of an external source of myrosinase buffered at pH 7.0 should eliminate the formation of nitriles.

In this study the autolysis of the diced sample was kept to a minimum. The GC analysis of the methylene chloride extract of the freeze dried solids showed some nitriles present. These were not removed from the solids during the freeze drying process because of the more intact structure of the diced material. Autolysis would have been caused by the rupture of cells and release of myrosinase (Kjaer, 1960) in the cutting and freezing processes. The most prominent glucosinolate hydrolysis product found in the diced solids was OZT. In the mashed autolysed sample a considerable reduction in the isothiocyanates and OZT was observed. OZT was reduced to one tenth of the amount found in diced rutabaga (Table 1) and nitriles were found in higher concentrations than their parent isothiocyanates. The reduction in OZT by autolysis should have been accompanied by the appearance of hydroxy nitriles (Daxenbichler *et al.*, 1977). These nitriles were not observed in the freeze dried solids or the methylene chloride extract of the freeze dryer condensate. Small amounts of compounds I–VI were found in the freeze drier condensate extracts. Not surprisingly the involatile SCN^- and OZT were not detected in the freeze dryer condensate extract.

From these results it is obvious that sample preparation plays a major role in the concentration and relative proportions of the glucosinolate hydrolysis products remaining in rutabaga. In practical terms, the time between preparation

and cooking will have a major effect. The amount of isothiocyanates and nitriles remaining in the cooked product will depend on the method of cooking. Boiling in an open vessel should reduce the concentration but microwave oven or pressure cooking would lead to retainment of glucosinolate hydrolysis products. Endogenous myrosinase would be inactivated by boiling or blanching during processing. In the analysis scheme used in this study there is no differentiation between the nitriles and isothiocyanates formed and trapped in the dried products before analysis and those formed from intact glucosinolates. The proportions of intact to hydrolysed glucosinolates in cruciferous vegetables is the subject of a future study.

Acknowledgments

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The resistance of dry spores of *Bacillus subtilis* var. *globigii* (NCIB 8058) to solutions of hydrogen peroxide in relation to aseptic packaging

Q. J. SMITH* AND K. L. BROWN

Summary

The resistance to solutions of hydrogen peroxide of dry spores of *Bacillus subtilis* var. *globigii* (NCIB 8058) was studied between concentrations of 10 and 30% (w/v) at temperatures from 20 to 50°C. Logarithmic relationships were obtained between decimal reduction time and temperature at different concentrations of hydrogen peroxide. The difference between the resistance of wet and dry spores to hydrogen peroxide is discussed.

Introduction

Many aseptic packaging systems utilize plastics, paperboard or foil containers in which to pack the sterilized product. Hydrogen peroxide is frequently used to sterilize the packaging material (Hedrick, 1973a,b; Sacharow, 1973; Toledo, 1973) since it is readily decomposed to products which will neither taint the food nor render it toxic (Cukor, 1973). Hedrick (1973b) has also reported that trace residues of hydrogen peroxide in food do not have a harmful effect when consumed.

Commercial packaging systems employ hydrogen peroxide at concentrations of 10–35% at either room or elevated temperatures (Buchner, 1978; Hedrick, 1973b; von Bockelmann, 1974; von Bockelmann & von Bockelmann, 1972) in the form of a spray or immersion bath (Buchner, 1978). The sporicidal action of hydrogen peroxide has been reviewed by von Bockelmann & von Bockelmann (1972). Both linear (Swartling & Lindgren, 1968; Ito *et al.*, 1973; Toledo, Escher & Ayres, 1973) and non linear (Cerf & Hermier, 1972) relationships between log number of survivors and time of exposure to different concentrations of hydrogen peroxide have been reported.

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Von Bockelmann & von Bockelmann (1972) in reviewing the subject, emphasized the need to know more about the differences in sensitivity of wet and dry spores. For example, Ito *et al.* (1973) have reported dry spores of *Clostridium botulinum* strain 169B to be more resistant than wet spores, whereas Toledo *et al.* (1973) working with *Bacillus subtilis* SA22 showed wet spores to be more resistant. In practice, dry spores are more likely to be encountered on packaging material.

The work reported here has been carried out using dry spores of *Bacillus subtilis* var. *globigii* (NCIB 8058), which is identical to the strain ATCC 9372 used by Toledo *et al.* (1973). This organism produces spores which are among the most resistant to hydrogen peroxide. Sterilization procedures using hydrogen peroxide based on resistance data for dry spores of this organism should therefore be more than adequate to destroy most other bacterial spores on the packaging material.

Materials and methods

Organism

Bacillus subtilis var. *globigii* (NCIB 8058) produces two colony types, translucent (T) and dense (D). Spores from type T colonies have been reported to be resistant to hydrogen peroxide (B. Fitzpatrick, Londreco Ltd., personal communication), and were used in this study.

Cultures were maintained on slopes of plate count agar (Oxoid CM183) at 30°C. Spores were harvested from lawn growths on plates of nutrient agar (Oxoid CM3) after 5 days incubation at 30°C, by suspension in sterile distilled water. The suspensions were pasteurized in 150 ml round bottles by placing the bottles in a steamer at 100°C for 5 min. By experiment, this method gave a final equilibrium temperature between 65 and 70°C which was sufficient to kill the vegetative cells. Spore suspensions were then stored at 4°C.

Heat resistance

Small glass spheres, approximately 5–7 mm diameter, blown from melting point tubes were filled, using an 'Agla' micro-syringe, with 0.025 ml of spore suspension (4.28×10^8/ml) and sealed in a flame. They were heated in a water bath at 71.7 and 96.0°C for a series of time intervals. After removal from the bath, the spheres were immersed in 95% ethanol to cool and clean the external surfaces. They were then transferred aseptically to 1 oz bottles containing 10 ml sterile distilled water. The spheres were then crushed and shaken, and survivors were enumerated in nutrient agar plates after incubation at 30°C for 48 h.

Hydrogen peroxide

Solutions of required concentrations were prepared from 50% (w/w) solution (BDH) by dilution with distilled water and were stored at 4°C. Working solution strengths were checked regularly by hydrometer and pH measurement while stock solutions were checked by titration with potassium permanganate solution.

Recovery medium

Spores were enumerated in nutrient agar (Oxoid CM3) to which neutral red had been added to a final concentration of 0.005% (w/v). This indicator changed from red to blue in the presence of hydrogen peroxide and therefore acted as an indicator of carry-over of hydrogen peroxide to the recovery medium. Acid production by the test organism during incubation caused a change in colour from red to yellow which aided colony counting.

Preparation of slides

Microscope slides (3 × 1″) were degreased overnight in hydrochloric acid (50% conc. HCl, 50% water) and were then washed well in distilled water and dried. One end was marked off for handling with forceps. The slides were sterilized by autoclaving at 121°C for 15 min. After each experiment they were recycled by autoclaving in water and returning to the acid soak.

Treatment with hydrogen peroxide

Tenfold dilutions of the stock spore suspension containing 4×10^8 spores/ml were prepared in distilled water and 0.25 ml aliquots were dried onto the slides at 55°C overnight. There was no evidence of reduction of initial spore count using this treatment which produced dried smears within a reasonably short time.

The spores were treated by dipping the slides into solutions of hydrogen peroxide in staining jars, the temperatures of which were controlled to within ± 0.5°C by a water bath. Following treatment, the slides were washed twice by dipping in sterile tap water to remove residual hydrogen peroxide. The slides were then placed into Petri dishes and the recovery medium poured over them. Air bubbles were released from beneath the slide by lifting one edge with a flamed scalpel during pouring of the agar.

Acidification of hydrogen peroxide

The hydrogen peroxide solutions employed here were naturally acidic (Fig. 1). Cerf & Hermier (1972) reported that the acidification of 15% hydrogen

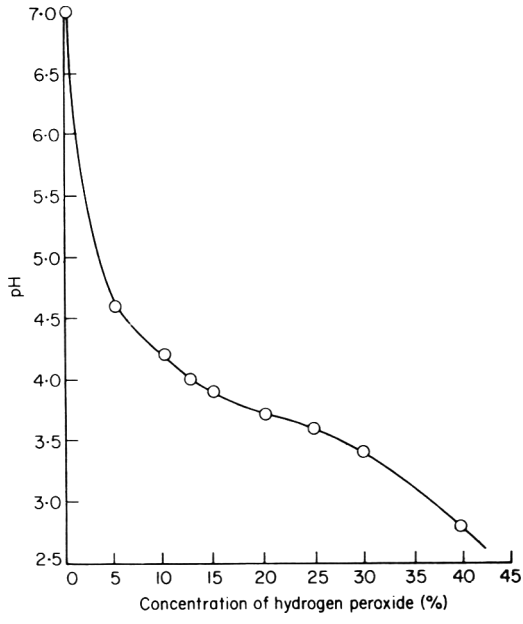

Figure 1. pH of solutions of hydrogen peroxide at room temperature (20–22°C).

peroxide at 80°C increased its effectiveness against *B. subtilis* SJ2 spores but reduced its effectiveness against *B. cereus* III spores. The effect of lowering the pH of 10% hydrogen peroxide with 3,3, dimethylglutaric acid (DMGA) (Koch Light Ltd.) was investigated. This acid has been used by the authors in a buffer system (Stafford, Watson & Rand, 1955) in studies on the heat resistance of bacterial spores.

Acidification was achieved by mixing equal volumes of 20% hydrogen peroxide and 50 mmol/l DMGA just prior to use to produce a 10% solution of hydrogen peroxide with a pH of 2.5. The normal pH of 10% hydrogen peroxide is 4.2. Treatment of the spores with the acidified hydrogen peroxide was carried out as described previously.

Incubation and recovery

In order to determine the optimum incubation time and the effect of drying of the spores after treatment, the following trial was carried out. Spores which had been treated with 5% hydrogen peroxide were either dried at 55°C after the washing procedure or were left wet. The agar was then poured on as described earlier, and colonies counted after various incubation times at 30°C.

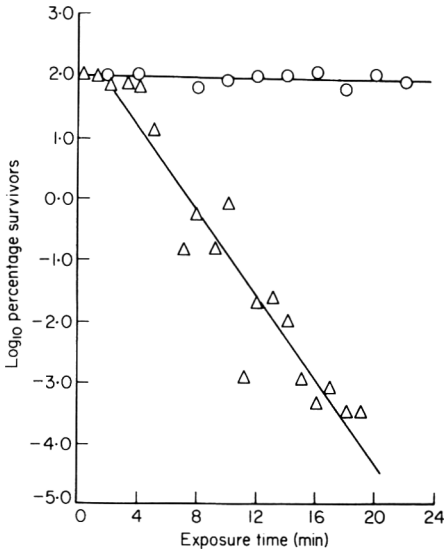

Figure 2. Thermal destruction of spores of *B. subtilis* var. *globigii* at 71.7°C (○) and 96.0°C (△).

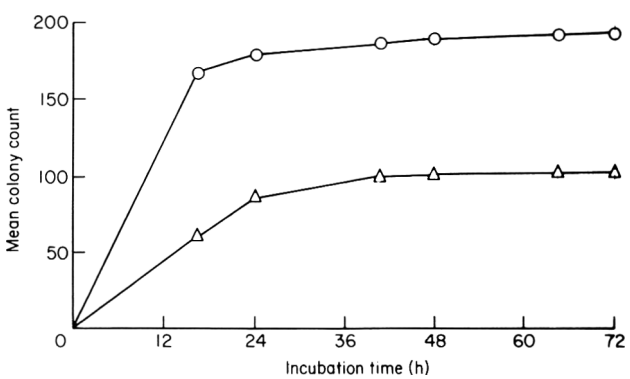

Figure 3. Comparison of wet (○), and dry (△) recovery of spores of *B. subtilis* var. *globigii* after treatment with 5% hydrogen peroxide for 3 min at room temperature.

Results

Heat resistance

Results were plotted (Fig. 2) as log percentage survivors against exposure time and curves fitted by linear regression. The time taken for a tenfold reduction in surviving spores ('D' or decimal reduction time) was calculated. At 96°C the D-value was 3.0 min while at 71.7°C the D-value was approximately 4 h.

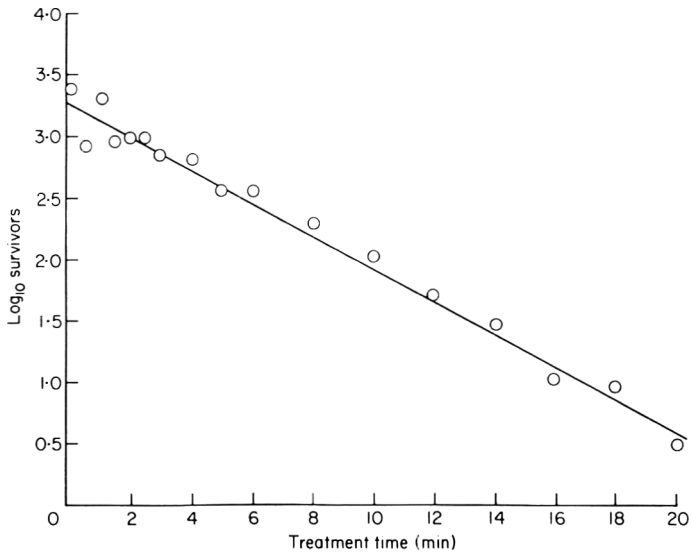

Figure 4. Reduction in number of viable spores of *B. subtilis* var. *globigii* with time of treatment in 15% hydrogen peroxide at room temperature.

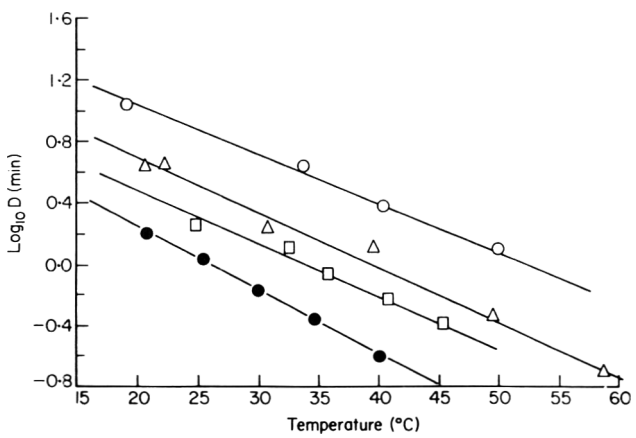

Figure 5. Relationship of decimal reduction time (D) to temperature, for spores of *B. subtilis* var. *globigii* at hydrogen peroxide concentrations of 10%, (○); 20% (△); 25%, (□); and 30%, (●).

Incubation and recovery

Drying the spores following treatment with hydrogen peroxide significantly impaired recovery (Fig. 3). Colony development appeared to be complete after 48 h. Consequently in all the resistance experiments spores were recovered 'wet' with an incubation of 48 h at 30°C.

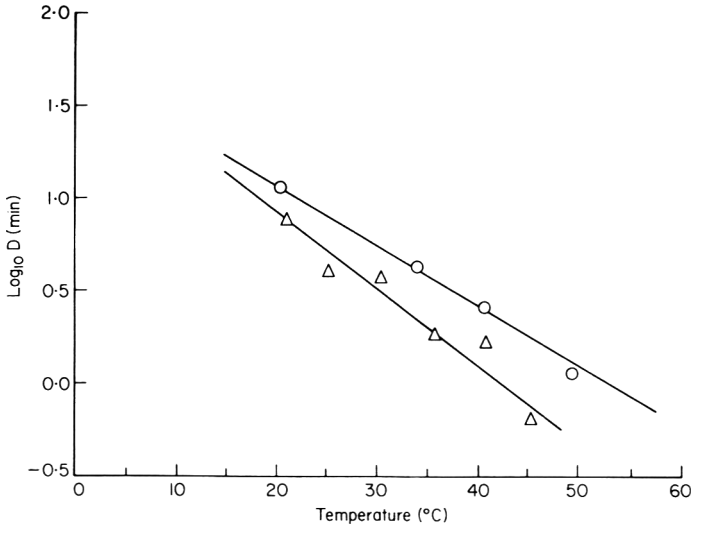

Figure 6. Sporicidal action of 10% hydrogen peroxide non-acidified, (○), or acidified with 0.025 M 3,3, Dimethylglutaric acid, (△).

Hydrogen peroxide resistance

The number of survivors per slide was multiplied by the appropriate dilution to relate all counts. For each treatment the log number of survivors was then plotted against exposure time and the best straight line fitted by linear regression. A typical result is shown in Fig. 4. D-values were calculated from the slopes of the survivor curves. Plotting log D against temperature produced a series of near parallel regression lines corresponding to different concentrations of hydrogen peroxide (Fig. 5).

Acidification of hydrogen peroxide

The resistance of the spores in the acidified solution was compared with the resistance in non-acidified hydrogen peroxide (Fig. 6). Acidification reduced the resistance and also increased the slope of the regression line of log D against temperature. Part of this effect may in fact have been due to the formation of organic peroxides with the buffer solution.

Discussion and conclusions

Bacterial spores are usually present in low numbers on packaging materials used in aseptic systems. Swartling & Lindgren (1968) reported 0.04 spores/cm^2 on Tetra Pak paper while Buchner (1978) found the bacterial count on synthetic material foils to be in the range 0.004–0.1/cm^2 and on layered cartons and

lacquered aluminium foil in the range 0.01–0.02/cm². Such spores will be dry and although there is a substantial amount of published data on resistance of wet spores to hydrogen peroxide, there is comparatively little on the resistance of dry spores (Ito *et al.*, 1973; Neal & Walker, 1977; Swartling & Lindgren, 1962; Toledo *et al.*, 1973).

It is well known that bacterial spores are more resistant to dry heat than wet heat and that *z*-values (the number of degrees Celcius to effect a tenfold decrease in the D-value) obtained from dry heat resistance data may be two or three times greater than those obtained from moist heat resistance data (Russell, 1971). In comparison, the resistance of the dry spores of *B. subtilis* var. *globigii* to hydrogen peroxide reported here is approximately half that of the wet spores of the same strain studied by Toledo *et al.* (1973). Calculation of *z*-values gave figures of 30.4, 24.2, 28.1, 31.5 and 23.8°C at hydrogen peroxide concentrations of 10, 12.5, 20, 25 and 30% respectively for the dry spores of *B. subtilis* var. *globigii* studied here. Toledo *et al.* (1973) however obtained a *z*-value of 40°C for wet spores of the same strain in 25.8% hydrogen peroxide. Calculation of *z*-values from the data of Swartling & Lindgren (1968) using only the linear portions of their curves gave values of 46, 52 and 47°C for wet spores of *B. subtilis* in 10, 15 and 20% hydrogen peroxide respectively. From the work of Curran, Evans & Leviton (1940), *z*-values calculated for wet spores of *B. albolactis*, *B. cohaerens*, NCA 9499 and NCA 1518 were 27, 31, 28.5 and 21°C respectively in 1% hydrogen peroxide. The resistance of wet and dry spores to hydrogen peroxide does not therefore appear to be related to wet and dry heat resistance. Comparing the data here with that of Toledo *et al.* (1973) shows dry spores of *B. subtilis* var. *globigii* to have lower resistance to hydrogen peroxide and lower *z*-values than wet spores which is the reverse of the published data on heat resistance.

With the exposure times and temperatures employed here, there would be little effect from thermal destruction of the spores (Fig. 2). This was also found by Swartling & Lindgren (1968).

The *z*-value curve of Toledo *et al.* (1973) based on the D-values of *B. subtilis* var. *globigii* in 25.8% hydrogen peroxide crosses the *z*-value curve of the 25% hydrogen peroxide data presented here at about 27°C. Toledo *et al.* (1973) found that wet spores were more resistant than dry spores at 24°C in 25.8% hydrogen peroxide. From Fig. 5, the resistance of the dry spores studied here was estimated at this temperature and concentration and compared with the data of Toledo *et al.* (1973) for wet spores. Although the data are not exactly comparable, the results suggest that wet spores would be more resistant than dry spores under these conditions, but below about 23°C dry spores would appear to be more resistant. Cross over of wet and dry *z*-value curves for the spores of the same organism when exposed to the same concentration of hydrogen peroxide may explain why Ito *et al.* (1973) found dry spores of *Clostridium botulinum* to be more resistant than wet spores at 25°C. In practice, therefore, comparisons of hydrogen peroxide resistance of wet and dry spores at a single temperature appear to be of limited value and may be misleading.

It has been shown by a number of workers including Murrell & Scott (1966), Härnulv & Snygg (1972), Senhaji, Bimbenet & Le Maguer (1976) and Lubieniecki-von Schelhorn (1972) that the heat resistance of bacterial spores is dependant on the water activity of their surroundings. Maximum resistance occurs with a water activity around 0.2 to 0.5. Since wet spores appear to be more resistant to peroxide than dry spores it would be interesting to know what effect, if any, water activity has on peroxide resistance.

It has also been shown that the shape of heat resistance survivor curves depends on whether the spores are exposed to wet or dry heat (Härnulv & Snygg, 1972; Fox & Eder, 1969), with initial shoulders being reported for wet heat and an initial concavity for dry heat. Cerf & Hermier (1972) obtained both initial shoulders and concavities in peroxide resistance curves for wet spores of a number of species. When the wet and dry peroxide resistance curves obtained by Toledo *et al.* (1973) for *B. subtilis* and by Ito *et al.* (1973) for *Cl. botulinum* are compared there is little difference between the shapes of the survivor curves obtained. The curve presented here (Fig. 4) for dry spores of *B. subtilis* var. *globigii* appears to have a small initial shoulder which was typical of the results obtained. The linear portions of the survivor curves were used for calculation of the D-values.

Tailing of survivor curves was not experienced here. Curran *et al.* (1940) found less than 1% of the surviving spores present in the tail, while Swartling & Lindgren (1968) only obtained tails at low survivor levels and ignored them. Cerf & Metro (1977) investigating tailing in more detail, concluded that tailing of survivor curves was not due to a mutual protective effect of the spores and the tail did not represent a resistant fraction.

The sporicidal properties of hydrogen peroxide have been shown to increase with a decrease in pH (Cerf & Hermier, 1972; Curran *et al.*, 1940) although Wallen (1976) found no significant effect on sporicidal activity by varying the pH of hydrogen peroxide between 2.2 and 7.2. The results obtained here showed that acidification of 10% hydrogen peroxide increased its sporicidal activity (Fig. 6).

Neal & Walker (1977) used a similar technique to that reported here, drying spores onto tinplate and then dipping this into 9.2% hydrogen peroxide at 33°C. The spores were then dried at 34°C before recovery which from the results obtained here (Fig. 3), would tend to depress recovery. Swartling & Lindgren (1962) also found that heating following hydrogen peroxide treatment increased the sterilizing effect.

Replotting the data of Swartling & Lindgren (1968) for wet spores of *B. subtilis* with log D-value against temperature also produced a series of near parallel lines corresponding to different concentrations of hydrogen peroxide (Fig. 7). However when compared with Fig. 5 it can be seen that the resistance of the dry spores of *B. subtilis* var. *globigii* was greater up to 60°C.

In conclusion, dry spores of *B. subtilis* var. *globigii* (NCIB 8058) were less resistant than the wet spores studied by Toledo *et al.* (1973). Increasing temperature, concentration of hydrogen peroxide and increasing acidity all

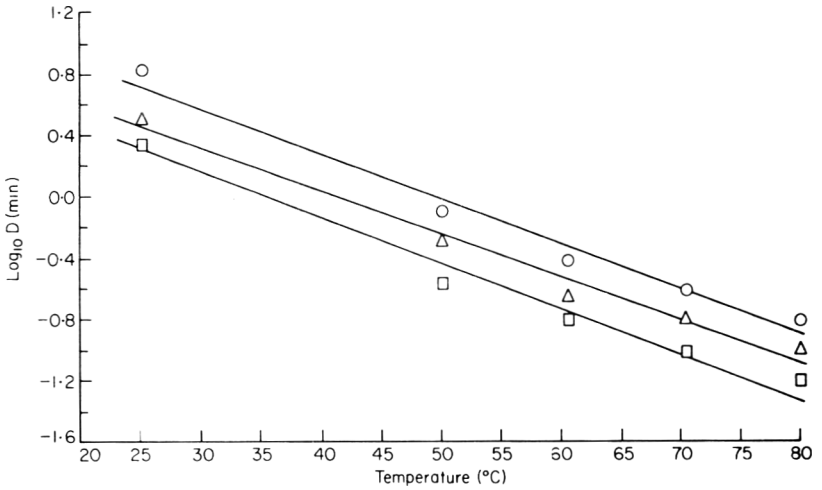

Figure 7. Relationship of decimal reduction time (D) to temperature, for spores of *B. subtilis* NCDO 736 at hydrogen peroxide concentrations of 10%, (○); 15%, (△); and 20%, (□). (from Swartling & Lindgren, 1968.)

increased sporicidal activity. Crossover of z-value curves of wet and dry spores suggests that under certain conditions, dry spores may be more resistant to hydrogen peroxide than wet spores. This would have to be taken into account when setting sterilization procedures for aseptic packaging. Heating following hydrogen peroxide treatment, as used in some systems, (Buchner, 1978) increased the sporicidal effect.

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Dehydration of onion: some theoretical and practical considerations

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Summary

Yellow globe type onion slices were dehydrated with air at different temperatures and flow rates. Drying-rate curves were constructed and used for the calculation of critical moisture content, drying constant, effective diffusivity of moisture through the slices and energy of activation for diffusion. Rehydration rates at 25 and 40°C were also determined and found to be independent of drying conditions. An attempt to relate the process of moisture removal to the process of rehydration was made and a possible diffusion mechanism based on the concept of internal and external resistances is discussed.

Introduction

Dehydrated onion has become a standard ingredient in nearly every processed food product in which raw onion can be used. A large part of the dehydrated onion production is used as seasoning in production of catsup, chili sauce and meat casseroles, as well as cold cuts, sausages, potato chips, crackers and other snack items. Food service outlets also use dehydrated onion because of its convenience in storage, preparation and use. The quantity of dehydrated onion and other dehydrated horticultural crops sold to the retail market is, however, still very small and this can be attributed, in part, to the large loss of flavour which occurs during processing.

In spite of the considerable effort and some progress made in recent years, in the understanding of the chemical and biochemical changes, that occur during dehydration and in some isolated studies on the mechanism of food dehydration (Jason, 1958; Fish, 1958; Saravacos & Charm, 1962), drying of solid foods remains still largely an art. Improvement of the drying process is essential if further growth of the dehydration industry is to be expected.

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The drying of solid foods, such as onion, is usually taken to mean the removal of moisture from the solid by evaporation (Fulford, 1969). The heat required for evaporation has to be supplied to the material, therefore, heat and mass transfer occur simultaneously. There are many published mathematical models available for estimating simultaneous heat and moisture transfer in dehydrated material (Henry, 1948; Krischer, 1963; Lykov & Mikhailov, 1965; Whitney & Porterfield, 1968; King, 1968; Harmathy, 1969; Berger & Pei, 1973; Hayakawa & Russen, 1977). The main difficulty in describing transport of heat and mass inside porous food materials, based on microscopic analysis, is that the geometry of the structure is not easily described quantitatively, while the individual transport process relate to local values of temperature, pressure and composition.

The mathematical model provided by Henry (1948) accounts for the interaction which occurs during the simultaneous transfer of moisture and heat. According to this model, moisture transport is assumed to occur only in the vapour phase, and the interaction between heat and mass transfer is accomplished with the assumption that water vapour concentration is at all times during the transfer process, a linear function of moisture content and temperature. Capillarity within the air space and hysteresis are neglected. Krischer (1963) provided a model consisting of differential heat and mass transfer equations which accounts for simultaneous transfer of water by capillary forces and by vapour diffusion, in series, in parallel, or in more complex series and parallel combinations. This model requires the use of two diffusion coefficients to account for the two mechanisms of moisture transfer. Unfortunately, both these quantities depend on the nature of the material, the nature of the pore structure, the moisture content and temperature. The lack of these coefficients and the complicated calculating procedure are pointed out by Fulford (1969) as major factors detracting from the use of this model. Another approach to generalizing the problem of internal heat and moisture transfer during drying has been made by Lykov & Mikhailov (1965). This approach has been based on the application of the methods of the thermodynamics of irreversible processes to the case of internal heat and moisture transfer during drying. Essentially, the moisture transfer is split into two parts, one due to the moisture transfer driving force, which is specially defined in an attempt to encompass most of the mechanisms of moisture transfer and which is characterized by a moisture diffusivity coefficient, and one due to the temperature gradient, which is characterized by the thermo-gradient coefficient. Lykov & Mikhailov's analysis, however, is not rigorous from the non-equilibrium thermodynamic point of view. The solutions they give for the set of differential equations all assume constant transport coefficients, making the solutions unsuitable for description of drying foods.

Whitney & Porterfield (1968) modified Henry's mathematical model to account for internal heat generation to simulate heating of peanuts. King (1968) provides an interesting theoretical analysis of simultaneous heat and mass transfer in dehydrated foods which is then successfully used to account for

seemingly anomalies in observations by various workers relating to various moisture diffusivity values. The author, through the combined use of Fick's first law for binary gaseous diffusion, Fourier's law of heat conduction in solid, and a modified form of the Clausius-Clapeyron equation, derives a variable diffusivity equation wherein the effective diffusivity is a function of both temperature and moisture content. The assumptions made are vapour-phase diffusion only, vapour-sorbed moisture equilibrium at each point within the body, constant sorption heat, and negligible sensible heat.

Harmathy (1969) developed a theory for heat and mass transport based on the assumption that all movement of moisture in porous material takes place in the gaseous phase. This theory seems a good approximation to drying of materials with low initial moisture content. At higher moisture contents, however, capillary transport and/or surface diffusion will take place in addition to the transport of water in the gas phase (King, 1968). The mathematical model comprises a set of second order, non-linear partial differential equations and was solved numerically with convective boundary conditions.

Berger & Pei (1973) used a mathematical model similar to Krischer's to describe drying of capillary-porous solids. Their model differs in that they use the sorption isotherm in the hygroscopic region and the Clausius-Clapeyron equation at greater than maximum sorptional moisture content.

Hayakawa & Rossen (1977) examined a procedure for estimating simultaneous heat and moisture transfer in capillary-porous material of an infinite slab shape when the values of the heat transfer Fourier number were large. For this examination, they used analytical formulae obtained from the Lykov & Mikhailov model and found that the transfer potentials could not be estimated accurately.

In summary, despite efforts made to develop a theoretical model for the drying process, the experimental approach still has a place in the study of food dehydration. It is, therefore, the purpose of this paper to present the results of a study aimed at understanding the dehydration of onion slices in terms of evaporation, diffusion and sorption processes. Rehydration rates at 25 and 40°C are also presented and an attempt to relate the mechanism controlling rehydration to the one controlling moisture removal is made.

Materials and methods

Onion

Yellow globe type onion (*cv* Improved Autumn Spice) grown to maturity in experimental plots at the Alberta Horticultural Research Center, Brooks, Alberta were used. The onions were planted in early April, 1977, harvested the middle of September when the tops were down, and cured and graded indoors before storage in bins at 1–2°C. The onions were held in storage for about 1 week before the dehydration experiments were initiated. At this stage, the

mean dry matter content of the fresh onion, as estimated by the loss in weight of 10–15 g samples on drying in a vacuum oven at 70°C and 48.8 mmHg for 6 hr, was 12.8%.

Pilot-plant scale dehydration

Medium sized bulbs (4.5–7.5 cm in diameter) were peeled, sliced (1.5 mm thick) and dehydrated in a 0.3125 m^2 bed area Vibro Fluidizer (Niro Atomizer, Copenhagen). Three temperatures (40, 50 and 65°C) and three air flow rates (5.5, 8.1 and 10.3 m^3/min) were studied. The dryer consisted of a perforated plate built into a long, narrow, enclosed chamber. The unit was equipped with an air filter, an air supply fan of the centrifugal type, with built-in damper, an electric air heater, a vibrator, a cyclone, an exhaust fan, also of the centrifugal type with built-in damper, and connecting ducts and control panel. The air velocity was measured using a pitot tube connected to a Mark 5 Testing Set (Airflow Developments Ltd., High Wycombe, England) and it was changed by adjusting the damper in the air supply and exhaust fans. The dry-bulb and wet-bulb temperatures (T_{DB} and T_{WB}) were measured with thermocouples connected to a Honeywell Electronik 16 temperature recorder (Honeywell Ltd., Scarborough, Ontario). The wet-bulb temperature was obtained by covering the end of a thermocouple with a wick immersed in a bottle containing distilled water.

Dehydration rate: effect of air temperature and flow rate

Drying curves (X *vs* time) were obtained by graphical integration of the thermographs and/or by periodic weighing of onion samples during dehydration. The equilibrium moisture content (X_e) of the dehydrated product, required for the drying calculations, was determined by the saturated-salt-solution method (Mazza & LeMaguer, 1978). The values of the critical moisture content (X_c) were obtained from the drying-rate curves of the abscissa (X) corresponding to the end of the constant-rate period. The falling-rate period was studied by plotting the data on a semilog paper as log ($X-X_e$) *vs* time (θ). The slope of the curves so obtained were measured and expressed as the drying constants. The effective diffusivity of moisture was determined by applying the procedure suggested by Perry (1950). One-half of the average thickness of the fresh onion slices and one-half the thickness of the dry slices were used for the drying calculations. The thickness of the onion slices after various lengths of drying, was determined from specific volume measurements made by the displacement of toluene.

Rehydration rate

Rehydration was measured in distilled water at 25 and 40°C. Five grams of dehydrated onion were added to 150 ml of distilled water in a 250 ml beaker,

mixed thoroughly, and allowed to rehydrate for various lengths of time (see Fig. 6). At the end of the rehydration period the onion was filtered off using a No. 4 Whatman filter paper and slight vacuum, and weighed. The rehydration was expressed as kg water per kg dry material. The rehydration rate was studied by plotting the data on a semilog paper or $\log (X_{00}-X)$ *vs* time (θ), where X_{00} refers to the moisture content, expressed as kg H_2O/kg DM, at the end of rehydration and X refers to the moisture content at time θ. The slopes of the curves so obtained were measured and expressed as the rehydration constants. The diffusivity of moisture in onion slices was determined as outlined above.

Results and discussion

The effectiveness of increasing the drying air temperature in accelerating dehydration of onion slices is illustrated in Fig. 1, the advantages being especially apparent in the later stages of dehydration. The increasing effectiveness of increased air temperature as the moisture content of the product is reduced to lower and lower levels, is in accordance with the mechanisms of drying at various moisture intervals and has been briefly discussed by Van Ardel, Copley & Morgan (1973).

Figure 2 illustrates the effect of temperature on the rate of drying of onion slices. The drying rate curves pattern is similar to that reported for other foodstuffs (Roman *et al.*, 1979) and this behaviour was observed repeatedly throughout our experiments.

It is, of course, difficult to obtain precise information about the initial stage of drying, since the weight of the slices is falling very rapidly, and the temperature

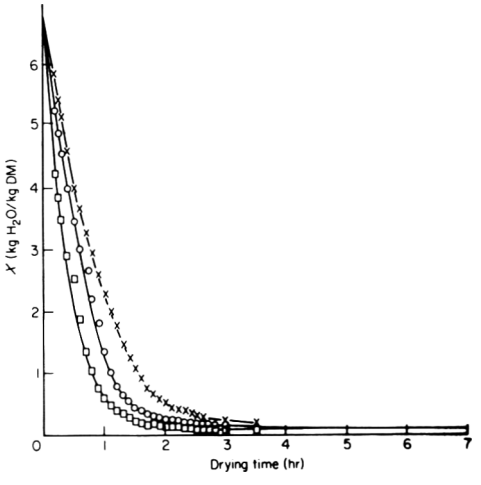

Figure 1. Effect of temperature on the moisture content of onion slices. Drying conditions: yellow globe type onion slices 1.5 mm thick; air flow rate 8.1 m³/min. X, 40°C; ○, 50°C; □, 65°C.

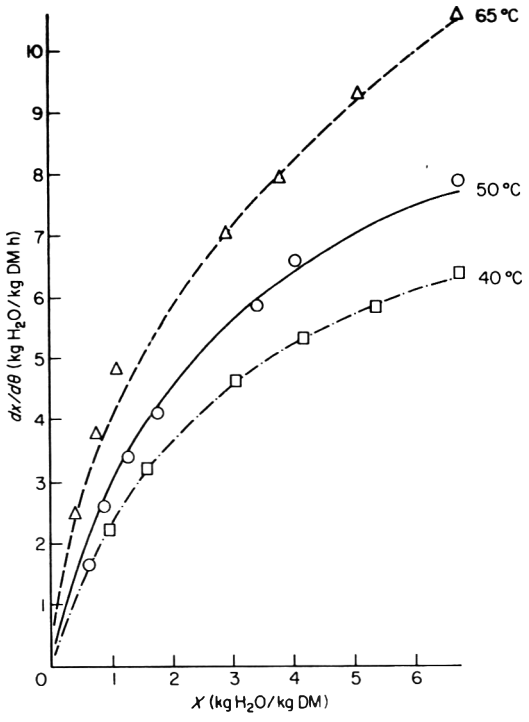

Figure 2. Rate of dehydration of onion slices at 40°C (□), 50°C (○) and 65°C (△).

of the outgoing drying air is rising just as rapidly. A very short constant-rate drying period was observed with onion slices dried comparatively slowly in air at 40°C, but as the temperature was increased to 50 and 65°C the constant-rate period disappeared.

It is well documented (Charm, 1971) that drying proceeds at constant rate as long as evaporation from the surface controls the rate. During the constant-rate period, moisture from the interior migrates to the surface by various means and is vaporized. As the moisture content is lowered, the rate of migration to the surface is lowered and finally the rate of movement to the surface becomes the limiting factor. When drying occurs relatively fast, as it did for onion slices, the amount of water available at the surface soon becomes inadequate to maintain the supply and the rate rapidly declines to a value controlled by liquid diffusion within the food piece.

The critical moisture content (X_c) of the onion slices is considerably higher than those of inorganic materials reported in the literature (Perry, 1950). This may be ascribed to the colloidal and hydrophilic nature of the food materials which causes the water molecules to be held more tightly. As a consequence nearly all of the drying of onion takes place during the falling-rate period. During this period the migration of moisture occurs through the mechanism of diffusion.

The equations governing the transfer of moisture through diffusion are

analogous to the transfer of heat in the transient conduction heating. With a constant diffusion coefficient the following equation (Perry, 1950) expresses the moisture content as a function of time in a slab:

$$\frac{X - X_e}{X_c - X} = \frac{8}{\pi^2}\left[e^{-D\theta(\pi/2L)^2} + \frac{1}{9}e^{-9D\theta(\pi/2L)^2} + \frac{1}{25}e^{-25D\theta(\pi/2L)^2} + \ldots\right] \quad (1)$$

where X, X_c and X_e = average-moisture contents (dry basis) at any time θ, at the start of the diffusional flow period, and at equilibrium with the external conditions, repectively (D = Liquid diffusivity; and L = one-half the thickness of the solid layer through which moisture is diffusing). This equation assumes that drying occurs from both sides of the slab. When evaporation occurs from only one surface, L is total thickness of the solid layer. When the time becomes large, a limiting form of equation (1) is obtained as follows:

$$\frac{X - X_e}{X_c - X_e} = \frac{8}{\pi^2}e^{-D\theta(\pi/2L)^2} \quad (2)$$

By plotting the logarithm of $(X - X_e)$ as a function of time, on the basis of equation (2), one should obtain a straight line.

When the data obtained by drying the onion at different temperatures were plotted as log $(X - X_e)$ *vs* time, two well-defined lines were obtained (Fig. 3).

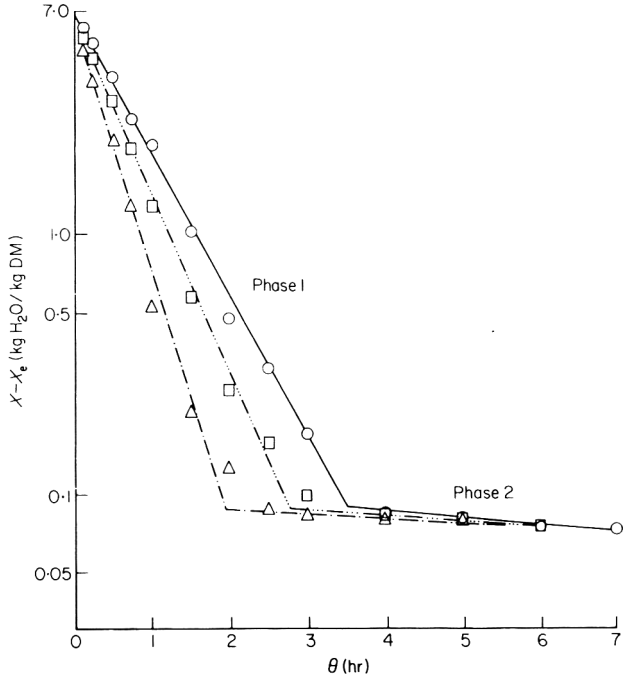

Figure 3. Removal of water from onion slices at different temperatures. ○, 40°C; □, 50°C; △, 65°C.

Table 1. Average diffusivity of moisture from onion slices dried at different temperatures

Temperature (°C)	Diffusivity (m^2/S)	
	Phase I	Phase II
40	7.60×10^{-11}	3.90×10^{-12}
50	9.81×10^{-11}	3.96×10^{-12}
65	13.90×10^{-11}	3.96×10^{-12}

The moisture content at which the transition took place was about 0.1 kg H_2O/kg DM. From the straight-line portions of the curves the average diffusivities of moisture in the onion slices during the two rate periods were calculated and are shown in Table 1. The calculation of these liquid diffusivities was made through equation (1) where $(X-X_e)$ is a function of $D\theta/L^2$. The value of L used in this equation was, as mentioned previously, half the thickness of the onion slice. Because shrinkage takes place during the drying of onions we have calculated diffusivity values for the fresh onion slice and the dried onion slice. To do this, it was assumed that the shrinkage takes place equally in all directions and consequently a change in L^2 is associated with a change in the volume at the power 2/3. Volume changes were measured for different water content, as indicated in the experimental sections, and are presented in Fig. 4.

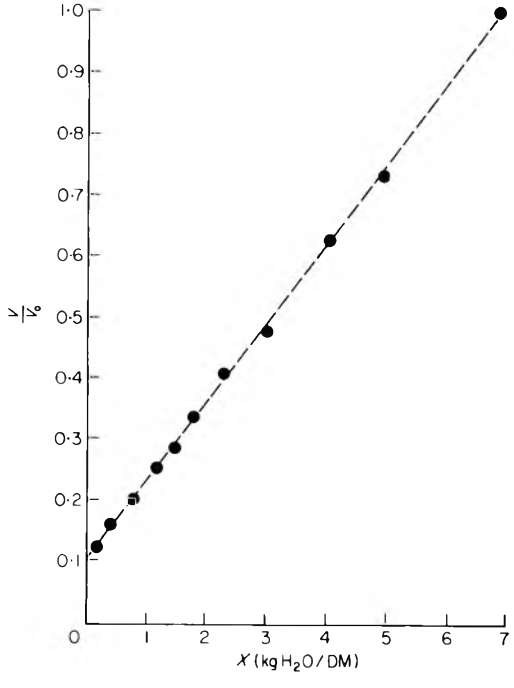

Figure 4. Relationship between volume as a proportion of the original volume and moisture content of onion slices.

Upon examining the results in Table 1, it is obvious that the moisture diffusivity for the first phase increased with temperature. From consideration of the diffusivity values at 40, 50 and 65°C, and on the basis of the applicability of equation (1), one would expect the drying times necessary to achieve the same residual moisture content in the onion to be twice as long at 40°C than at 65°C. This was observed experimentally throughout this work, as exemplified by Fig. 1. Also, at 40, 50 and 65°C, diffusivities in the first phase of drying were about 20, 25 and 35 times higher respectively, than for the second phase. This indicates that during the higher dehydration rate period the rate was sensitive to changes in temperature while during the second period of drying, which corresponds to low moisture contents, the rate was not sensitive to external factors.

The diffusivity values obtained at 40, 50 and 65°C are plotted against the reciprocal of absolute temperature, T (Fig. 5) together with the diffusivity values obtained by taking shrinkage into account. Each set of results may be represented by an Arrhenius type of relationship which is of the form

$$\frac{d\ln D}{dT} = \frac{\Delta E}{RT^2} \tag{3}$$

Where ΔE is the energy of activation for diffusion, and R is the gas constant = 8.314 J/κ mole. The energy of activation calculated from line A was 21,666 J/mole and that calculated from line B was 19,800 J/mole.

Diffusivity for onion slices apparently has not been reported previously, but has been determined for other foods such as fish muscle (Jason, 1958), potatoes (Saravacos & Charm, 1962; Fish, 1958), pepperoni (Palumbo *et al.*, 1977), and apple pieces (Roman, Rotstein & Urbicain, 1979). Our results are comparable to those reported in the literature.

One of the most important characteristics of a dehydrated product is the capacity for rapid and complete rehydration. Rate of rehydration *vs* time at 40

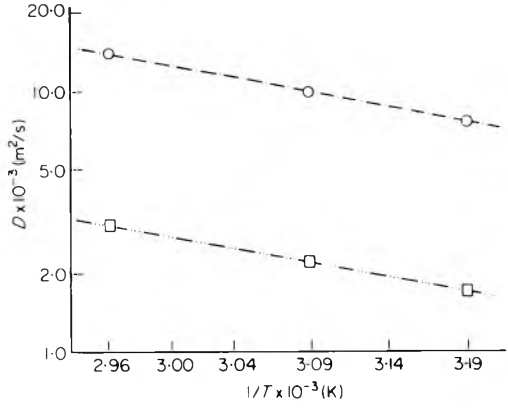

Figure 5. Effect of temperature on the diffusivity of moisture through onion slices during the first phase of drying. ○, neglecting shrinkage; □, with shrinkage.

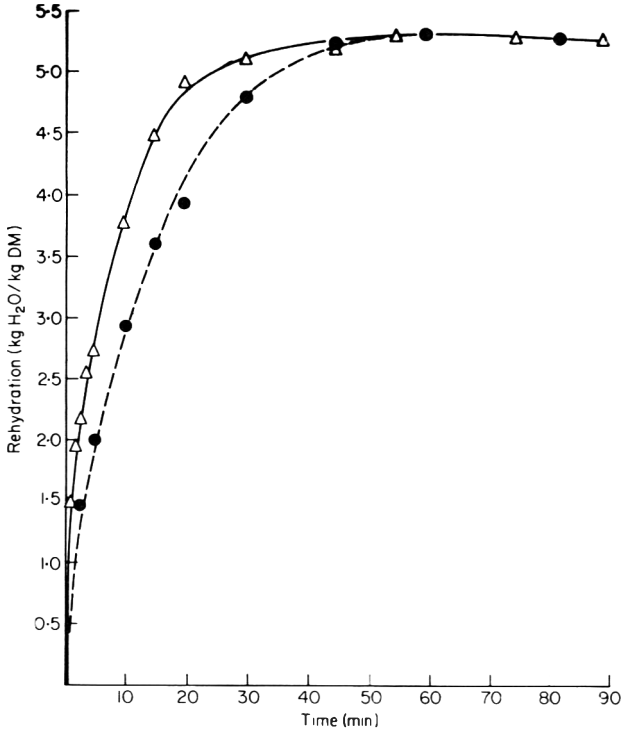

Figure 6. Rehydration of yellow globe onion slices dehydrated at 50°C. △, Rehydration at 40°C; ●, rehydration at 25°C.

and 25°C is shown in Fig. 6. The onion samples used for the dehydration experiments were dried with air at 50°C. Upon examining the results shown in Fig. 6, it is immediately apparent that at 40°C the rate of rehydration was faster than at 25°C. After approximately 1 hr the amount of water absorbed at the two temperatures is about the same and rehydration ceases. No real differences were found, both in rate and final volume of water absorbed, between samples rehydrated at different air temperatures or air flow rates. These results agree with those reported for white globe onion (Shimazu, Sterling & York, 1965). The present study showed small decrease in rehydration volume and rehydration rate as the dehydration rate increases, but the differences were not significant.

When the rehydration data obtained at 25 and 40°C were plotted as log $(X_{\infty}-X)$ *vs* time, straight lines resulted for the region of moisture contents of 6.2×10^{-2} kg H_2O/kg DM to about 5.2 Kg H_2O/kg DM (Fig. 7). Following the same procedure used for the dehydration data, diffusivities were calculated. As expected, diffusivities were higher at 40°C than at 25°C. The diffusivity values are also shown in Fig. 7.

The values of diffusivity of water during dehydration, $D_{\text{dehydration}}$, and rehydration, $D_{\text{rehydration}}$, were compared. It was found that at the same temperature $D_{\text{rehydration}}$ is about twice the value of $D_{\text{dehydration}}$ (2.33×10^{-10} m²/s *vs* 7.69×10^{-11} m²/s).

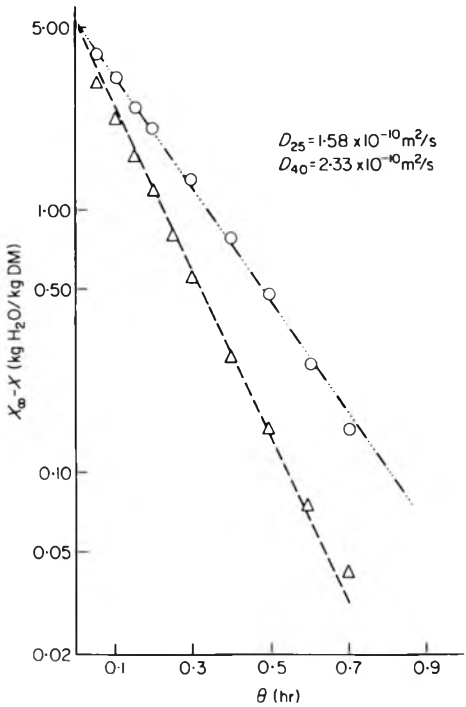

Figure 7. Rehydration rate of onion slices at 25°C (○) and 40°C (△).

The diffusion coefficients discussed up to this point have been defined according to Fick's Law, in which the driving force for diffusion is the concentration gradient. This means that the values obtained from equation (2) are in fact effective diffusivities and represent the interaction of the various resistances which occur during drying. Following King (1968), we calculated the value of α for the first phase of drying, from the equation

$$\alpha = \frac{k R R_v T^3}{(\Delta H_s)^2 D^1 r P_w^0} \tag{4}$$

where k is the thermal conductivity of solid plus moisture, R and R_v are gas constants, T is the absolute temperature, ΔH_s is the molar heat of sorption, D^1 is the effective vapour space diffusion coefficient, r is the relative humidity, and P_w^0 is the vapour pressure of water. The value of α, when the quantities in equation (4) were expressed in the same units used by King, was well over 1, implying internal mass transfer control.

Examination of the diffusivity values for the first phase of drying shows that these are temperature dependent; but the temperature change also modifies the external resistance between the air and the product, therefore contributing to the overall effect observed. If one was to assume, on the basis of other observations, that external resistances are not controlling, the variation in effective

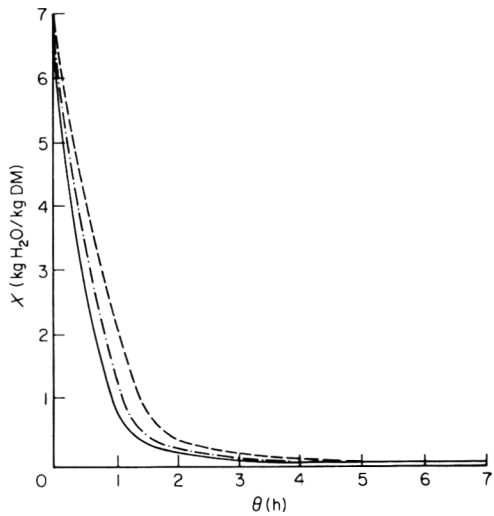

Figure 8. Effect of drying air flow rate on the moisture content of onion slices. Drying conditions: yellow globe type onion slices 1.5 mm thick, dry bulb temperature of the air, 50°C. —, 5.5 m³/min; —·— 8.1 m³/min; ---, 10.3 m³/min.

diffusivity could then be attributed to the internal mass transfer control. However, the experiments conducted at constant temperature and variable air flow rate (Fig. 8) show that the external resistances contribute significantly to the overall resistance. In this case the internal resistance is not modified by the change in the flow rate and therefore the increase in drying rate is totally attributable to the improvement in heat and mass transfer at the surface of the product.

Considering now the second phase of drying, the first relevant observation pertains to the order of magnitude of the effective diffusivities. These are between 20 and 35 times lower than the first phase diffusivities. However, as evidenced from Fig. 3, it is obvious that these are practically temperature independent and it follows that in this phase internal resistances are totally controlling the process.

If it is assumed that the transition point where the process ceases to be mass transfer controlled, and becomes heat transfer controlled is associated with the uncovering of the unimolecular layer of water after the outer layers have been removed, an energy balance equation for the processes of monolayer adsorption, diffusion and evaporation can be written

$$\Delta H + \lambda = E_{D_2} - E_{D_1} \tag{5}$$

E_{D_1} being the activation energy for diffusion of molecules in the second and higher adsorbed layers, E_{D_2} the activation energy for diffusion of molecules in the first layer, λ the heat of vaporization of water, and ΔH the heat of sorption.

If we take the value of E_{D_1} to correspond to the experimental values calculated from

line A and/or line B in Fig. 4 and the value of $\Delta H + \lambda$ (2,535 kgJ/kg DM) to correspond to the value calculated from the sorption isotherms (Mazza & LeMaguer, 1978), by the use of equation (5) the value of E_{D_2} can be calculated. The value of E_{D_2} will be 67,296 J/mole and 65,432 J/mole, depending on whether shrinkage is neglected or not. These values are comparable to the energy of activation of water migrating by surface diffusion along molecular fibril in starch gel of very low water content given by Fish (1958), who suggested that these values are consistent with the breakage of two hydrogen bonds in order to attain the activated state of a water molecule. The agreement between the values of activation energies of onion slices and starch gels, therefore, suggests that a similar process occurs in the diffusion of water through onion.

Conclusion

The air drying and rehydration characteristics of yellow globe-type onion slices have been investigated. From the drying and rehydration curves at different temperatures, the effective diffusivity of moisture together with energy of activation were estimated, and an attempt to relate the values of these functions to the way water moves within onion slices was made.

Acknowledgments

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Long term storage of some dry foods: a discussion of some of the principles involved

D. J. McWEENY

Summary

Foods which have been dried to the point where microbiological growth is inhibited can still deteriorate through chemical, biochemical and physical changes. Keeping foods cool and dry is normally the best way of minimizing these changes but this is not universally the case. Some exceptions are discussed in relation to the scientific principles underlying storage practice with flour, fats, yeast, sugar and dried milk. The mechanisms involved in loss of baking quality of flour, β-carotene deterioration in fats, loss of gassing power in yeast, syrup formation in sugar and loss of solubility in dried milk are discussed.

Introduction

Urban societies rely on supplies of food which have been treated so as to ensure they reach the consumer in a wholesome and nutritious condition. With large scale movements of food on a worldwide basis – and with the need to ensure stocks are adequate to even out seasonal variations in production – modern society relies on foods which have been stabilized in some way so as to retard the processes which otherwise would lead to losses. These losses may be due to infestation, microbial growth and biochemical, chemical and physical changes. As far as possible major commodities are dried before storage and transport to the point at which infestation and microbial growth are adequately controlled but in many cases the conditions are such that biochemical, chemical and physical changes can still take place. With a few notable exceptions food items deteriorate in quality in a progressive manner but the nature of the changes, their rate, their causes and their effects can vary enormously as also can the control measures adopted. The present paper examines some of the principles involved in controlling these changes and exemplifies the applications and the

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limitations of these principles in relation to some processed foods (flour, fats, dried yeast, sugar and dried milk). Microbiological and infestation effects can be controlled effectively by heat processing, preservatives/fumigants and reduction in water activity either separately or in combination and for the purposes of this paper it is generally assumed that the moisture content is low enough to prevent microbial and insect attack. Some of the changes are abnormal in so far as they have been studied systematically only in storage experiments with time-scales far in excess of those encountered in normal commercial practice. Quite apart from the scientific curiosities they occasionally reveal these studies are of interest for the insight they may provide into the problems encountered in more normal circumstances as sporadic incidents which do not lend themselves to systematic investigation.

The primary practical rules in controlling storage changes are that both temperature and moisture content should be kept low. These rules are generally applicable to most forms of change – but the scientific basis for these practical rules can be markedly different depending on whether a particular change is chemical, biochemical or physical. An appreciation of the scientific basis of the practical rules can indicate the reasons why they operate only within certain limits (which differ from one type of change to another) and can provide an understanding of the situation in which departures from the general rules can be experienced. Some of the general principles involved and some problems encountered during long term storage are discussed below.

Chemical and biochemical changes

(a) General principles

The effects of heat and of dryness on chemical changes during storage are not always those which would be predicted by the application of the simple injuction to keep commodities dry and cool. In the case of certain forms of deterioration the effects of temperature on the rate of a chemical change can be unexpectedly high. Thus for instance the rate of discolouration due to non-enzymic browning may increase two-fold for a temperature rise of only 3 or 4°C (Ross, 1948). Non-enzymic browning is frequently an important form of deterioration in dehydrated and intermeciate moisture foods and the situation with this particular form of deterioration is complicated by the dependence of the reaction on the moisture content – or more correctly the water activity of the food. The problem can be exemplified by some studies on a model system of glucose and glycine dispersed in a micro-crystalline cellulose matrix (McWeeny, 1973). When this was held at 37° at various water activities the rate of colour development showed a very marked maximum at a_w around 0.55 – with a steep dependence on a_w throughout the ranges 0.2 to 0.5 and 0.6 to 0.8 (Fig. 1). In the latter region where the effect of a_w on microbial growth is also important there

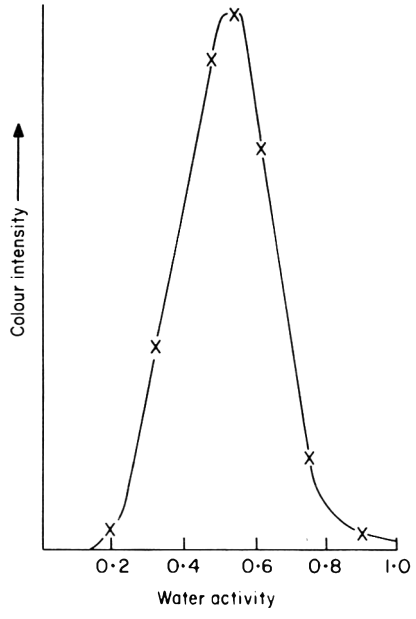

Figure 1. Effect of water activity on non-enzymic browning of glucose/glycine/avicel (8 days at 38°C).

can be some difficult compromises to make if both microbial growth and non-enzymic browning are storage problems in the same commodity i.e. conditions which would help to control microbial growth tend to enhance browning – and vice versa. In deciding on the compromise to be adopted there could be clear advantage in terms of colour stability if even a marginally higher a_w can be achieved without prejudicing the control of microbial growth. It is in situations of this nature where control of microbial growth by chemical preservatives can be particularly advantageous even at relatively low levels of use.

Non-enzymic browning is frequently encountered during the later stages of vegetable dehydration i.e. when the a_w has been reduced to the critical zone around 0.5 to 0.6 At this point in many processes it is customary to reduce the temperature of the drying air and this action reflects two considerations. Firstly, as drying progresses the rate of evaporation decreases and hence the amount of evaporative cooling also decreases; this allows the product temperature to rise to a higher level than that existing in the earlier stages unless steps are taken to control this by reducing the air temperature. Secondly as drying reaches the a_w 0.5 to 0.6 zone the rate of non-enzymic browning increases very rapidly and control of this is achieved by reducing the temperature. Because the reaction rate is highly dependent on temperature a relatively small reduction in temperature causes a marked reduction in reaction rate (e.g. 6–8 fold for a 10°C reduction) and by taking advantage of this relationship an effective control of non-enzymic browning can be achieved without unduly extending the time-span of the drying process.

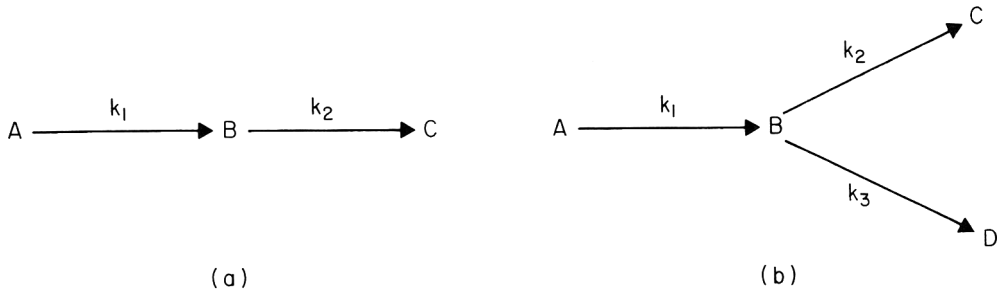

Figure 2. Reaction scheme capable of showing unusual effects of change in temperature (a) consecutive reactions (b) competing reactions.

Another aspect of the effects of temperature on chemical changes during storage should be mentioned before describing some specific observations on storage behaviour of commodities. The normal expectation that a reaction rate will approximately double for each 10°C rise in temperature is based on a number of assumptions about the order of the reaction involved and its isolation from other reactions. In this last respect the involvement of competing or consecutive reactions (Fig. 2) can lead to some startling departures from the rule. If reactions of these sorts are taking place then the fact that they will each have their own activation energy – and hence their own temperature coefficient – can lead to marked shifts in the rate of accummulation of a particular product as the temperature is changed and indeed situations can be encountered where a reaction appears to be more rapid as the temperature is lowered. Thus in the situation depicted in Fig. 2a the abundance of the intermediate B will depend upon the relative values of the rate constants k_1 and k_2 at any particular temperature; if k_2 increases more rapidly than k_1 as the temperature is raised then the steady state concentration of B will decrease at higher temperatures. Similarly where competing reactions exist (Fig. 2b) the abundance of the product C at any temperature will be determined by the relative values of k_2 and k_3; if k_3 increases more rapidly than k_2 as the temperature is raised then the rate of formation of C will not increase in the normal fashion at higher temperatures. If k_3 is sufficiently greater than k_2 the rate of formation of C can actually decrease as the temperature is raised.

Situations of this sort underlie a number of practical procedures (e.g. the thermal decomposition of hydroperoxides during deodorization of oils and fats) in food processing but they can also be responsible for unexpected temperature effects which occur from time to time in food processing and storage. A number of situations of this sort have been reviewed in the literature (McWeeny, 1968d) and one particular example is described in some detail later. Other examples concern: (i) the stability of fish oils as affected by the presence of certain amines (Harris & Olcott, 1966), (ii) the stability of vegetable oils as affected by certain dicarbonylic compounds (Anderson & Huntley, 1964), (iii) the stability of fats in some fish as affected by the drying temperature (Banks, 1950), (iv) protein denaturation in chilled and frozen fish during storage at

temperatures just below 0° (Love & Elerian, 1964), (v) oxidative changes in foods at low temperatures (i.e. down to −30°C) due to the effects of free radicals (Hannan, 1955; Greene & Watts, 1966), (vi) losses in tocopherol and vitamin A in various commodities at temperatures down to −35°C (Bunnell *et al.*, 1965; Hayes & Steele, 1964). Not all of these examples relate directly to long term storage but they are mentioned for two reasons. Firstly because mechanisms analogous to those at work in causing these changes are, in principle, capable of operating in the course of long-term storage. Secondly, although some of these effects operate only at elevated temperatures which are not in themselves relevant to storage conditions they do relate to temperatures which are used for accelerated storage/stability tests and there seems to be the possibility that they could give rise to misleading predictions about stability during long-term storage. For instance a test at 100°C of an oil containing an amine contaminant or a dicarbonyl contaminant could lead to a substantial overestimation of its stability at lower temperatures.

(b) Flour storage

When wheat flour of the type marketed in the UK for commercial breadmaking is stored for a few years it ceases to bake into normal sized loaves (Greer, Jones & Moran, 1954; Cuendet *et al.*, 1954). If the moisture content is kept sufficiently low there are no infestation problems and it can be stored in paper sacks for some time and still appear to be in sound condition. It makes normal dough and rises during 'proving' in the normal fashion but when placed in the baking oven there is no 'oven spring' and the loaf remains much the same size as the proved dough piece. As such it is commercially unacceptable. The immediate cause appears to be that the dough becomes more permeable in the oven and the gases which should cause the dough to rise merely leak away; the underlying reasons for this enhanced dough permeability at elevated temperature are less readily identified (Daniels & Fisher, 1976; Bell, Daniels & Fisher, 1977).

Traditionally the protein quality is regarded as the key to good bread making characteristics but at least on first sight this does not appear to provide the explanation of this particular problem. The extractable protein in the flour is unchanged in quantity (Shearer, Patey & McWeeny, 1975) and when fractionated by the usual electrophoretic methods shows no marked change from the original pattern other than the loss of purothionin; other tests indicate this loss may not be important to baking quality (Patey, Shearer & McWeeny, 1976). On the other hand changes in the lipids can be fairly dramatic; these are only 1½–2% of the flour but they show some remarkably extensive changes. There is (i) extensive accumulation of free fatty acids, mostly due to hydrolysis of triglycerides, (ii) a loss of some polar lipids and (iii) some loss of measurable linoleic acid. Lipase and lipoxidase both appear to be active in this relatively dry material and many of the changes can be regarded as due to enzyme action.

Over a period of years more than half the lipids may be converted to free fatty acids and this rate of change is retarded by reducing the moisture content of the flour during storage. However these changes do not appear to be the primary cause of the quality loss and although free fatty acids can cause loss of baking quality even the relatively large degree of conversion of lipids to this form does not seem enough to induce the observed changes. The question of whether the loss of quality is due to loss of a factor which is necessary for good loaf formation, or to the production of a deleterious substance is not easy to answer unequivocally. All that can be said is that there is no evidence for the production of an *extractable* agent of this sort and the formation of a deleterious agent which becomes strongly *bound* somewhere in the flour matrix at a point which is closely involved in the process of bread making cannot be excluded. Clear evidence of differences between binding of various components and additives when doughs are formed from fresh and stored flours have been reported in studies on work input and protein extractability from these doughs (Patey, Shearer & McWeeny, 1977). These effects appear to be linked to changes in baking quality and lend credence to the idea that loss of baking quality could be due to formation and binding of a deleterious agent. Work on the problem continues and a better understanding of it may contribute significantly to an appreciation of the mechanisms at work in normal bread-baking and might suggest an approach to the use of flour from wheat varieties which are not currently useful for bread making.

(c) Storage of hydrogenated fats

Studies were conducted some years ago on anhydrous hydrogenated fat with added BHA, β-carotene and retinol produced by three processors from a single batch of crude groundnut oil. Two produced fats in which there was a wide incidence of an unusual deterioration; fats from the third processor rarely showed the problem. The striking features of the problem were two-fold. Firstly it was observed that during storage the colour of the fat changed from yellow to green/blue and secondly the change appeared to be substantially faster at 5°C than it was at ambient temperature (approx 11°C).

The effect was reproduced in the laboratory with a wide range of hydrogenated palm kernel and coconut oils (McWeeny, 1968 a,b,c). These studies showed that the change was oxygen dependent, but was not retarded by the usual free radical scavenging phenolic antioxidants. Examination of the non-saponifiable fraction of the fats showed the presence of several products derived from β-carotene and prominent amongst these were several 5,6-epoxides and their 5,8-furanoxide isomers. It is known that per-acids can be involved in the formation of 5,6-epoxides. The per-acids are thermolabile and accordingly they are used in the cold in the laboratory preparation of epoxides; it is also known that their action as oxidising agents does not involve a free radical mechanism. Finally it is known that the yellow 5,6- and 5,8-epoxides

turn green/blue in the presence of acids. It was possible to propose a reaction mechanism which involved oxidation of β-carotene by per-acids (derived from aldehydo-glycerides formed during deodorization) which could also engage in a competing reaction (thermal decomposition) with a relatively high temperature coefficient and which removed them from the system at higher temperatures but allowed them to exist in the cold and to exert their oxidising action on β-carotene. This hypothesis accounted satisfactorily for the oxygen dependence of the reaction, the inability of phenolic antioxidants to control it, the ability of amines to control the reaction and also for its negative temperature coefficient. It also successfully predicted two methods of controlling the onset of the colour change.

(d) Dried yeast storage

Dried yeast is not normally kept commercially for extended periods (although the same may not apply in the home) but storage trials have established that under the right conditions it can be kept for a number of years. This commodity differs from most other dry goods in that it is a living organism and that throughout storage it is essential to retain a high proportion of the enzymes involved in CO_2 production. This requirement to retain a high level of enzyme activity is in marked contrast to the situation on other commodities where the aim is often to eliminate biochemical activity as far as possible.

Dried yeast is produced by extruding a yeast biomass and drying this slowly in a rotating drum in a stream of warm air. It comes in the familar 'bead' form and is not normally stored for more than a year. By gas packing in hermetically sealed containers longer storage lives may be obtained with only slight loss of activity. In the course of the development of gas-packing procedures a simple means of gas packing without the use of an evacuation/inflation cycle has been developed by Hearne & Thomas (1960). This involves a hollow needle with a series of holes in the side. If this simple 'probe' is inserted into a container and nitrogen passed through it under pressure for a few minutes residual oxygen contents of the order of 1% can be routinely obtained.

By taking high quality yeast, ensuring the initial moisture content is correct and gas packing in this way it is possible to keep dried yeast for a number of years with only a small loss in activity. The reason for this loss is itself of some interest. Normally it is important in prolonged storage that biochemical activity is suspended as completely as possible and its resumption at the end of storage is not normally important. It has been shown by Biltcliffe (1972) that more than one system is involved in the CO_2 production and that at least one of these is relatively easily disrupted during storage – the remainder being much more robust. The ability to produce CO_2 by the fermentation of the polysaccharides of flour is damaged more than ability to ferment simple hexoses and specifically there seems to be a loss of activity of the enzymes involved in fermentation of maltose which is the substrate normally formed at a result of natural amylase

action on starch. Having established the specific nature of the biochemical damage it is, in this case, not difficult to establish procedures for optimizing the residual activity and counteracting the effects of storage in so far as they affect the strain of yeast employed in these studies.

Physical effects

(a) Moisture effects in granulated sugar

Newly refined sugar in paper sacks can be expected to have a moisture content below 0·03% and if stored in a suitable manner will remain usable for a number of years. If external moisture is prevented from entering the sack the main change which occurs during storage is the formation of lumps. These are produced by the movement of traces of water initially present in the sugar. This leads to cementing together of individual crystals and the process is aided by the compression of sacks in a stack. However, provided the moisture content of the sugar is satisfactory most lumps which form can be broken down without undue effort. Higher moisture contents will lead to the formation of harder lumps not so easily dealt with. At yet higher levels caking will progress more rapidly and the lumps may become so hard that they are broken down only with great difficulty (J. F. Hearne, *et al.* unpublished data).

Other physical/chemical relationships in stored sugar can lead to problems in storing sugar for extended periods. In the presence of water sucrose is slowly converted to invert sugar and consequently the sucrose dissolved in the film of moisture around each crystal in damp sugar is partly converted to invert sugar. This has a lower a_w than a pure sucrose solution and the formation of invert sugar depresses the relative humidity close to the film of saturated sucrose solution on the sugar crystal. In turn this tends to draw moisture from other regions in the bag; more sucrose dissolves, more invert sugar is formed, the a_w is reduced and so on. Given sufficient time presumably this cycle of events can cause some considerable amplification of minor initial differences in moisture content. This phenomenon illustrates the need to consider the range of moisture a_w conditions within the bulk of a product, rather than merely the average condition. It also illustrates how the influence of temperature fluctuations during prolonged storage can be important; in this case a temperature gradient within a bag may lead to moisture migration and provide the 'trigger' for the dissolution/hydrolysis/reduced a_w/moisture migration cycle.

(b) The role of packaging in food storage

There is a continuous interchange between the moisture contained in a material and the moisture contained in the surrounding air. If a number of materials are enclosed in a single moisture-proof container their moisture

contents will adjust until they all have a common a_w. The processes may be slow, but in the time scale involved in long-term storage, this may not be a limiting factor. A significant hazard in the storage of commodities in packaging made from fibreboard is the growth of mould and normally mould growth on this medium is not found at $a_w < 0.80$. So for example, in order to define a specification for sugar and its packaging suitable for safe prolonged storage it is necessary to know the moisture content of the sugar and of packaging at an a_w of 0.80 and particularly to have some knowledge of how these parameters change at various temperatures.

The curves relating moisture content ot a_w for sugar have long been established and curves relating the moisture content to a_w for different types of fibreboard can be constructed fairly readily. The curves for sugar indicate that the moisture content of sucrose with a_w 0.80 is about 0.03% at 25°C. It is likely that ambient storage temperatures in the UK will rarely exceed this figure and since the sugar has greater capacity to hold moisture at lower temperatures, the value of 0.03% may safely be taken as the maximum allowable moisture content of the sugar for storage. On the other hand the moisture content of fibreboard at a_w 0.80 is much more than 0.03% and perhaps more important the change in moisture content of fibreboard in going from say a_w 0.82 to 0.78 is very much greater than that involved in a similar a_w change in sugar.

If these considerations are applied to a storage situation taking, as an example, cube sugar in small boxes within a large moisture-proof outer case, one can establish the relative weights of sugar and fibreboard and it is a simple arithmetical exercise to show that a significant amount of water can be removed from the sugar by using fibreboard at only slightly below the a_w 0.80 target figure. Conversely if the packaging a_w is only slightly too high then in time the moisture content of the sugar will rise to a level at which deterioration begins. In effect once the pack is sealed the final a_w of the contents will be determined by the initial condition of the fibreboard (J. F. Hearne *et al.*, unpublished data).

In situations where production of one component in a pack is difficult to produce commercially at the target a_w (e.g. because of damage to the quality of an expensive item in the final stages of conventional dehydration) then there may be an advantage in stopping short of the target a_w and conditioning other items, or the packaging itself to an a_w somewhat below the target figure before assembling the composite pack and subsequently allowing the contents to come to the desired equilibrium.

(c) Moisture effects in dried milk

Usually when moisture content is specified in a food for prolonged storage the deteriorations which are in mind are microbiological or chemical. However, they can also be physical. Dried milk powder shows some physical changes at a_w 0.42 to 0.52 i.e. at water activities far below those considered in relation to microbiological damage. The change which affects dried milk is concerned

primarily with the lactose component. As produced commercially the lactose in dried milk exists as an amorphous glass. This is a relatively stable condition but at a_w 0.42 crystallization can begin to occur and moisture is liberated. The moisture release leads to a number of effects, i.e. lumpiness and caking of the powder leading eventually to formation of a solid cake. Possibly more serious is the finding that when the lactose crystallization occurs the protein becomes insoluble and on rehydration the milk separates into two layers. At this stage the product may become unacceptable for human use and may have to be allocated for animal feed at a much reduced price. A description of the development of this deterioration under conditions which are normally regarded as suitable for prolonged storage has recently been published by Warburton & Pixton, (1978).

Conclusion

Although reduction of temperature and of moisture content may be successfully employed in controlling a wide range of effects in foods during prolonged storage there are in fact a number of quite distinct scientific principles at work underlying these practices. An appreciation of the mechanisms involved can improve our understanding of the limitations which exist in the operation of the general rule that keeping foods dry and cool is the way to store them successfully for prolonged periods. This general rule is quite rightly a cornerstone of our system for ensuring that food reaches the consumer in a wholesome condition, but by carefully examining the foundations upon which the rule is laid it may be possible firstly to devise means of enhancing stability by a controlled departure from the normal procedures and secondly to appreciate that failure to recognize the limitations in the rule can contribute to some unexpected and unusual forms of deterioration.

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Colourless sunflower protein products: chemical and nutritional evaluation of the presence of phenolic compounds

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Summary

This study describes a simple process for preparing a sunflower product from dehulled sunflower seeds. The processed products, apart from the high content of lipid (39%), are whole foods, white in colour, with a fibrous or granular texture and acceptable odour. They contain 27–29% proteins, 4% ash, 3.9% fibres and small amounts of phenolic compounds. Furthermore, their PER values can equal that of casein when 2% lysine is added. However, the extraction process causes a loss in lipid (25–30%), a fall in lysine and cystine content and a slight fall in soluble protein.

Introduction

Although sunflower seeds are used mainly to produce edible oil, defatted sunflower meal is an appreciable source of protein which, although deficient in lysine, contains no toxic substances (Clandinin, 1958; Smith, 1968). The potential uses of this protein resource for human consumption are however limited by the presence of phenolic substances, particularly chlorogenic and caffeic acids, and by the presence of reducing sugars (Pomenta & Burns, 1971; Sabir, Sosulski & Finlayson, 1974; Milic, Stojanovic & Vuvurevic, 1968).

Defatted whole sunflower flakes without removal of the seed coat contain considerable quantities of phenolic substances and reducing sugars (Mikolafczak, Smith & Wolf, 1970) which, depending on extraction conditions (pH, oxidation and heat), can cause considerable darkening of the product and reduce its acceptability. A reduction in nutritional value may also result due to the formation of covalent bonds between proteins and oxidized phenolic substances (Pierpoint, 1969).

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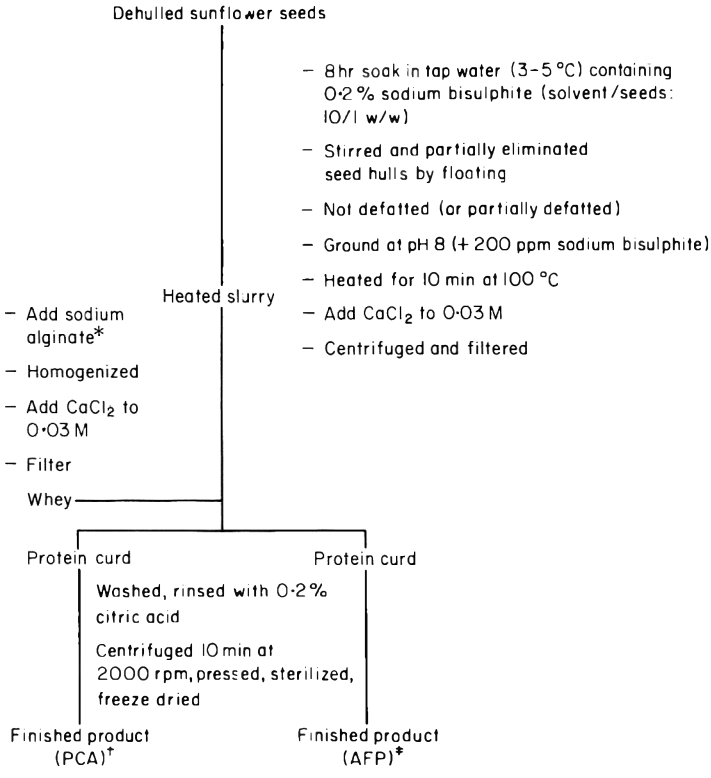

Figure 1. Preparation of food product. *2% sodium alginate (w/w: sodium alginate/seeds, dry basis) †product containing sodium alginate (see text for details); ‡alginate free product (see text for details).

Here we describe a process for the removal of sugars and phenolic substances from dehulled sunflower seeds in order to obtain a non-coloured product with an acceptable odour. We have also determined the effect of processing on the composition of the products obtained, particularly as regards soluble phenolic compounds and phenolic compounds bound to insoluble proteins as well as extraction yields, physico-chemical properties and *in vitro* and *in vivo* digestibility.

Materials and methods

Preparation of protein fraction

The protein fractions were prepared from dehulled sunflower seeds (DHSS) (Institut National de la Recherche Agronomique, France) containing approximately 24% protein (N × 6.25) and 41% fat. The process is outlined in Fig. 1.

A 'polytron PT 10–35' (Kinematica GmbH, 6005 Luzerne CH Switzerland) was used to grind the samples in hot water (90–95°C) so as to inhibit enzymatic

oxydation (peroxydase and lipoxygenase). After thermal treatment (10 min at 100°C) in aqueous medium, the protein curd was obtained by precipitation with calcium chloride (0.03 M final concentration) in the presence and absence of sodium alginate. The precipitated curd was then washed, rinsed in an 0.2% citric acid solution, centrifuged 10 min at 2000 rpm and freeze dried. The texture of the finished product was fibrous or granular, depending on whether or not sodium alginate was added. Sodium bisulphite was used as an antioxidant during extraction. One product containing alginate was designated, PCA, and the other product was defined as alginate free product (AFP). 2% sodium alginate w/w: sodium alginate/seeds, dry basis) was added for the preparation of PCA, this end-product presents a fibrous texture.

Proximate analysis

Nitrogen was measured by the micro-Kjeldahl procedure (AOAC, 1970) and fibre was estimated by Lees' method (1971). Lipid content was determined by hexane extraction, using a Soxhlet apparatus, sugars were extracted with 80% alcohol (Bau *et al.*, 1978) and measured by the anthrone method (Loewus, 1952).

Determination of phenolic compounds

Phenolic compounds were measured according to the method of Monties & Rambourg (1978). Three- to five-hundred mg of finely ground sample mixed thoroughly with 25 ml Fontainebleau sand (acid washed, Prolabo, France) was transferred into a column (25 cm glass tube, 2 cm diam.) containing a teflon tap plugged with glass wool. The sample was eluted with a series of solvents. The following solvents were used successively: petroleum ether containing 2% methanol (extraction of chlorophyll pigments, carotenoids and lipids); diethyl ether (final extraction of liposoluble pigments); methanol and distilled water (extraction of polyphenolic compounds).

The eluted methanol and distilled water extracts were separately collected in a brown graduated flask containing a drop of 6 N hydrochloric acid. The extracts of polyphenolic compounds were measured by absorbancy at 330 nm. To analyse for protein bound phenolic substances, the samples were defatted and cleared of soluble phenolic compounds by first washing with methanol and water, and then treating with a mixture of acetyl bromide and glacial acetic acid (1 : 3 v/v). This treatment dissolved cell walls and released the bound phenolic compounds.

Amino acids analysis

Amino acid analysis was carried out in duplicate according to the method of Moore, Spackman & Stein (1958), using a Technicon TSM auto-analyser

Model II. The samples were sealed in tubes in a nitrogen atmosphere and then hydrolyzed in 6 N HCl at 110°C for 24 hr. Cystine and methionine were analyzed after oxidation to cysteic acid and methionine sulphone respectively (Schram, Moore & Bigwood, 1954).

In vivo *Digestion by pepsin and trypsin*

Trypsin (SERVA from bovine pancreas, 40 u/mg 2 × cryst. reference 37260) was suspended in tris-buffer (tris-hydroxymethyl aminomethane-0.05 M-pH 8.2) containing 0.02 M sodium chloride. It took approx. 8 hr to dissolve the substrate and to stabilize the pH of the substrate medium at 8.2. Pepsin (SERVA pepsin procine, 30 Anson units/mg, 2 × cryst. reference 31820) digestion was carried out in 0.06 M HC1-pH 1.8. Enzyme/substrate ratio was 2.5/1000 and 2/1000 for trysin and pepsin respectively. Incubation time varied from 0 to 120 min (0, 10, 20, 30, 60 and 120 min at 37%C). Digestion was terminated by the addition of trichloroacetic acid (0.8 M final concentration). Nitrogen soluble in 0.8 M TCA was designated non-protein nitrogen (NPN).

PER determination

All the samples for the PER determination were freeze dried and finally ground to powder (100 mesh).

Protein efficiency ratio (PER) was determined by the AOAC procedure (1970). A 28-day feeding trial was carried out with male weanling rats (Wistar strain, 28-days-old, initial weight, 55–65 g) separated into groups of ten, housed in individual cages and fed the diets *ad libitum*. The rats were weighed twice a week. PER values of protein fractions with a supplemented 2% lysine (lysine/protein; dry basis) were also determined.

Results and discussion

Extraction yields

The results (Table 1) refer to laboratory assay runs with a batch size of 10 litres. The extraction yield of dry weight, 80.3% (89.9 nitrogen recovery) was obtained with the product PCA and 74.2% (88.9 nitrogen recovery) with the AFP. The use of sodium alginate increased the yield, probably due to the formation of protein: alginate complexes cross linked to calcium ions.

Composition of products

Results are given in Table 1. Protein content of the PCA was 27.1% and of the AFP 29%. Both contained about 39% lipids, small quantities of ethanol

Table 1. Proximate analysis and extraction yields of sunflower protein products (dry basis).

Sample	Protein (%)	Ash (%)	Lipid (%)	Fibre (%)	Ethanol-soluble sugars (%)	Dry wt recovery (%)	Nitrogen recovery (%)
DHSS*	24.2	6.05	41.2	6.7	5.1		
PCA†	27.1	4.04	39.2	3.9	0.06	80.3	89.9
AFP‡	29.01	3.94	38.1	3.8	0.05	74.2	88.9

*: dehulled sunflower seeds. See text for details.
†: product containing sodium alginate. See text for details.
‡: alginate free product. See text for details.

soluble sugars, 4% ash and 3.9% fibre. Our extraction process eliminated about 40% of the fibre and almost all the ethanol soluble sugars but it caused a partial removal of soluble protein and of above all, lipid (25–30%) which passed into the serum during the different extraction stages. The calculation of the loss of nutrients was taken into account in the dry weight recovery values.

Phenolic compound content

Table 2 gives the content of phenolic compounds. We found 1.92% phenolic substances in dehulled seeds, of which 65.9% was soluble phenolics, 34.1% protein-bound phenolics. Our technological treatment eliminated about half of these phenolic substances from sunflower seeds (0.89 and 0.99% for the PCA and AFP products respectively). The products obtained were white in colour and had a low content of soluble phenolics, however the concentration of bound phenolics increased slightly during extraction from 34.1 to 44.2% of total phenolic content in DHSS for the PCA product and to 38.4% for the AFP product. It would appear that soluble phenolics are very sensitive to oxidation, so it is indispensable to use an antioxidant during the extraction process.

About one third of the phenolic component (34.1%) in the sunflower seeds was not soluble but was bound to the proteins of the seeds before processing, and was not eliminated by aqueous extraction.

Table 2. Phenolic content of sunflower protein products.

Sample*	Phenolic content (%)	Phenolic compounds (%)† Free	Bound
DHSS	1.92	65.9	34.1
PCA	1.03	9.48	44.2
AFP	0.93	10.00	38.4

*DHSS: dehulled sunflower seeds.
PCA: product containing sodium alginate.
AFP: Alginate free product.
†% of total phenolic content in DHSS.

Table 3. Amino acid composition of protein fractions (mg/16 mg nitrogen).

Amino acid	Sample			
	DHSS	PCA	AFP	FAO*
Lysine	4.20	2.85	2.74	5.4
Methionine	2.65	2.44	2.37	3.5
Cystine	1.42	0.95	0.86	
Threonine	4.41	4.15	4.02	4.0
Valine	5.92	5.21	4.41	5.0
Isoleucine	5.48	5.20	4.66	4.0
Leucine	7.54	7.10	6.82	7.8
Tyrosine	3.10	2.96	2.71	6.1
Phenylalanine	5.20	4.94	4.4	

*Food and agriculture organization reference protein (FAO/WHO, 1973).

Amino acid content

As shown in Table 3, the essential amino acid content of PCA and AFP protein products was reduced compared to dehulled sunflower seed. The reduction in lysine and cystine was 34 and 37% respectively for both PCA and AFP; most likely the loss of lysine and cystine was due to their removal in the whey fraction with the soluble proteins (see Fig. 1). The loss in the amino acid content of AFP is greater than that of PCA. This might suggest that the cross linkages formed between proteins and alginate molecules in PCA retain a certain proportion of amino acids.

Determination of protease activity (pepsin and trypsin)

Table 4 shows the variations in digestibility for pepsin and trypsin. There was a considerable difference between the two types of digestion for dehulled sunflower seed meal (DHSS), which had the highest pepsin proteolysis rate but the lowest trypsin hydrolysis rate. The drop in trypsin digestibility was probably due to the formation of trypsin resistant covalent bonds between free amino groups of lysine and arginine residues, and phenolic substances as a result of oxidation in alkaline medium (pH 8.2, TRIS buffer for 8 hr). These results confirmed those of Lahiry *et al.* (1977).

Proteolysis did not, on the other hand, have the same effects on the processed products. After 2 hours' digestion, the PCA and AFP products, like casein, were digested to a greater extent by trypsin than by pepsin. After 2 hours' digestion increases in non-protein nitrogen (NPN) for PCA and AFP respectively were 51.15 and 48.18% with tryspin and 44.64 and 38.31% with pepsin.

Table 4. Trypsin and pepsin digestibility of sunflower meal and protein products.

Sample	NPN % of total N (before proteolysis)	Increase of NPN % of total N (after 2 hours' proteolysis)	
		Trypsin	Pepsin
Casein	2.9	56.25	45.0
DHSS	11.03	29.62	61.21
PCA	9.3	51.15	44.64
AFP	9.28	48.18	38.31

NPN = non-protein nitrogen

The initial NPN content of the sunflower products varied from 9.3% for PCA to 11.03% for DHSS. The presence of a gelation agent (2% sodium aliginate) did not greatly affect pepsin or trypsin proteolysis.

PER determinations

PER values (Table 5) showed that the lysine content of unprocessed sunflower meal (DHSS) was below the rats' nutritional requirements, since the addition of 2% lysine raised the PER value from 2.07 to 2.45. For the processed products (PCA and AFP), PER values were lower than that for sunflower meal. After the addition of 2% lysine, PER values were comparable to those obtained with both the casein and sunflower meal diets.

Although the proportion in phenolic compounds bound to proteins of PCA was slightly greater than that of AFP (Table 2), the PER value of PCA was somewhat higher than that for AFP. This would indicate that differences in amino acid content rather than the presence of bound phenolics were responsible for the differences in PER values between PCA and AFP.

Table 5. Nutritive value of sunflower protein products.

Sample	PER* (± s.d.) Diet	Diet + 2% lysine
Casein	2.5 ± 0.18	—
DHSS	2.07 ± 0.21	2.45 ± 0.12
PCA	1.56 ± 0.07	2.48 ± 0.14
AFP	1.29 ± 0.12	2.24 ± 0.09

Protein efficiency ratio corrected on a basis of PER = 2.5 for casein.

Conclusion

The technology involved in the procedure used is simple, inexpensive, and can be adapted to other types of high protein seeds. Soaking in an aqueous medium and precipitating the protein close to neutral pH, eliminate 50% of the phenolic compounds, 42% fibre and virtually all of the ethanol soluble sugars from the sunflower seeds. However, the extraction process resulted in a considerable loss in lipid (25–30%), a slight loss in soluble proteins and a large fall in lysine and cystine content. One third of the phenolic substances in sunflower seeds was not eliminated by aqueous extraction and remained bound to the protein. The processed products contained about 40% of the total phenolic compounds in dehulled sunflower seeds. In the absence of reducing sugars and lowered amounts of residual phenolic substances, light coloured products were obtained, however, because of high lipid content, a tendency towards rancidity was observed during storage. By varying the processing conditions, it may be possible to control the lipid content of the protein products of fit nutritional and functional requirement in food systems containing PCA and AFP products. Partial defatting also reduces the occurrence of 'painty' and 'beany' odours. Since partial defatting may cause a slight loss of phenolic compounds, this study was carried out with dehulled full fat seeds so as to evaluate the correlation between the chemical and nutritional properties and the presence of phenolic compounds.

PCA and AFP, apart from their high lipid content and white colour have a fibrous or granular texture and an acceptable odour. They contain 27–29% proteins, 4% ash, 3.9% fibres and small amounts of phenolic compounds. The PER values of PCA and AFP nearly equal that of casein when supplemented with 2% lysine. Based on the results described in this report, it shows that it is possible to incorporate these sunflower meal + 2% lysine diets into a variety of food systems.

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Development of quick-cooking dehydrated pulses by high temperature short time pneumatic drying

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Summary

Quick-cooking dehydrated pulses were made from husked split grains of red gram, black gram and Bengal gram using high temperature short time (HTST) pneumatic drying technique wherein porosity was brought about in the dried pulses by exposure of the cooked grains initially to air at a high temperature (170–200°C) for a short duration (4–6 min) in a laboratory model HTST pneumatic drier followed by finish drying at a lower temperature (60–70°C) in a conventional tray or fluidized bed drier. Optimum temperature and time for the HTST drying of the grains were worked out and the HTST dried products were evaluated with respect to their drying behaviour, rehydration characteristics and shelf stability vis-a-vis the conventional hot air dried products.

Considerable reduction in drying and rehydration times could be achieved by the HTST process. The increase in porosity achieved and the HTST treatment did not adversely affect the shelf stability of the grains to any measurable extent.

The technique involves simple equipment and less capital investment as compared to other methods of drying, such as explosive puffing, achieving the same objective. It is amenable to continuous processing as the time of high temperature drying is very short.

Introduction

Pulses form an important source of proteins in the Indian diet and therefore form an essential component of the service rations. Raw pulses, both as whole gram and the husked split grains (dals) are, however, unsuitable as components of pack rations in view of their considerably prolonged cooking times (Bhatia *et al.*, 1967). While by simple precooking and air drying their cooking times could be reduced significantly, further improvements were found necessary to make them quick cooking especially at high altitudes.

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0022–1163/80/0400–0217 $02.00

It is well known that during air drying shrinkage causes irreversible textural changes in most foodstuffs and the air dried food particles do not rehydrate into a texture resembling the original cooked material but remain tough and hard. Further, diffusion of solutes during drying causes formation of a tough, leathery skin described as 'case hardening' which delays rehydration (Van Arsdel & Copley, 1963). There has been, therefore, a constant and continuing search for processes which will minimize texture damage to air dried foods and yield products which will reconstitute almost instantly in water.

Several special techniques have been tried by other workers to produce quick cooking dehydrated foods. With specific reference to pulses and beans, subjecting the cooked grains to the action of proteolytic enzyme, papain, was used by Bhatia *et al.* (1967) to produce a variety of quick cooking dehydrated pulses and beans which reconstitute in boiling water to smooth slurry in a short time. A process was developed by Rockland & Metzler (1967) for the preparation of quick cooking Lima and other dry beans consisting of intermittent vacuum treatment ('Hydravac process') for 30 to 60 min in a solution of inorganic salts (chloride, tripolyphosphate, carbonate and bicarbonate of sodium), soaking for 6 hr in the same solution, rinsing and drying.

Increasing the porosity of the product by expanding the structure has been successfully applied by a number of workers to vegetables to achieve rapid dehydration and reconstitution. Methods utilized so far include explosive puffing (Cording *et al.*, 1963), vacuum puffing (Eapen & Ramanathan, 1966) and deep fat frying wherein the flashing of water vapour from within the food pieces creates a porous structure that permits a much faster drying and rehydration. Neel *et al.* (1954) applied high temperature pneumatic drying for dehydration of potato granules and Harrington & Griffith (1950) for potato 'puffs' suitable for direct eating.

In the study reported here, the high temperature short time (HTST) pneumatic drying method as applied to pulses is described wherein porosity was brought about in the dried pulses by exposure of the cooked grains initially to air at a high temperature (170–200°C) for a short period (4–6 min) followed by conventional method of drying at lower temperature (60–70°C) thereby achieving considerable reduction in drying and rehydration times. The HTST dried products were evaluated with respect to their drying behaviour, rehydration characteristics and shelf stability vis-a-vis the conventional hot air dried products.

Materials and methods

Raw materials

Husked split grains (dals) of red gram (*Cajanus cajan*), black gram (*Phaseolus mungo*) and Bengal gram or chick pea (*Cicer arietinum*) procured from the local market were used in the studies. These were chosen because of

their prolonged cooking times and because they are commonly used in service rations in India. The grains were hand picked free of extraneous matter and broken pieces prior to use.

Cooking

The grains were soaked in sufficient tap water (total hardness 68 p.p.m. as $CaCO_3$; pH 7.4) for 2 hr under ambient conditions, drained, spread in trays and cooked in an autoclave using steam at a pressure of 15 lb/in^2 for 10 min for red gram dal and 15 min for black gram and Bengal gram dals.

Dehydration

The cooked grains were exposed initially to a high temperature for a short time (between 170 to 200°C for 4 to 6 min depending upon the dal) in a laboratory model HTST pneumatic drier specially designed and fabricated for the purpose (Fig. 1).

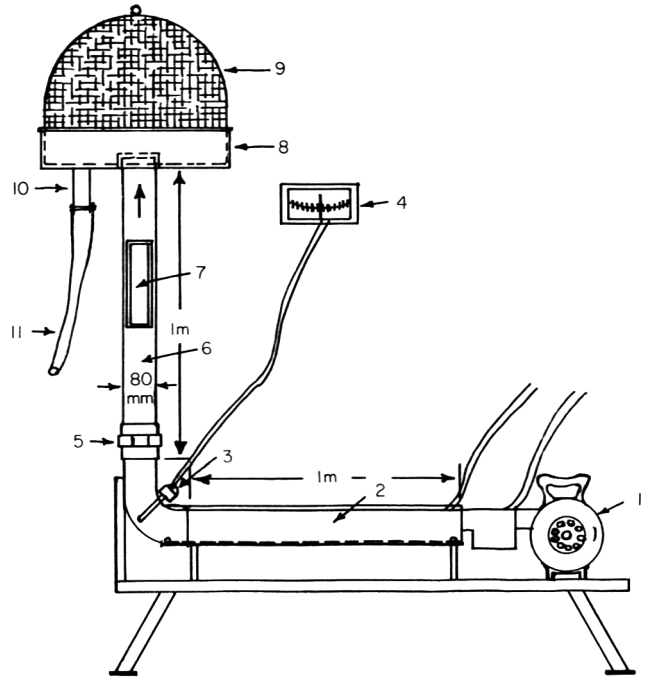

Figure 1. Schematic diagram of experimental HTST pneumatic drying unit. 1. Blower; 2. heating unit; 3. thermocouple; 4. temperature controller; 5. wire mesh trap; 6. drying section; 7. glass window; 8. receiving hopper; 9. wire mesh cover; 10. product outlet; 11. flexible tube.

The drier consisted of a blower connected to a heating unit (horizontal GI pipe with heating elements) and a vertical drying unit (GI pipe of 8 cm diam. and 1 m height) with a wire mesh trap and glass window in the middle. A thermocouple planted after the heating unit and connected to a temperature controller enabled automatic control of the temperature of the hot air.

After attainment of the desired air temperature, the cooked grains were charged into the drier through the mouth of the vertical pipe and kept fluidized in hot air by suitably regulating the inlet air to the blower unit (air velocity about 1500 ft/min). At the end of the HTST drying the material was removed by ejection using full blast of air (velocity about 2000 ft/min) from the blower onto a hopper with an outlet fitted to the mouth of the drying pipe along with a wire mesh cover for trapping the ejected product.

The drying was batchwise and material was fed to the drier at the rate of 250 g/batch. Experiments were carried out in 3 kg lots.

The cooked and HTST dried grains were collected and subsequently finish dried to 5% moisture in a conventional hot air drier. A cabinet drier with an air velocity of 250 ft/min at 65–70°C and a laboratory model fluidized bed drier (Glatt Drier Type TR-2, Chemical and Pharmaceutical Industry Co. Inc., New York; Capacity: 2 kg wet meterial) with air at 60°C were used for the purpose.

Different time-temperature combinations were tried for each type of grain and the optimum conditions were chosen based on maximum puffing effect coupled with minimum heat damage (scorching) and rapid rehydration to give a soft product.

Dehydration curves

Samples were drawn at intervals of 1 min during HTST drying and every 15 min during subsequent drying and their moisture content were estimated by drying in an air oven at 100°C to constant weight. Dehydration curves were drawn by plotting gram moisture per gram solids against time of drying in minutes for the various modes of drying, namely, direct tray drying and fluidized bed drying, HTST plus tray drying and HTST plus fluidized bed drying with a view to evaluate the various methods comparatively.

Bulk density

In order to assess the extent of porosity imparted to the product by the HTST drying as compared to other conventional methods, bulk density (g/cc) of the processed grains was determined using rape seeds. The product (50 g) was mixed with 100 g of rape seeds, the total volume was measured using a 250 ml measuring cylinder and the bulk density calculated.

Reconstitution time, rehydration ratio and rehydration curves

Cooking (rehydration) time was assessed organoleptically by the time taken for the product to become soft in the core when boiling 10 g of the material with 100 ml of water.

Rehydration ratio was determined by adding 5 g of the material to 50 ml of boiling water, bringing to boil, simmering for 5 min, filtering over a Büchner funnel and immediately weighing. The ratio was calculated as weight of material after cooking over that before cooking.

A rehydration curve was drawn by plotting against time of cooking the percentage moisture in the product after boiling 10 g in 100 ml of water for varying periods of time.

Storage studies

Since the precooked and HTST dried pulses have a porous and expanded structure as compared to ordinary precooked hot air dried products, the possible influence of HTST drying on the shelf stability of these products was assessed by packing them in low density polythene (300 G) pouches as well as paper (60 BC Kraft) – aluminium foil (0.04 mm) – polythene (150 G) laminate (PFL) pouches and storing at 0°C (control), room temperature (25–30°C) and 37°C. Samples were drawn periodically and subjected to organoleptic tests after rehydration in boiling water by a panel of judges. Rehydration ratio was also evaluated and compared.

Results and discussion

Dehydration characteristics

Optimum temperature and time for the HTST drying of the husked and split grains of red gram, black gram and Bengal gram are given, along with the percentage moisture of the grains at various stages of processing, in Table 1. These conditions enabled achievement of optimum porosity in the grains leading to quick drying and rehydration without causing any heat damage.

Dehydration curves for the HTST drying followed by finish drying by tray drying as well as fluidized bed drying for the three types of grains are given in Figs 2, 3 and 4 along with the curves for the control samples, namely, direct tray drying and fluidized bed drying of the cooked grains. As seen from the curves, HTST drying brought down the moisture from about 50–55% in the cooked grains to about 20% in 4–6 min thereby cutting down the constant rate drying period considerably. This sudden flashing of water vapour from the grains results in an expanded structure which further reduces the time for finish drying (falling rate period) in tray or fluidized bed drier.

Table 1. Moisture content at various stages of processing and optimum temperature-time for HTST drying of pulses

Material	Moisture content (%)					Optimum temperature time for HTST drying
	Raw	Soaked	Cooked	HTST dried	Final dried (Tray)	
Red gram dal	6.5	54.2	53.4	20.9	4.9	180°C for 4 min
Black gram dal	7.0	54.5	56.0	16.9	4.5	170°C for 6 min
Bengal gram dal	7.1	52.3	52.8	21.7	4.6	200°C for 4 min

As seen from Table 2 there is considerable reduction in the total drying time of the HTST dried products as compared to control. By a combination of HTST drying and tray drying, the total drying time could be reduced to almost half for red gram and Bengal gram dals and to one third for black gram dal as compared to direct tray drying. By combining HTST with fluidized bed drying the extent of reduction was about half for black gram and Bengal gram dals and one fourth for red gram dal as compared to direct fluidized bed drying and the whole drying operation could be completed within 45 min for red gram and black gram and 75 min for Bengal gram dal.

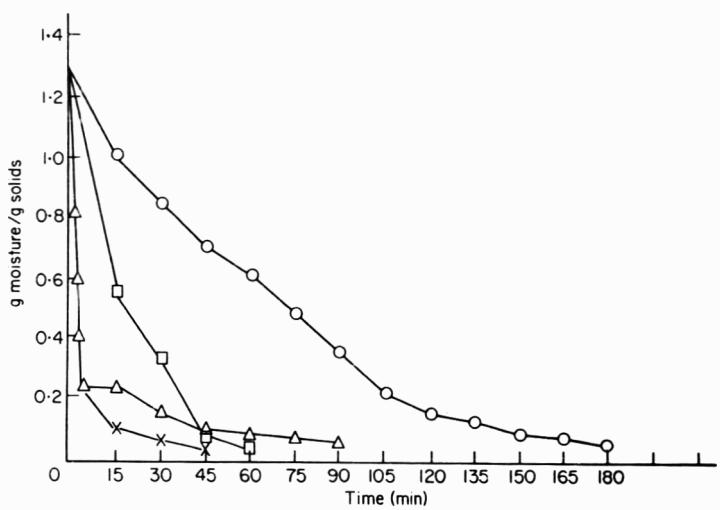

Figure 2. Dehydration curves for HTST drying of precooked red gram dal as compared to conventional modes of drying. ○. Direct tray drying; □. direct fluidized bed drying; △. HTST plus tray drying; ×. HTST plus fluidized bed drying.

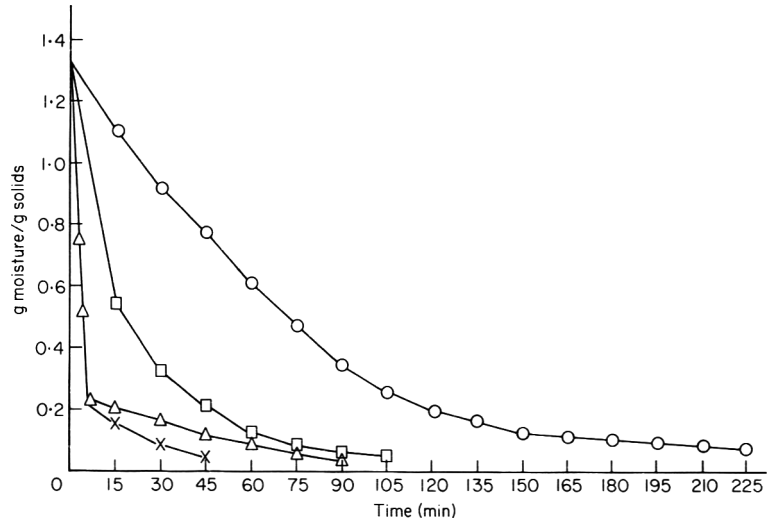

Figure 3. Dehydration curves for HTST drying of precooked black gram dal as compared to conventional modes of drying. ○, Direct tray drying; □, direct fluidized bed drying; △, HTST plus tray drying; ×, HTST plus fluidized bed drying.

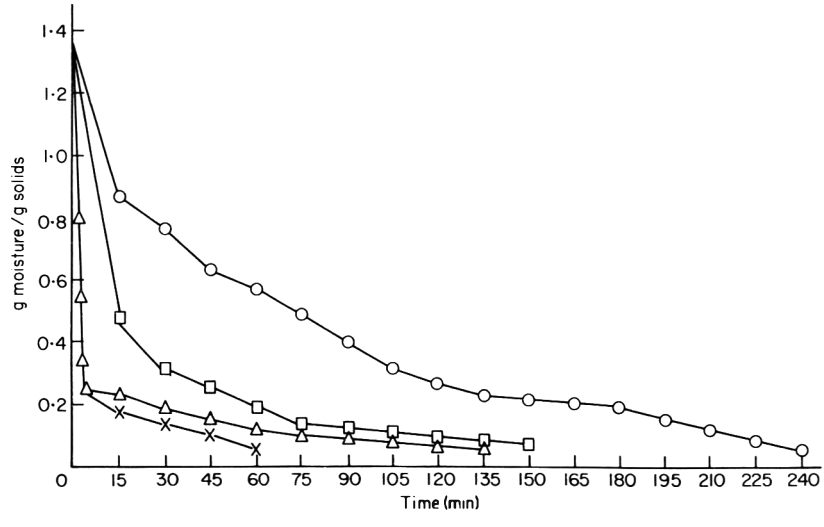

Figure 4. Dehydration curves for HTST drying of precooked Bengal gram dal as compared to conventional modes of drying. ○, Direct tray drying; □, direct fluidized bed drying; △, HTST plus tray drying; ×, HTST plus fluidized bed drying.

Bulk density

Data on the bulk density of the grains processed by the HTST drying are given in Table 2 along with the figures for the controls. There was considerable decrease in bulk density in HTST dried grains as compared to controls especially in black gram and Bengal gram dals indicating puffing effect. The bulk

Table 2. Drying time, bulk density, reconstitution time and rehydration ratio of precooked and HTST dried pulses as compared to direct hot air dried pulses

	Type of dal		
	Red gram dal	Black gram dal	Bengal gram dal
Total drying time (min)			
Direct tray drying	180	210	240
Direct FB drying	60	105	150
HTST + tray drying	90	75	135
HTST + FB drying	45	45	75
Bulk density (g/cc)			
Raw	0.96	1.04	1.04
Direct tray drying	0.71	0.81	0.96
Direct FB drying	0.70	0.71	0.86
HTST + tray drying	0.67	0.59	0.69
HTST + FB drying	0.62	0.48	0.66
Reconstitution time (min)/ rehydration ratio*			
Direct tray drying	10(2.2)	10(2.9)	13(2.3)
Direct FB drying	8(2.5)	8(2.9)	12(2.4)
HTST + tray drying	5(2.9)	5(3.5)	7(2.5)
HTST + FB drying	4(3.1)	4(3.5)	6(2.6)

* Figures in parentheses represent rehydration ratio.
FB = Fluidized Bed.

density was the lowest, indicating maximum expansion, in HTST plus fluidized bed dried products. Red gram dal did not show much increase in bulk in view of the flat nature of the grains but the HTST dried grains were more porous as seen from the cracks developed in the grains.

Rehydration behaviour

The cooking times given in Table 2 for the HTST dried dals show that they reconstitute in boiling water in half the time as required for the control samples.

Rehydration curve for black gram dal precooked and then dehydrated by HTST plus tray drying vis-a-vis control (direct tray drying) and raw is given in Fig. 5, which clearly shows the superiority of the HTST dried product over control with regard to percent water uptake and reconstitution time.

Rehydration ratio for the different grains processed by the HTST technique

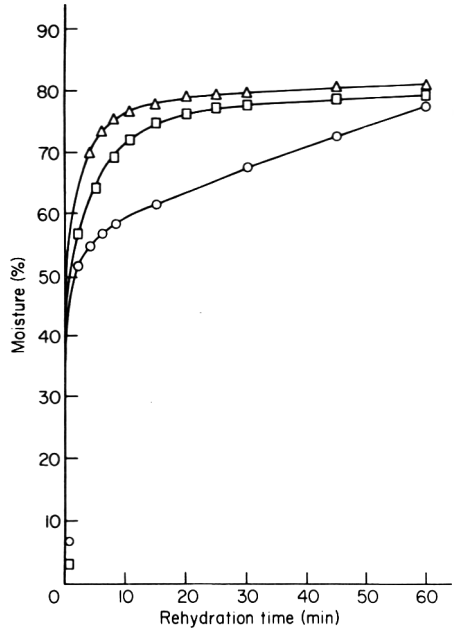

Figure 5. Rehydration curve for HTST plus tray dried precooked black gram dal as compared to direct tray dried and raw. ○, Raw; □, direct tray dried; △, HTST plus tray dried.

as well as the controls are given in Table 2. These again show the HTST dried samples to have higher values than the conventionally dried controls indicating higher water uptake.

Storage stability

Evaluation of the HTST dried dals during storage at different temperatures in polythene and PFL pouches up to 12 months showed that there was negligible change in the reconstitution time, rehydration ratio and organoleptic quality of the HTST dried dals. While red gram and black gram dals remained acceptable up to 12 months in both types of packages at both RT and 37°C, without any rancidity or browning, Bengal gram dal showed signs of slight rancidity and browning beyond 8 months in both types of packs, the HTST dried sample exhibiting a slightly higher rancidity than the control. Both were, however, still acceptable after reconstitution.

Amenability of the process for continuous production and its applicability to other food products

The technique enumerated above involves simple equipment with less capital investment as compared to other methods of drying, like explosive puffing,

achieving the same objective and is amenable to continuous production as the time of high temperature drying is very short. A continuous HTST drier similar to the equipment employed by Ferrel & Pence (1963) for dry-heat expansion of bulgur could be employed.

We have applied the technique to a variety of vegetables including green peas, diced potato, carrot and other root vegetables such as elephant yam, colocasia and sweet potato with encouraging results. Results of these studies will be published in a subsequent communication.

Conclusions

It is possible to reduce the rehydration and drying times of precooked dehydrated pulses considerably by exposing the cooked grains initially to a current of air at high temperature (170–200°C) for a short period (4–6 min) in a pneumatic drier followed by conventional method of drying at 60–70°C in a cabinet or fluidized bed drier. This initial HTST drying results in an expanded structure in the grain due to the sudden flashing of water vapour which helps in quicker drying and reconstitution of the dried material. The increase in porosity and the treatment at high temperature for a short time do not adversely affect the shelf stability of the grains.

The technique involves simple equipment and less capital investment compared to other methods of drying such as explosive puffing and is amenable to continuous processing as the time of high temperature drying is very short.

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Control of spoilage in vacuum packaged dark, firm, dry (DFD) meat

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Summary

Early spoilage of vacuum-packaged DFD meat, due to green discoloration and development of undesirable odours and flavours, can be prevented by addition of small quantities of citrate buffer to the meat before packaging. This treatment extends the storage life to that of vacuum-packaged normal meat, both appearance in the pack and flavour being acceptable after 12 weeks storage at −1°C. However, steaks cut from the vacuum-packed primal cuts remained darker in appearance than normal pH controls and spoiled more rapidly during aerobic storage.

Introduction

Aerobic spoilage of normal ultimate pH meat at chill temperatures occurs when the developing spoilage flora exhausts the glucose at the meat surface and attacks amino acids (Gill, 1976). DFD, or high pH, meat is deficient in glucose and so amino acids are attacked without delay, giving spoilage at far lower bacterial cell densities than normal. The aerobic shelf life can be extended by addition of glucose but not by reduction of the pH (Newton & Gill, 1978).

Normal meat can be stored at chill temperatures (*ca* 0°C) under anaerobic conditions for periods in excess of 10 weeks, whereas under aerobic conditions the shelf life is only 3 to 4 weeks. This has led to an increasing use of vacuum-packaging to extend the shelf life of chilled prime beef cuts. However, DFD meat spoils rapidly when vacuum packaged, green discoloration and putrid odour appearing after only 4 to 6 weeks (Taylor & Shaw, 1977). This can result in considerable financial loss as on occasion up to 40% of prime animals may yield DFD meat which must be downgraded and used for manufacturing pruposes. It is therefore desirable to find an acceptable method of delaying spoilage in vacuum-packaged DFD meat.

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0022–1163/80/0400–0227 $02.00

The green discoloration of DFD meat is caused by *Alteromonas putrefaciens* and is due to production of H_2S which converts the muscle pigment to green sulphmyoglobin (Nicol, Shaw & Ledward, 1970). The putrid odours are produced by *Enterobacter liqueraciens* attacking amino acids (Gill & Newton, 1979). Growth of *A. putrefaciens* and *E. liquefaciens* is apparently favoured by high pH (> 6.0) and oxygen limitation in vacuum packed DFD meat. Production of putrid odours by *E. liquifaciens* is prevented by addition of a preferentially utilized substrate such as glucose or citrate, but production of H_2S by *A. putrefaciens* is not. *In vitro* studies revealed that both organisms can utilize certain amino acids in the presence of glucose under anaerobic conditions. Therefore, the growth of *A. putrefaciens* must be stopped to prevent greening of vacuum packed DFD meat (Gill & Newton, 1979). The possibility of extending the shelf life of vacuum-packaged DFD meat by inhibiting growth of *A. putrefaciens* has therefore been examined.

Materials and methods

The investigation was divided into three stages.

(1). *Meat slices*

Initially, 50 g slices of DFD meat (pH 6.0) were packaged in the manner previously described (Gill & Newton, 1979). Both sterile slices and slices carrying a natural microflora were used. Each package received one of the additive treatments shown in Table 1 and was inoculated with a culture of *A. putrefaciens*, previously isolated from greened beef (Gill & Newton, 1979), to give an initial cell density of about $10^2/cm^2$. On sealing the package the film became closely applied to the meat so that the added solutions were distributed over all meat surfaces by capillary action. For study of the inhibitory activity of *Lactobacillus* the meat was inoculated with a suspension of an organism origi-

Table 1. Treatment of 50 g slices of DFD meat.

Additive	Concentration of solution or suspension	Amount added (μl/g meat)
Acetic acid	10% (w/v)	10, 20
Lactic acid	10% (w/v)	10, 20
Citric acid	10% (w/v)	10, 20
Glucose	50% (w/v)	1
Lactobacillus	10^9 cells/ml	1
Glucose : *Lactobacillus*	50% (w/v) : 10^9/ml	10 : 1
Disodium citrate : lactic acid	1.3M : 1.5M (pH 4.0)	3, 6, 9
Disodium citrate : lactic acid	1.3M : 0.7M (pH 4.5)	3, 6, 9
Disodium citrate	1.9M (pH 4.8)	2, 4, 6

nally isolated from vacuum-packaged meat. The *Lactobacillus* was cultured for 24 hr at 25°C in APT broth, centrifuged, and resuspended in 0.1% (w/v) peptone water for use as the inoculum. Packs were stored at 10°C and examined daily for appearance and odour. Bacterial counts and the pH of the meat slice were determined from a homogenate of half of the meat slice in 20 ml 0.1% (w/v) peptone water.

(2). *Small packs*

Pieces of DFD beef striploin (pH 6.2 to 6.7, 750 g) were packaged, using a commercial machine, in film with similar characteristics to that used for the meat slices. The solutions and suspensions added to packs are shown in Table 2. Two buffers were used alone, with glucose, with *Lactobacillus* and with glucose and *Lactobacillus*. Treated and control packs were stored at −1°C to 0°C. They were examined weekly for appearance, and at 6 and 12 weeks for bacteriological and sensory evaluation. Determinations of pH for all packs, and glucose and lactate determinations for selected packs, were made on exudate, meat samples 2–3 mm thick cut from the surface, and meat from the interior of cuts. Approx. 2 g of meat were homogenized in 10 ml distilled water for pH determinations, and glucose and lactate were determined as described by Gill (1976). Steaks were grilled and assessed by an *ad hoc* taste panel of six people.

(3). *Commercial packs*

Whole DFD striploins (pH 6.4–6.7, 3–4 kg) were treated with disodium citrate buffer (1.9 M, pH 4.8, 6 ml/kg) without or with glucose (10% w/v, 3 ml/kg). Treated DFD striploins, control striploins of untreated DFD meat, and meat of normal pH were packaged as in normal commercial practice. The packs were stored at −1° to 0°C. Duplicate packs were withdrawn at 0, 6 and 12 weeks for bacteriological and sensory assessment. Two steaks 2.5 cm thick were cut from both ends of each striploin to give two end and two middle steaks from each pack. The steaks were grilled and presented to a trained six-member panel who rated them for tenderness, juiciness, flavour acceptability, off flavours

Table 2. Solutions and suspensions used for treatment of 750 g samples of DFD striploins.

Treatment	Additive	Concentration of solution or suspension	Amount added (μl/g meat)
1	Disodium citrate : lactic acid	1.3M : 1.2M (pH 4.2)	9
2	Disodium citrate	1.9M (pH 4.8)	2.6
3	Treatment 1 + glucose	+ 20% (w/v)	+ 1.5
4	Treatment 2 + glucose	+ 20% (w/v)	+ 1.5
5	Treatment 2 + *Lactobacillus*	+ 10^9/ml	+ 1
6	Treatment 4 + *Lactobacillus*	+ 10^9/ml	+ 1
7	Glucose : *Lactobacillus*	20% : 10^9/ml	0.5, 1.5, 5, 15 : 1
8	Untreated control		

Table 3. Growth of *A. putrefaciens* on vacuum packed 50 g DFD meat slices held at 10°C.

Additive	Generation times (hr)	Final counts (log_{10} no./cm²)
Untreated control	4.2	7.5
Glucose	4.2	8.0
Lactobacillus	15.6	5.4
Glucose : *Lactobacillus*	NG*	<4.0
Buffers (lower concentrations)	11.6	4.7–5.9
Buffers (highest concentration)	NG	<4.0

* NG = no growth.

(microbial and chemical) and general acceptability. The taste panel results were subjected to analysis of variance. Additional steaks were wrapped in stretch polyethylene, held at 6° to 7°C, and observed daily to determine display life.

Results

(1). *Meat slices*

Addition of acetic, lactice or citric acid reduced the meat pH but caused severe brown discoloration on its surface. Buffers at pH 4.0 and 4.5 cause some brown discoloration initially, although this disappeared during storage. Buffer at pH 4.8 caused little discoloration. The pH 4.0 and 4.5 buffers prevented growth of *A. putrefaciens* only at 9 µl/g of meat, and the pH 4.8 buffer only at 6 µl/g of meat. Lower concentrations delayed greening by slowing the rate of growth and reducing the final counts of *A. putrefaciens* (Table 3). The pH 4.0 buffer reduced the pH of the meat slice to below 6.0, but pH 4.5 and 4.8 buffers did not.

Adding glucose to the meat in the presence of the natural flora did not delay greening. *Lactobacillus* delayed greening by slowing the rate of growth and reducing final counts of *A. putrefaciens*. Addition of glucose plus *Lactobacillus* prevented growth of *A. putrefaciens* and therefore greening by reducing the pH from an initial value of 6.4 to 5.8 after 4 days. In appearance this meat became indistinguishable from normal pH meat.

(2). *Small packs*

Green discoloration was apparent in the DFD control packs at 5 to 6 weeks. The pH 4.2 buffer caused irreversible brown discoloration, although greening was prevented and the meat was acceptable to the taste panel. The pH 4.2 buffer reduced the pH of the exudate and the meat surface by up to 0.7 unit

Table 4. Assessment of treated 750 g packs of DFD striploins after 12 weeks at −1° to 0°C

Treatment	Additive/g meat	Attribute*				*A. putrefaciens* (log_{10} no./cm^2)
		Appearance	Odour	Colour regain	Taste	
1	Buffer pH 4.2, 9 µl	1	3	2	2	<3.4
2	Buffer pH 4.8, 2 µl	1	2	2	1	5.4
2a	Buffer pH 4.8, 6 µl	3	4	3	3	<3.4
3	Treatment 1 : glucose 0.3 mg	1	3	2	2	<3.4
4	Treatment 2 : glucose 0.3 mg	1	2	2	1	<3.4
4a	Treatment 2a : glucose 0.3 mg	4	3	3	3	<3.4
5	Treatment 2 : *Lactobacillus* 10^3	3	2	4	1	<3.4
5a	Treatment 2a : *Lactobacillus* 10^3	3	4	4	1	<3.4
6	Treatment 4 : *Lactobacillus* 10^3	4	3	4	1	<3.4
6a	Treatment 4a : *Lactobacillus* 10^3	4	2	4	1	<3.4
7	Glucose 0.1, 0.3, 1, 3 mg : *Lactobacillus* 10^3	4	2	4	1	<3.4
8	Untreated control	0	0	2	0	6.7

* Scored on a 0–4 scale where 0 = unacceptable, 2 = marginal, 4 = good. Scores were assigned for the four attributes from taste panelists' reports.

after 6 and 12 weeks storage. The pH 4.8 buffer reduced the pH of the exudate and surface by up to 0.5 unit. In both treatments the internal pH was unaffected. Meat which received a glucose plus *Lactobacillus* treatment was paler than untreated meat and the appearance was improved. The surface pH was reduced 0.2 to 0.4 unit after 6 and 12 weeks storage but the internal pH was unaffected. However, all meat which received a *Lactobacillus* inoculum was unacceptable at 12 weeks because of the development of 'dairy' flavours (Table 4).

Brown discoloration produced by the buffers occurred only on the meat surface and glucose and lactate determinations, in addition to pH, confirmed that the effects of treatment were largely confined to the exudate and meat surface.

Consideration of all the parameters: appearance of the meat, odour, colour regain, bacterial counts and taste, indicated that treatments with disodium citrate pH 4.8 at 6 μl/g of meat or this buffer plus glucose (0.3 mg/g of meat) gave the most acceptable results (treatments 2a and 4a, Table 4).

(3). *Commercial packs*

The untreated DFD controls were spoiled by green discoloration at 6 weeks and were not presented to the taste panel. The treated DFD meat was darker than the normal pH control both in and after removal from packs, but this did not detract greatly from its appearance. The exudate contained some precipitate in treated packs, but was clear in control packs. The colour regain of all cuts

Table 5. Taste panel results for steaks cut from vacuum packed striploins stored 12 weeks at −1° to 0°C.

Attribute	DFD : Buffer middle and end steaks		DFD : Buffer : glucose middle and end steaks		Normal pH middle and end steaks	
* Tenderness	6.2	6.7	6.8	6.2	7.3	6.8
* Juiciness	6.9	6.7	6.8	6.2	7.3	6.8
† Off flavours 1.microbiol	4.5	4.0	4.8	4.5	5.0	4.7
2.chemical	5.4	5.6	5.2	5.3	5.3	5.2
* Flavour acceptability	5.4	4.9	6.2	5.1	6.4	6.3
* General acceptability	5.4	4.8	5.9	4.9	6.5	6.2

* Scored on a 1–9 scale where 1 = highly unacceptable
5 = marginal
9 = highly acceptable.

† Scored on a 1–9 scale where 5 = no off flavours
1 = strong microbial off flavour
4 = slight
9 = strong chemical off flavour
6 = slight.

was good and no abnormal odours were apparent when packs were opened. *A. putrefaciens* was undetectable ($<10^3/cm^2$) in treated packs at any sampling time and greening was prevented. After 12 weeks storage there was little difference between the internal pH of the meat and the pH at or near its surface. The pH ranged from 6.35 to 6.71. However, the pH of the exudate was about 0.2 pH unit lower than that of the meat.

At all sampling times the treated DFD meat and the normal pH control meat were acceptable to the taste panel in the attributes tested. After six weeks storage there were no detectable differences between treated DFD meat and the control. The tenderness of all meat increased with time, but the flavour acceptability of treated DFD meat decreased between 6 and 12 weeks storage. This decrease was reflected in the 'general acceptability' scores. Time of storage made no significant differences to the other attributes, nor did the presence or absence of glucose (Table 5).

The display life of DFD steaks was 2 days, while that of steaks from normal pH was 3 days. DFD steaks were darker in appearance and putrid odours occurred after 2 days.

Discussion and Conclusions

The solutions added to vacuum packs of DFD meat and the effects produced by them were initially confined to the meat surface and the exudate in the pack. This was advantageous because the bacteria are confined here also, and treatments designed to limit their growth can thus be relatively mild since the effects need not extend in to the bulk of the meat.

Lactobacilli inhibit growth of competing species (Gilliland & Speck, 1975). Although inoculation with *Lactobacillus* suppressed *A. putrefaciens* and produced vacuum packed DFD meat with enhanced appearance, taste deterioration reduced the effectiveness of this treatment. Use of other species of lactic acid bacteria may overcome this difficulty, and the treatment would then produce meat almost indistinguishable from vacuum packed normal pH meat. Use of lactic acid starter bacteria is commonplace in the dairy industry and in the manufacture of fermented sausages, but such treatment of DFD meat might pose problems in determining whether the product could legally be described as fresh meat or would be deemed to be processed.

The success of mild buffer treatments in prolonging storage life was apparently due to the initial inhibition of *A. putrefaciens* by the low pH at the meat surface. The subsequent rise in surface pH due to equilibration with the bulk meat did not result in growth of *A. putrefaciens*, probably because the organism had by then been inhibited by the developing population of lactobacilli. It should be possible to use salts of other organic acids to achieve the same end. Unfortunately, sodium lactate is not suitable as it has little buffering capacity in the pH range involved. Treatment is by the addition of a solution of the buffer to the meat in the plastic bag just before evacuating and sealing, and could be done

routinely without interferring with the flow of meat in the packaging room. The treated vacuum packaged DFD meat then has a storage life comparable with that of vacuum packaged normal pH meat.

Acknowledgments

The authors gratefully acknowledge the assistance of staff of the Auckland Farmers' Freezing Co-operative, and of Dr V. J. Morre, MIRINZ, who performed the taste panel assessments and analysed the results.

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Book reviews

Food Processing Enzymes . . . recent developments, Food Technology Review No.52 By Nicholas D. Pintauro.
New Jersey: Noyes Data Corporation, 1979. Pp. xii + 420. ISBN 0–8135–0748–8. U.S. $42.00.

This is another skilfully prepared runner from the NDC stables. Set out in splendidly clear type, arranged into obvious and useful chapters and coming at a time of rapid expansion in the field of food processing, Pintauro has provided the means for the reader to explore a wide range of application for enzymes and yet remain well within the discipline of the food industry.

In the foreword to this collection of United States Patents granted between roughly 1970 and 1978 the author sets out most explicit claims for the objectives of the book. 'As a source of technical information and a guide to the U.S. Patent Literature in the field' it fulfils its goals well, but the reader should remain in constant awareness of the limitations of that claim. Having the prime requirement to substantiate a patentable condition in law, the patent literature rarely provides the essential detail that makes the difference between an economically viable process and plain inventiveness. Thus the reader will be left with the very real question as to the feasibility of commercially performing the described steps, but the answers reasonably lie within the expected range of knowledge of the worker in the field. This brings out the difficulty of accepting another suggestion made as a case for the value of the book, *viz.* a source of sound background knowledge for new starters in the field of enzymes applied to the food industry.

The most attractive facet of this book may well be the manner in which the author has disentangled the concepts of many complex patents and has constructed some excellent introductions for individual sub-headings within the main chapters. This feature is particularly well presented in the last, and sadly all too short, chapter on 'By-Product and Waste Utilisation and Animal Feed Production'.

If a serious limitation to the achievement of the main aim of the book is to be found at all, it lies in the absence of a reference-cross referenced index of the subjects treated. It is to be understood that the manner of rapid production of these reference works places severe limitations on the details of indexing that one expects from them, but in these times of computer word handling it might have proved a worthy additional feature of the book to produce a key-word index. Again, one could also wish for an index listing the location of references to enzymes by type; e.g. carbohydrases (starch and non-starch modifying),

proteases, lipases, esterases, etc. After asking the text a few basic questions, this particular failing proved a definite irritation in attempts to follow a particular train of application through the chapters.

In conclusion, at the price of approximately £20, this numbers amongst the top thirty books that should be ready at hand for anyone who wishes to remain at the forefront of food processing technology. A definitely worthwhile presentation of data and ideas but not a book to be considered a 'good read'. If the reader can formulate the problem to conform to the very logical way the book has been set out, then many solutions will be found within its covers.

A. Godfrey

Liquid Chromatographic Analysis of Food and Beverages, Vol. I. Ed. by G. Charalambous.
New York: Academic Press, 1979. Pp. xiii + 236, ISBN 0 12 169001 6. £10.40.

This book makes a valuable addition to the rapidly increasing literature on food analysis by high performance liquid chromatography (HPLC). It consists of the proceedings of a symposium on the analysis of foods and beverages by HPLC held in Honolulu, Hawaii, 1–6 April 1979.

The topics covered include many up to the minute developments in HPLC and as such the book will be found most useful to those readers with a basic knowledge of the instrumentation and techniques of this method. It is not conceived as an introduction to HPLC, nor indeed would it be of any use in this role.

The thirteen chapters consist of several papers dedicated to HPLC methodology and others directed to specific food analyses, not all of which use HPLC techniques. In the former category the first chapter describes the use of spectroscopy for the identification of compounds by stopped-flow scanning. A subsequent chapter (4) discusses the utilization of a microprocessor-based variable wavelength detector for the optimization of detection conditions. Chapter 3 deals with several comparatively new chromatographic techniques such as paired-ion chromatography (PIC) and on-column concentration. Chapter 5 illustrates some of the, at present, very limited applications of ^{13}C nuclear magnetic resonance spectroscopy to food analysis, although here the chromatographic separations are based on low pressure gel-filtration. In Chapter 6 the power of HPLC, as applied to amino-acid analysis, is clearly demonstrated.

The remaining papers concentrate on applications of HPLC to specific food components including naturally occurring capsaicins, aflatoxins, sterols in soybeans, anthocyanins in fruits, vitamins in citrus juices and monosaccharides in avocado. A further paper on aflatoxins demonstrates the use of high performance radial chromatography (HPRC), a recent acquisition to the chromatographer's growing armoury. An excellent paper is also included on the character-

isation of Amadori compounds from model systems, which illustrates the complementary nature of gas chromatography (GC) and HPLC.

This book will prove very useful to the practising chromatographer working in the field of food analysis. However, it is always a pity that rapid publication of symposia proceedings appears to necessitate the photoreproduction of authors' typed scripts, with the associated problems of variable type face and indifferent diagrams.

Robert Macrae

Microbiology of Food Fermentations, 2nd edition by C. S. Pederson. Westport: AVI, 1979. Pp. viii + 384. ISBN 0 87055 277 5. U.S. $28.00.

The author of this book seeks, within the confines of some 370 pages, to introduce the reader to the plethora of fermented foods that are prepared throughout the world, and it is hardly surprising, therefore, that the treatment of individual fermentations appears rather superficial. The justification for this approach is that the 'treatise will give readers a broader concept of the importance of this method of preparing foods in the feeding of the populations of the world', and if the text is read with due consideration to this intention, then it may be regarded as a readable and entertaining book.

The introductory chapters have been up-dated from the first edition, and are designed to provide non-microbiologists with a 'working knowledge' of the micro-organisms involved in food fermentations. This section, which occupies nearly one-third of the book, is followed by chapters dealing with various fermented foods, such as milk products like cheese and yoghurt, as well as vegetable products ranging from sauerkraut through to the standard loaf of bread. Another chapter deals briefly with the gamut of alcoholic beverages from Kaffir beer to Champagne, while a separate chapter describes the industrial production of vinegar and lactic acid. Whether these latter fermentations, or indeed the commercial production of Champagne, should be described as 'food fermentations' is a moot point, but it becomes clear at an early stage that had these marginal topics been excluded, then more space could have been devoted to those fermentations that occupy a central position in the lives of less developed communities. Kaffir beer, for example, is accorded a brief, and rather dated, mention as being important in 'the diet of the natives of Nyasaland', and yet this traditional fermentation occupies a vital role in the social life of many southern African communities, as well as being responsible for the relative absence of pellagra in the same area.

The selection of contents for any book is, of course, a matter of personal taste, but if Professor Pederson were really seeking to 'fire the imagination' of his readers concerning the potential of fermentation, then it is curious that many of the 'age-old practices' are viewed almost as quaint relics, rather than as having a possible niche 'in feeding the populations of the world'. Some traditional

processes are obviously of limited application, but readers are given little guidance as to which are 'museum pieces' and which have, or could have, a viable role in improving the nutritional status of under-privileged communities. The reader will also gain little inspiration from the illustrations, which in terms of quality, or even relevance in some cases, are quite appalling. Thus, a plate with the legend 'Tea, a white-flowered evergreen plant', reveals nothing beyond a few hazy farm buildings, while two gentlemen reported to be 'Harvesting coffee cherries in the Philippines' could, as far as one can see, be doing anything. Obviously one accepts that publishers are under considerable pressure to reduce costs, but it is to be hoped that the standards accepted in this text will never become the 'norm' for scientific works.

The overall impression is, therefore, of a book that offers to reveal to the reader all the mysteries and untapped potential of food fermentations, and yet, in the end, never quite 'lives up' to expectation. No doubt many people will enjoy it as a glimpse of the more benign aspects of food microbiology, but the feeling remains that, in revising the first edition, the author has done less than justice to a subject that is extremely relevant to present-day problems.

R. K. Robinson

Books received

Composite Flour Technology Bibliography. Supplement 2 to Publication G 89 (Report G 124). By D. A. V. Dendy and R. Kasasian.
London: Tropical Products Institute, 1979. Pp. vi + 74. ISBN 0 85954 104 5. £2.00.

World Review of Nutrition and Dietetics, Volume 34. Edited by G. H. Bourne.
Basel: S. Karger, 1980. Pp. xii + 272. ISBN 3 8055 3069 2. Sw.Fr. 166, U.S. $99.50.

The topics reviewed in this volume comprise: the contribution of large-scale feeding operations to nutrition; meat in human nutrition; some naive questions and thoughts on vitamin D and its relatives; cocoyam – a neglected tuber; Zn metalloenzyme activities; aflatoxin-induced coagulopathy in different nutritionally classified animal species; mercury in marine seafood; the scientific medical margin of safety as a guide to the potential risk to public health.

Advances in Food Research, Volume 25. Edited by C. O. Chichester, E. M. Mrak and G. F. Stewart.
New York: Academic Press, 1979. Pp. vii + 292. ISBN 0 12 016425 6. U.S. $28.00.

This volume contains monographs on: wine deacidification; dehydrated mashed potatoes – chemical and biochemical aspects; xylitol and oral health; metabolic and nutritional aspects of xylitol; frozen fruits and vegetables – their chemistry, physics and cryobiology; *Byssochlamys* spp. and their importance in processed fruits.

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Arrangement. Papers should normally be divided into: (a) Summary, brief, self-contained and embodying the main conclusions; (b) Introduction; (c) Materials and methods; (d) Results, as concise as possible (both tables and figures illustrating the same data will rarely be permitted); (e) Discussion and conclusions; (f) Acknowledgments; (g) References.

References. Only papers closely related to the authors' work should be included; exhaustive lists should be avoided. References should be made by giving the author's surname, with the year of publication in parentheses. When reference is made to a work by three authors all names should be given when cited for the first time, and thereafter only the first name, adding *et al.*, e.g. Smith *et al.* (1958). The '*et al.*' form should always be used for works by four or more authors. If several papers by the same author and from the same year are cited, a, b, c, etc. should be put after the year of publication, e.g. Smith *et al.* (1958a). All references should be brought together at the end of the paper in alphabetical order. References to articles and papers should mention (a) name(s) of the author(s) (b) year of publication in parentheses; (c) title of journal, underlined, abbreviated according to the *World List of Scientific Publications*, 4th edn and supplements; (d) volume number; number of first page of article. References to books and monographs should include (a) name(s) and initials of author(s) or editor(s); year of publication in parentheses; (b) title, underlined; (c) edition; (d) page referred to; (e) publisher; (f) place.

Standard usage. The *Concise Oxford English Dictionary* is used as a reference for all spelling and hyphenation. Statistics and measurements should always be given in figures, i.e. 10 min, 20 hr, 5 ml, except where the number begins the sentence. When the number does *not* refer to a unit of measurement, it is spelt out except where the number is one hundred or greater.

Abbreviations. Abbreviations for some commoner units are given below. The abbreviation for the plural of a unit is the same as that for the singular. Wherever possible the metric SI units should be used unless they conflict with generally accepted current practice. Conversion factors to SI units are shown where appropriate.

SI UNITS

gram	g	Joule	J
kilogram	kg = 10^3 g	Newton	N
milligram	mg = 10^{-3} g	Watt	W
metre	m	Centigrade	°C
millimetre	mm = 10^{-3}m	hour	hr
micrometre	μm = 10^{-6} m	minute	min
nanometre	nm = 10^{-9} m	second	sec
litre	l = 10^{-3} m^3		

NON SI UNITS

inch	in	= 25·4 mm
foot	ft	= 0·3048 m
square inch	in^2	= 645·16 mm^2
square foot	ft^2	= 0·092903 m^2
cubic inch	in^3	= 1·63871 × 10^4 mm^3
cubic foot	ft^3	= 0·028317 m^3
gallon	gal	= 4·5461 l
pound	lb	= 0·453592 kg
pound/cubic inch	lb in^{-3}	= 2·76799 × 10^4 kg m^{-3}
dyne		= 10^{-5} N
calorie (15°C)	cal	= 4·1855 J
British Thermal Unit	BTU	= 1055·06 J
Horsepower	HP	= 745·700 W
Fahrenheit	°F	= 9/5 T°C + 32

Figures. In the text these should be given Arabic numbers, e.g. Fig. 3. They should be marked on the backs with the name(s) of the author(s) and the title of the paper. Where there is any possible doubt as to the orientation of a figure the top should be marked with an arrow. Each figure must bear a reference number corresponding to a similar number in the text. Photographs and photomicrographs should be unmounted glossy prints and should not be retouched. Line diagrams should be on separate sheets; they should be drawn with black Indian ink on white paper and should be about four times the area of the final reproduction. Lines and lettering should be of sufficient thickness and size to stand reduction to one-half or one-third. Whenever possible, the originals of line diagrams, prepared as described above, should be submitted and not photographs. The legends of all the figures should be typed together on a single sheet of paper headed 'Legends to figures'.

Tables. There should be as few tables as possible and these should include only essential data; the data should not be crowded together. The main heading should be in bold with an Arabic number, e.g. **Table 2**. Each table must have a caption in small letters. Vertical lines should not be used.

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