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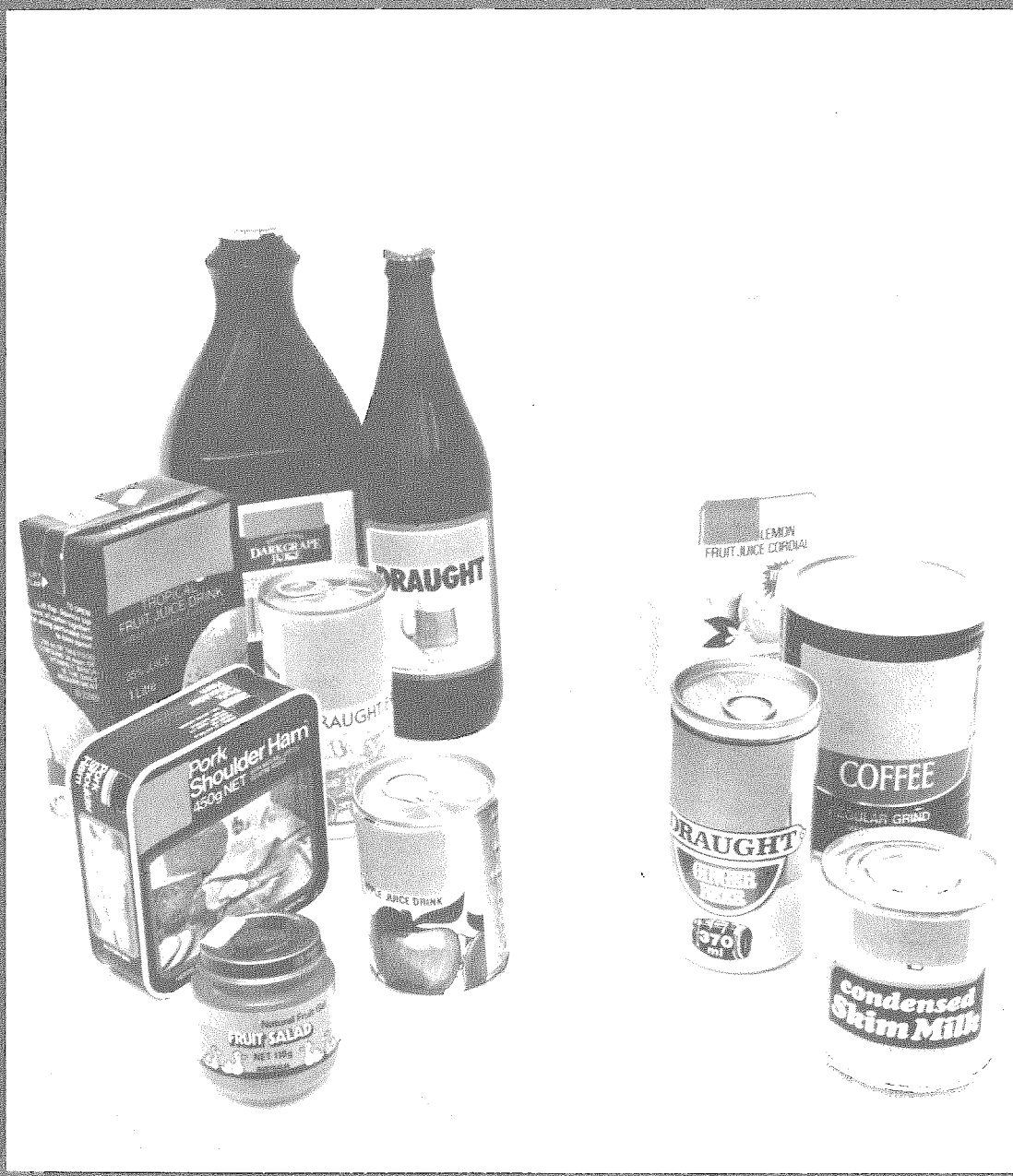

What are canned foods?

By P. W. Board

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Surprisingly few people know which foods are rightly called canned foods, or what characteristics canned foods are expected to have. Most would recognize a can of peas as a canned food but would probably reject a bottle of beer, a jar of baby food or a flexible pouch of ravioli as being canned foods, even though they are. Conversely, some people would argue that cans of cashew nuts, lemonade or sweetened condensed milk are canned foods, although they are not, being simply foods packed in a convenient container which happens to be a can.

The canning process

What is and is not a canned food is determined by the procedure used to manufacture the product. Canned foods are those that are manufactured by the canning process which involves two essential operations:

- the food must be heated at a sufficiently high temperature and for a sufficient time to make it commercially sterile, and
- the food must be sealed in a hermetic container (not restricted to metal cans) which will prevent recontamination of the product after it is sterilized.

These operations may be carried out in any of three sequences: most canned foods are produced by heating the product after it is sealed in the container, some foods are filled hot into the container, which is then sealed and cooled, and thirdly, some products are heated and cooled continuously before being filled into sterilized containers which are then sealed under aseptic conditions.

Commercial sterility

The term *commercially sterile* is used to describe foods that are free of microorganisms capable of growing under the conditions that the product is likely to encounter during storage and distribution. This term implies that canned foods may not be totally sterile and this is commonly the case. The microorganisms that survive the heat treatment do not reproduce or spoil the product and, in many instances, slowly die during storage of the product. Despite the presence of these surviving, but dormant, organisms the food is safe and it carries a much lower microbial load than other processed or fresh foods.

Factors governing the growth of surviving organisms in commercially sterile canned foods include the acidity or pH of the product, the absence of oxygen, the presence of certain inhibitory substances and the temperature the product encounters during storage and distribution.

Acid foods

The severity of the heat treatment required to achieve commercial sterility is determined to a major extent by the pH of the product. In simple terms, products having a pH less than 4.6, i.e. most fruits and many tomato products, are made commercially sterile by heating all parts of the product to about 95 °C and then cooling. Lower temperatures are sufficient for highly acid foods. These processes inactivate vegetative forms of contaminating organisms, while the acidity prevents the surviving spores from germinating and spoiling the product.

Low acid foods

The acidity of foods with pH above 4.6, i.e. most meat, fish and vegetable products, is insufficient to prevent spore germination and growth and consequent spoilage. These

products must therefore be processed at higher temperatures, usually in the range 115–125 °C, to inactivate spores that are capable of germinating and growing at the temperatures prevailing during storage and distribution.

Temperatures during storage and distribution

Most canned foods are intended for storage at temperatures ranging from about 5 °C to about 40 °C and so inactivation of mesophilic organisms is essential in these products. The mesophilic sporing bacterium having the greatest significance as a public health hazard in canned low-acid foods is *Clostridium botulinum*. Most heat treatments for low-acid canned foods are therefore designed to reduce to a vanishingly small value the probability that any spores of *Cl. botulinum* will survive. Thus if viable mesophilic sporing bacteria are found in a low-acid canned food, the long-term stability and safety of that food must be suspect. Exceptions are the 'pasteurized' canned foods mentioned below. Viable mesophilic sporing bacteria may sometimes be cultured from these foods but in the intact product they are dormant.

If proper precautions are taken during the storage and distribution of low-acid canned foods, the temperature of these products will seldom exceed 40 °C even in tropical regions. If for some reason the temperature of the canned foods reaches say 45–55 °C during storage and transport, there is a risk that the product will be spoiled by thermophilic organisms. Spores of thermophilic bacteria are often highly resistant to inactivation by heat and so some may survive the usual heat sterilizing processes, germinate and grow if temperature conditions become favourable.

Thermophiles

The heat resistance of spores is commonly specified as the D_{121} value which is defined as the time in minutes at 121 °C required to reduce the number of surviving spores by a factor of 10. Spores of the thermophile, *Bacillus stearothermophilus*, have a D_{121} value of about 5 min and spores of *Cl. botulinum* (Types A and B) have a D_{121} value of about 0.2 min. A typical heat sterilizing process for a low-acid food, equivalent in sterilizing effect to exposing the entire product to 121 °C for 5 min (i.e. $F_0 = 5$ min), would reduce the number of surviving spores of the thermophilic organism by a factor of 10 and the number of spores of *Cl. botulinum* by a factor of 10^{25}. Even if the product contained several thousand spores of *Cl. botulinum*, the probability of one spore surviving the heat treatment would be extremely small (about 10^{-20}). However, if the product contained only 10 spores of the thermophile at the thermal centre, there is a 10% chance that one of these spores would survive the process. Clearly, the heat sterilization processes used commercially will often be insufficient to inactivate all the spores of thermophilic organisms, even when they are present in low numbers. Hence, the stability of most low-acid canned foods is dependent on storage at sub-thermophilic growth temperatures. The added benefit of storing canned foods at moderate temperatures is that many deteriorative processes are retarded and the product retains quality for longer periods.

'Pasteurized' canned foods

Another group of canned products, whose stability depends on the maintenance of low storage temperatures is typified by 'pasteurized' canned hams which must be stored at temperatures below 5 °C. These products receive a heat treatment of low severity, which inactivates the heat-labile vegetative forms of potential spoilage organisms but not the spores. Pasteurized canned foods must be stored at temperatures less than 5 °C to prevent germination and growth of the surviving spores. The products will remain stable against spoilage as long as the specified temperature is maintained.

Summary

Canned foods are those that are produced by the canning process which involves heating the product to inactivate microorganisms that may cause spoilage, and sealing the product in a package which prevents recontamination. The heat process may be applied before or after packaging and the package may be a metal can, glass container, plastic pouch or any other container compatible with the food and having the required protective properties.

Most canned foods are heat processed to make them stable at storage temperatures ranging up to about 40 °C, a temperature which should not be exceeded even in the tropics provided established precautions are taken during storage and transport. When low-acid canned foods are exposed to temperatures in the range 45–55 °C there is a danger that thermophilic spoilage will occur.

The spores of some thermophilic bacteria are so heat resistant that it is often impractical to inactivate them with heat. The best protection against thermophilic spoilage is to maintain the temperature of the product below 40 °C. This approach also prolongs the shelf life of the product. Storage temperatures below 5 °C must be used to ensure the storage stability of 'pasteurized' products as these receive heat treatments of low severity that are insufficient to inactivate the spores of some mesophilic organisms.

Mycotoxins in human health*

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Between 1960 and 1970 it was established that some fungal metabolites, now called mycotoxins, were responsible for animal disease and death. In the decade following 1970 evidence steadily accumulated which showed that mycotoxins have been the cause of *human* disease in the past, are causing it now, and will continue to cause it in the future. There are at least 10 human diseases which are now known to be, or are suspected of being, mycotoxicoses. Each of them is reviewed below, and their possible implications for Australian are discussed.

Ergotism.

The association of one human illness with a fungus has been known for a long time. Ergotism occurred throughout the last millennium in central Europe, and has certainly killed hundreds of thousands of people. The relationship between ergotism and the formation of ergots in maturing grains was established by the 17th Century, and by 1750 it was known that ergots are the result of growth by the fungus *Claviceps purpurea* in the ovaries of grains, especially rye. During milling, ergots are not readily separated from sound grain, but become fragmented and dispersed throughout the flour.

The first symptom of ergotism is a feeling of coldness in hands and feet, followed by a sensation of intense burning. In extreme cases, gangrene, necrosis and death may follow. In the Middle Ages the disease was known as 'St Anthony's Fire', because it was believed that travelling to the shrine of St Anthony would relieve the burning sensation. Modern medicine is more likely to attribute the curative effect of this trip to removal of the victim from his contaminated environment.

The toxic principles in ergots are now known to be a range of alkaloids, all derivatives of lysergic acid, which have a wide spectrum of biological activities. In low doses, some have been used for many years as oxytocics.

The last known outbreak of ergotism occurred in the French village of Pont St Esprit in 1954. More than 200 people became ill and four died from cardiovascular collapse as a result of muscular spasms. This well-documented mycotoxicosis (Fuller 1968) was due to gross negligence by a miller. It was

* A paper presented at a seminar of the N.S.W. Branch of the Australian Society for Microbiology, Inc., Sydney, October 1979.

also notable because many people suffered from hallucinations, screaming that they were on fire or were being chased by wild beasts. Fuller suggests that the alkaloid responsible for these symptoms may have been lysergic acid diethylamide (LSD).

Ergotism can now be regarded as a disease of the past. Stringent controls on levels of ergot in grain have been established throughout the world.

Acute cardiac beriberi

Another human mycotoxicosis of significance, acute cardiac beriberi, was a common disease in Japan, especially in the second half of the 19th Century.

Beriberi is the general name given to vitamin deficiencies resulting from the consumption of polished rice. Painstaking and pioneering work by Uraguchi (1971) established that acute cardiac beriberi probably was not an avitaminosis but a mycotoxicosis. In 1910 the incidence of acute cardiac beriberi suddenly decreased: Uraguchi points out that this coincided with implementation of a government inspection scheme which dramatically reduced the sale of mouldy rice in Japan. The incidence of true beriberi, resulting from the consumption of polished rice, was unaffected.

The first symptoms of acute cardiac beriberi are heart distress and palpitation, with rapid breathing. After a few hours, breathing becomes laboured, nausea and vomiting are experienced, and within 2 to 3 days, anguish, pain, restlessness and sometimes maniacal behaviour occur. In extreme cases, progressive paralysis leading to respiratory failure may cause death. It is notable that victims of acute cardiac beriberi were often young adults without any history of disease.

Sakaki drew attention to the possible toxicity of 'yellow rice' in 1891, and its sale was banned in Japan in 1910. The possible involvement of fungi was studied by Miyake, who reported in 1940 that the probable cause was *Penicillium toxicarium*, a new species later considered to be a synonym of *P. citreoviride* and now known as *P. citreonigrum* (Pitt 1979). This fungus was reported by Miyake to grow on rice at moisture contents above 14.6%. By 1950, other Japanese workers had isolated the principal toxin, known as citreoviridin.

Uraguchi (1971) detailed a long series of studies on acute cardiac beriberi. This disease in humans, as reported in Japanese medical literature, is closely paralleled by that induced in dogs and other animals by injections of citreoviridin. Uraguchi's conclusion that acute cadiac beriberi was caused by citreoviridin appears to be well substantiated.

Alimentary toxic aleukia

A third disease caused by a mycotoxin is known as alimentary toxic aleukia (ATA). From 1942 to 1948 this disease caused the deaths of many people in Russia, especially in the Orenburg district north of the Caspian Sea, but also throughout most of the southern and central regions of the U.S.S.R. (Joffe 1978). In some localities, mortality was as high as 60% of those afflicted, and up to 10% of the population. The Russian authorities have apparently never released a figure for the total mortality, but it must have been at least one hundred thousand. Records show that ATA was prevalent in 1932 and in 1913, and, no doubt, outbreaks occurred in earlier years as well.

ATA is an exceptionally nasty disease: symptoms include fever, haemorrhagic rash, bleeding from the nose, throat and gums, necrotic angina, extreme leucopenia, agranulocytosis, sepsis and exhaustion of the bone marrow. These symptoms are surprisingly similar to those caused by radiation poisoning, and contrast with those caused by bacterial toxins or other mycotoxins (Joffe 1978).

Outbreaks of ATA were always associated with bread and other cereal products made from grain that was allowed to remain unharvested over the winter months. During and after World War II, agricultural labour in Russia was very limited, causing delays in harvest, and food was often very scarce, resulting in the consumption of poor quality grain.

Russian studies in the 1950s suggested that *Fusarium* and *Cladosporium* species elaborated the toxins responsible for ATA, and that alternate freezing and thawing of the grain was essential for toxin production. Two glycosides, named sporofusarin and poaefusarin, produced by *F. sporotrichioides* and *F. poae* were the principal compounds implicated. Because of the freezing and thawing effect, and the absence of reports of these toxins from elsewhere, Western mycotoxicologists concluded that ATA was confined to the U.S.S.R.

However, reports appeared in the 1970s

suggesting that the trichothecene mycotoxin known as T-2, another *Fusarium* metabolite, was capable of producing some of the effects of ATA and, moreover, that an original Russian sample of poaefusarin contained enough T-2 for the latter to be responsible for the whole ATA syndrome. Abraham Joffe, who now works in Israel, subsequently reexamined the *Fusarium* isolates with which he had worked in Russia during and after World War II. He and co-workers concluded (Yagen *et al.* 1977) that T-2 was the principal toxin responsible for ATA.

This finding is of great significance. Far from being confined to the U.S.S.R. or to temperatures oscillating about 0 °C, T-2 toxin is well known in the United States as a cause of animal disease. It is a member of a whole family of mycotoxins, the trichothecenes, the effects of which, apart from sometimes resembling radiation sickness, include haemorrhagic syndromes in cattle and pigs, vomiting in pigs and dogs, poor performance by laying hens and infertility in pigs (Pathre and Mirocha 1979). Although the symptoms of ATA have not been recognized in human populations outside the U.S.S.R, trichothecenes, and especially T-2, must now be treated with the greatest suspicion. A recent report (Marasas, *et al.* 1979) suggests that *Fusarium* toxins may be involved in the high incidence of oesophageal cancer that occurs in the Republic of Transkei (S.W. Africa).

Pellagra

Pellagra has recently been suggested as a new human mycotoxicosis (Schoental 1980). It is a skin disorder, accompanied by severe mental disturbance, and is almost entirely confined to people who subsist on maize of poor quality. Frequently, such maize is visibly mouldy. Pellagra has been considered for more than 50 years to result from vitamin B deficiency, but Schoental presents persuasive evidence that it is due to the growth of *Fusarium* species on moist corn and the consequent formation of T-2 and other trichothecene toxins.

Schoental also mentions outbreaks of disease among heavy beer drinkers in Quebec, Minnesota, Nebraska and Belgium in 1965–66. In Quebec, this syndrome became known as cobalt-beer cardiomyopathy. A number of deaths occurred. The accepted explanation of cobalt poisoning (arising from its use as an antifoam agent) is untenable in Schoental's view because of the low levels of that metal (0.5 mg l^{-1}) in beer. Schoental points out that the symptoms of this disorder were not dissimilar to those of pellagra.

Some properties of the mycotoxicoses mentioned so far are summarized in Table 1. Each is an acute disease syndrome. With the exception of the possible involvement of trichothecene toxins in cancer of the oesophagus, the mycotoxins involved are not known to have teratogenic, mutagenic, carcinogenic or other long-term effects.

The following second set of mycotoxicoses may involve acute effects, but their more significant disease implications relate to their chronic toxicity. The best known and most thoroughly studied of these toxicoses are caused by aflatoxins.

Table 1. Acute mycotoxicoses of human significance

Date	Disease	Toxin	Cause	Diagnosis
To 1954	Ergotism	Ergot alkaloids	*Claviceps purpurea* in rye	1800, fungal cause suspected 1850, fungal cause demonstrated
To 1910	Acute cardiac beriberi	Citreo-viridin	*Penicillium citreo-nigrum* in rice	1910, yellow rice sale banned 1969, fungal cause demonstrated
To 1948	Alimentary toxic aleukia	T-2	*Fusarium poae* in millet and rye	1950, fungal origin known 1976, toxin established correctly
1965-66	'Cobalt-beer' cardio-myopathy	T-2	*Fusarium* spp. in barley	1980, fungal origin proposed
Current	Pellagra	T-2	*Fusarium* spp. in maize	1980, fungal origin proposed
Current	Reye's syndrome	Aflatoxin	*Aspergillus flavus* in nuts and maize	1977, fungal origin proposed
1974	Hepatitis	Aflatoxin	*Aspergillus flavus* in maize	1975, fungal cause demonstrated

Aflatoxicosis

Aflatoxins were discovered in 1960 following the deaths of 100000 turkey poults in England and a high incidence of liver diseases in ducklings in Kenya and hatchery-reared trout in California. Perspicacious workers in England (Allcroft and Carnaghan 1963; Austwick and Ayerst 1963; Sargeant *et al.* 1963) established the cause of these problems to be toxins produced by the common moulds *Aspergillus flavus* and *A. parasiticus*. They devised assay techniques and carried out preliminary toxicological studies by 1963. The most potent aflatoxin, B_1, is usually associated with aflatoxin G_1 and smaller amounts of aflatoxins B_2 and G_2 in natural products. Aflatoxin M_1 is produced during mammalian metabolism of B_1, and is secreted in milk. Aflatoxins have both acute and chronic toxicity to animals, and they produce the following four distinct effects:

- acute liver damage
- liver cirrhosis
- induction of tumours, and
- teratogenic and other genetic effects.

Acute toxicity of aflatoxins to humans, fortunately, has been rarely encountered (Shank 1978). In 1967, 26 Taiwanese in two farming communities became ill with apparent food poisoning. Nineteen of these were children, of whom three died. Rice from affected households was blackish green and mouldy, and appeared to be of poorer quality than that from households that were unaffected. Samples of the mouldy rice contained about 200 $\mu g\ kg^{-1}$ of aflatoxin B_1 which was probably responsible for the outbreak; post-mortem examinations were not carried out.

It has been suspected for several years that Reye's syndrome, a common cause of death in South-East Asian children, may be attributable to aflatoxin. Shank *et al.* (1971) performed aflatoxin assays on autopsy specimens from 38 Thai children, 23 of whom had died from Reye's syndrome and the remainder from unrelated causes. Specimens from 22 of the 23 Reye's syndrome victims contained aflatoxins B_1 and B_2 at levels (1–4 $\mu g\ kg^{-1}$) similar to those found in specimens from monkeys in a U.S. study of acute aflatoxin poisoning. Traces of aflatoxin were found in specimens from most of the children who had died from unrelated causes — not surprising in view of the levels of aflatoxin in staple foods in north-eastern Thailand (Shank *et al.* 1972). Children who have died from Reye's syndrome in Czechoslovakia (Dvorácková *et al.* 1977) and in New Zealand (Becroft and Webster 1972) have also been found to have aflatoxins in their livers at autopsy.

In 1974 an outbreak of hepatitis that affected 400 Indian people, of whom more than 100 died, almost certainly resulted from aflatoxins (Krishnamachari *et al.* 1975). The outbreak was traced to corn heavily contaminated with *Aspergillus flavus*, and containing up to 15 mg kg^{-1} aflatoxin. Consumption of aflatoxins by some of the affected adults was estimated to be 2–6 mg in one day; and it can be concluded that the acute lethal dose for adult humans is in the range of 1–10 mg.

Aflatoxins and primary liver cancer

Scarcely 2 years after the discovery of aflatoxins came the first warnings that they might be able to cause human liver cancer. This disease has a high incidence in central Africa and South-east Asia. When epidemiological evidence suggested a possible correlation with mycotoxins in the food supply, field studies were initiated on an international basis. Epidemiological data were coupled with analyses of those foods that form the staple diets of stable indigenous populations. Stability in both diet and population is essential in studies of this kind because of the long induction period (10–20 years) for human liver cancer.

Such studies were carried out in Kenya, Swaziland, Uganda, Thailand, Mozambique and rural S.E. United States. Great care is needed to obtain meaningful results in such studies, but by 1976 sufficient data existed to allow plotting and statistical analysis (van Rensburg 1977). These indicated a positive correlation between the logarithm of aflatoxin intake and the occurrence of human primary liver cancer, at least in Africa and S.E. Asia.

Epidemiological studies in the U.S.A. have produced results differing from those above. Stoloff and Friedman (1976) estimated that children in rural communities in the southern states of the U.S.A. may ingest as much as 40 ng aflatoxin per kilogram of body weight per day, mostly from maize. From van Rensburg's figures such a level should produce 4–10 deaths from primary liver cancer per 10^5 population per year. The actual level encountered, however, is about 1,

i.e. less than in some other regions of the U.S. such as Wisconsin and California, where aflatoxin is unlikely to be ingested in significant amounts.

Ochratoxins

In the early 1970s, observers in Denmark noted a high incidence of nephritis – kidney inflammation – in pigs at slaughter. A search for possible causes eventually showed the presence of ochratoxin A, a mycotoxin originally reported from the common mould *Aspergillus ochraceus*. Analysis of pig feeds showed that 50% of samples contained ochratoxin A at levels up to 27 mg kg^{-1}. The mould responsible was found to be *Penicillium viridicatum* which often occurs in Danish barley (Krogh *et al.* 1973).

Danish law ensured that nephritic kidneys were condemned, but this did not result in the rest of the carcass being declared unfit for human consumption. The discovery of ochratoxin led to analyses of pork and bacon. These showed that a significant proportion of ingested ochratoxin lodged unchanged in depot fat. The risk to humans is difficult to assess, but since pig meats are popular in Denmark and rural populations would usually eat their own, uninspected, pigs, a risk has certainly existed for some time. Death rates owing to kidney failure are high in some Danish rural areas, and it is a reasonable hypothesis that the cause is ochratoxin.

Balkan endemic nephropathy

With evidence that ochratoxin may be involved in deaths in Denmark, European scientists turned their attention to a disorder of unknown and baffling etiology, known as Balkan endemic nephropathy, which occurs in eastern Europe. This disease has a long history in certain parts of Yugoslavia and Romania. Whole families have been struck down, resulting in towns with a proportion of houses boarded up because people could not be induced to occupy them after the mysterious deaths of the original inhabitants. At least one small Yugoslav town has been moved to a new location to avoid being wiped out.

The disease remains baffling, but the absence of any known causative agent and the presence of the nephropathic syndrome suggest that a mycotoxin may be to blame. Studies are continuing.

In summary, the known and suspected long term human mycotoxicoses are shown in Table 2.

The Australian scene

What is the current situation regarding mycotoxins of significance in human health in Australia? Although little information exists, an attempt will be made to appraise the situation realistically.

Ergotism

Local authorities advise that ergots do not occur on wheat – our staple cereal. It would be possible for them to occur on rye or triticale, the wheat-rye cross that is becoming popular. But there is no evidence that *Claviceps purpurea* is likely to be a problem here.

Acute cardiac beriberi

Rice production in Australia includes a mechanical drying stage which ensures that commercial rice is normally too dry to permit growth of *Penicillium citreonigrum* or other toxic *Penicillium* species traditionally associated with 'yellow rice'. But yellow rice has been seen here, and investigation of possible problems seems warranted.

Table 2. Chronic mycotoxicoses of human significance

Date	Disease	Toxin	Cause	Diagnosis
Current	Liver cancer	Aflatoxin	*Aspergillus flavus* in foods	1963, fungal cause known 1970-75, epidemiological studies 1977, statements of human risk
Current	Oesophageal cancer in Transkei	Deoxy-nivalenol zearalenone	*Fusarium* spp. in maize	1979, fungal cause suspected
Current	Nephropathy in Denmark	Ochratoxin	*Penicillium viridicatum* in barley fed to pigs	1973, fungal cause known in pigs: suspected in humans from residues in pork
Current	Balkan endemic nephropathy	?	?	1972, fungal cause suspected

Nephrotoxins

Although substantial information on the incidence of ochratoxin in Australia is lacking, there is no reason to suspect that it is a significant disease agent here. It would be prudent, nevertheless, to undertake further studies.

Aflatoxicosis

The policy of the National Health and Medical Research Council on aflatoxins is to set a 'zero tolerance' level which is consistent with limits of detection by present practical analytical methods, and levels achievable by good agricultural and manufacturing practice. For almost all foods this level is currently 5 $\mu g\ kg^{-1}$. Apart from being the practical assay limit, it is considered that the presence of aflatoxin in excess of this level is evidence of gross negligence. For peanuts and peanut products, the maximum permitted level is higher, 15 $\mu g\ kg^{-1}$, because in more humid years, even with the best farming and handling practice, the Australian peanut crop cannot meet the general 5 $\mu g\ kg^{-1}$ limit. Recent U.S. studies indicate that the risk to humans is negligibly increased at this higher limit and, indeed, the U.S. limit for raw peanuts is 25 $\mu g\ kg^{-1}$.

Figures for death rates from primary liver cancer in New South Wales (Health Commission of N.S.W. 1980) suggest that the risk from aflatoxin is low, but insufficient data on dietary habits is available to confirm this view.

Toxicoses from Fusarium species

There is no information on the incidence of *Fusarium* toxins such as T-2 and related trichothecene compounds in Australia. Analytical techniques are difficult, and so is the identification of *Fusarium* species. Studies in this area are urgently needed.

In summary, there is no direct evidence that Australians are in danger from mycotoxin-induced diseases. However, the magnitude of sickness and death caused by mycotoxins as revealed in the past few years, and the extreme toxicity of some of these compounds, leave no room for complacency.

Future research

Further studies on aflatoxin in Australia are urgently needed:

- to establish levels of incidence in Australian and imported nuts, cereals and other commodities;
- to survey food consumption patterns so that risks may be assessed; and
- to assess factors causing aflatoxin production in susceptible Australian crops and to indicate how to minimize its occurrence.

Research is also needed on the incidence of ochratoxin A, T-2 toxin, other trichothecenes, zearalenone and citreoviridin in Australian foods and feed stuffs in order to establish whether these mycotoxins are a possible hazard to the Australian population.

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Physico-chemical separation processes for food wastes*

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Introduction

A wide range of physico-chemical separation processes can be applied to food wastes, including the 90 x 10^6 t whey produced annually throughout the world from the manufacture of cheese, casein and similar products. This by-product contains some 5 x 10^6 t solids with a biological oxygen demand (measured in a 5-day test) of 3.0–3.5 x 10^6 t. Australia alone produces about 100 000 t whey solids.

These milk solids are potentially valuable but they also represent a real problem of waste disposal. It is not surprising therefore that studies on the profitable utilization of whey solids have been rather intensive, particularly in recent years. These studies have covered the majority of physico-chemical separation processes. This paper therefore aims to review briefly the studies on whey utilization in order to exemplify processes that could be more broadly applicable to food wastes.

*Paper presented at the Australian Academy of Technological Sciences workshop on 'Treating food wastes for profit' held in Melbourne in October 1980.

If the definition of physico-chemical separation processes did not include evaporation and drying, some whey products could be excluded. However, all the main processes currently in use or which have potential application are referred to, if briefly, to give a more complete picture.

Whey as a raw material

In the past, most whey arose from the manufacture of cheese. Today, it is more pertinent to define 'whey' as the lactose-rich effluent from the manufacture of cheese, casein (precipitated by mineral acids or by lactic fermentation), cottage cheese, quarg and the co-precipitates of casein and whey proteins. The definition is broadened, for the purpose of this paper, to include the permeate (protein-free whey) from the ultrafiltration of whey or milk.

The main types of whey, from cheese, casein, cottage cheese and quarg, are fluids containing 6–7% solids, of which protein is 10–15%, non-protein nitrogenous compounds (NPN) 3–5% (expressed as N x 6.38), minerals 5–10% and fat 0.5–1.5%, the balance of the solids being mainly lactose.

Apart from pH, the main difference between cheese wheys and the acid wheys from casein, cottage cheese and quarg lies in the content of calcium phosphate. Over half of the calcium phosphate of milk is retained in cheese. Hence acid wheys contain more than twice the level of calcium phosphate as compared with cheese whey.

Co-precipitates incorporate 60–80% of the whey proteins so that whey from this product is low in protein and may be high in calcium, as calcium chloride may be used as all or part of the precipitant. The effluent in this case could be described as protein-depleted whey. Permeates from the ultrafiltration of whey and milk are protein-free but still contain much of the NPN and minerals. The content of minerals, particularly calcium phosphate, decreases depending on whether the permeate is from acid whey, cheese whey or milk respectively.

These variations in composition have a marked effect on whey processing and influence the choice of process in attempting to make profitable use of the raw material. The components most likely to yield profitable products on separation are protein and lactose. However, whole solids can be valuable, as they contain most of the minerals and vitamins of milk, as well as the protein and lactose.

Whole whey products

Several traditional products are made from whole whey, especially from cheese whey, as its composition most closely resembles that of milk, except that casein is absent. The main products are outlined in Fig. 1. Concentrated whey is a useful ingredient in such foods as ice-cream and confectionery. The semi-solid concentrates are generally specific products such as the various types of whey cheese that are particularly popular in Scandinavia. Roller-dried or sprayed-dried whey is used in large quantities for stock food and, increasingly, as an ingredient in human foods. For the latter purpose, the non-hygroscopic form is proving popular. This results from spray-drying after holding the concentrate under conditions which encourage crystallization of α-lactose. Spray-dried, demineralized whey is an important component of infant foods. The choice of the demineralization process depends on end-user specifications. Some users prefer the demineralization to be carried out by electrodialysis, as this process is selective in first removing minerals of low molecular weight. The residual mineral ions are predominantly calcium, phosphate, magnesium, citrate and lactate which are useful in the infant food. Other users prefer the high degree of non-selective demineralization achieved by ion exchange, as they then have full flexibility in adjusting the mineral composition of their product.

Some new possibilities for whole whey products are outlined in Fig. 2. These possibilities are based on various combinations of demineralization and lactose hydrolysis. Partial demineralization, particularly by the selective process of electrodialysis, will reduce the saltiness of concentrated whey and could thereby increase its usefulness in various foods. Hydrolysis of the lactose to glucose and galactose, by processes to be described later, increases sweetness and substantially reduces the tendency for 'sandiness' to develop through crystallization of the rather insoluble lactose.

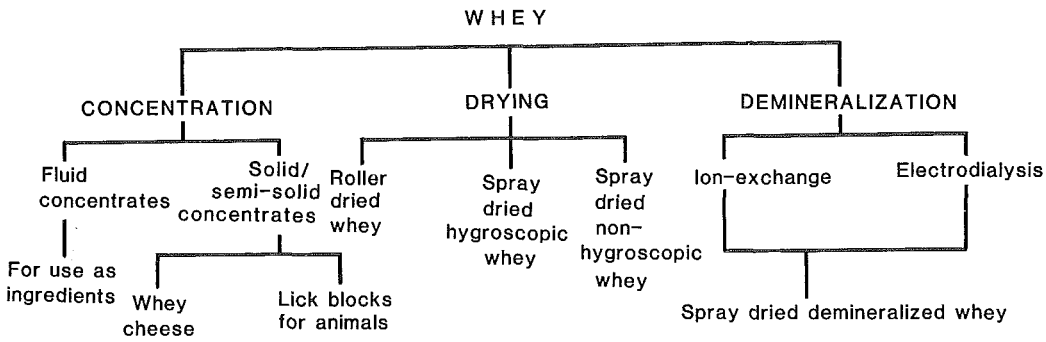

Fig. 1. Traditional products from whole whey.

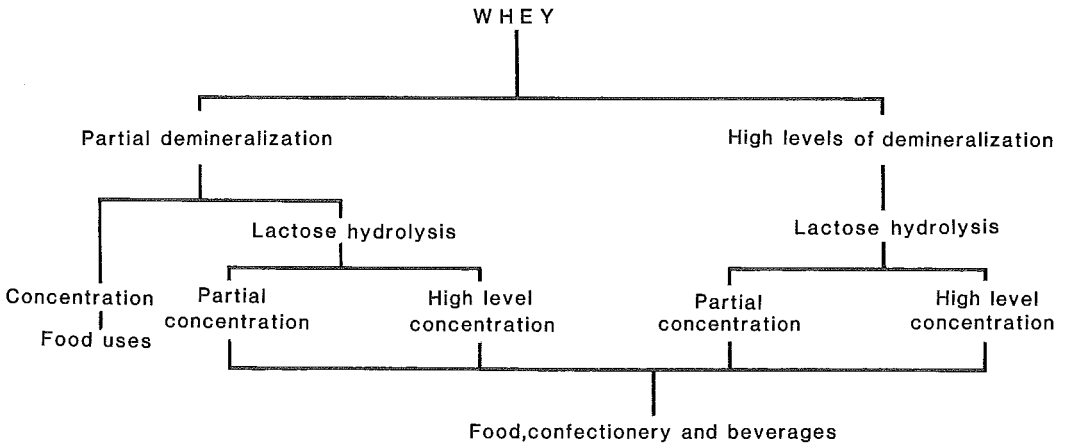

Fig. 2. Possible products from whole whey.

The combinations of part- or high-level demineralization and part- or high-level lactose hydrolysis can broaden the range of potential applications in foods, confectionery and beverages where the high quality whey proteins and the greater sweetness of the glucose and galactose are advantageous.

Whey protein products

A number of physico-chemical separation processes have been employed to recover proteins from whey.

The main traditional process results in the product called Lactalbumin. The process, as described by Robinson *et al.* (1976), consists of heating the whey for times and at temperatures that are related to pH and the level of calcium, and separating the precipitated proteins which are then washed to reduce the level of residual lactose before their recovery and drying. The product is used to improve the nutritional value of such food as speciality breads, biscuits, macaroni and pasta. The lack of solubility is advantageous in these applications, as the characteristic textural properties of the foods are unaltered (Morr 1979).

The Centri-whey process (Anon 1969) involves the centrifugal separation of heat-precipitated whey proteins and their recycling for inclusion in cheese milk with the aim of increasing the yield of cheese.

The most important of the newer fractionation processes are outlined in Fig. 3. At this stage ultrafiltration has emerged as the most attractive process commercially. From a recent summary of trends in whey processing (Zall *et al.* 1979) and from more recent information such as the news that three large ultrafiltration plants are now being commissioned in Australia, this process is now being used on whey in over 50 dairy factories around the world.

Ultrafiltration permits the manufacture of a range of whey protein concentrates with varying protein content and with functional properties that can be modified to suit a variety of end uses.*

References to the processes for the recovery of whey proteins as complexes and to the other physical separation processes in Fig. 3 can be found in review papers by Morr *et al.* (1973) and Marshall (1979). Further details are given in the discussion section (pp. 111-12) of the special issue of the *New Zealand Journal of Dairy Science and Technology* which contains the reference to Marshall (1979). That issue is devoted to the proceedings of a Whey Research Workshop.

Of the processes in Fig. 3, other than ultrafiltration, Sephadex gel filtration is, as far as I am aware, the only one that has been used on a commercial scale. Gel filtration has been used by a U.S.A. company as part of its process to fractionate whey in order to manufacture whey products ranging from

*Details of the ultrafiltration process and its products, together with an account of the related membrane process — reverse osmosis (RO) will be given in a paper by Dr K. R. Marshall, Assistant Director, N.Z. Dairy Research Institute, in *CSIRO Food Res. Q.* 41 (3).

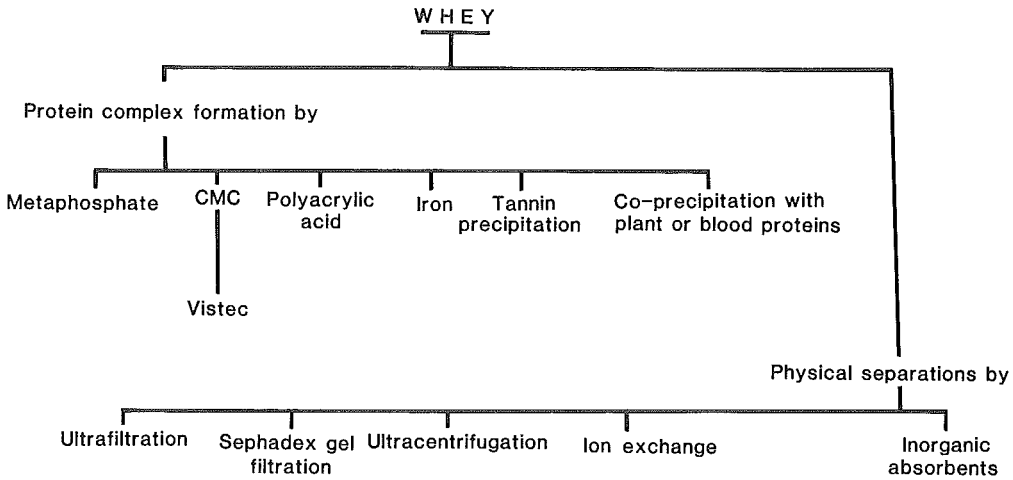

Fig. 3. Fractionation processes.

concentrates high in protein to low-protein, mineral- and lactose-rich products. This company intends to make a range of speciality products for use in different foods.

The potential of carboxymethyl cellulose (CMC) and polyacrylic acid as complexing agents has been given a good deal of attention. The original concept (Hansen *et al.* 1971) was to make a CMC-whey protein complex for sale as such. The complex is a highly functional, whippable product.

The process required dilution of the whey to reduce its ionic concentration, and this created problems in commercial application. Other workers (Zadow and Hill 1979) tried to overcome the need for diluting the whey by increasing the degree of substitution of the CMC, separating the protein from the complex and recycling the CMC. There were considerable problems in separating the protein and there was also a rapid loss of CMC reactivity.

The Vistec process (Palmer 1977) referred to in Fig. 3 is a further development in which a CMC, which appears to have the reactive material largely on the surface, is stirred with the whey at pH 3.2 and the protein then eluted at pH 9. Costs were high, as only about half the protein was recovered, but the product exhibited extraordinary gelation and foaming properties.

Higher recoveries of protein have been obtained by using polyacrylic acid as a complexing agent (Sternberg *et al.* 1976). Marshall (1979) summarizes further developments which involve cation exchange resins, inorganic adsorbents, or a combination of both techniques.

Lactose products

Each of the fractionation processes in Fig. 3 results in a protein-free or protein-depleted effluent containing lactose, minerals, vitamins and some of the lipids. For practical purposes, only lactose is present in sufficient concentration to be a likely raw material for making profits from this food waste. However, some of the products listed in Fig. 4 such as lick blocks for animals include all the components of the waste.

Fermentation to produce alcohol, methane or yeast is being applied commercially in some countries where the economics appear to be more favourable than in Australia. (These processes were also discussed during the Workshop.)

The processes for lactose crystallization and lactose hydrolysis were reviewed by MacBean (1979). He pointed out that, while processes for the production of crystalline lactose from whole whey and from protein-free or -depleted whey are well established, the capital costs of new plants are a deterrent where throughput or utilization of capital equipment is low. There is interest therefore in lower cost processes.

Continuous crystallization is being studied

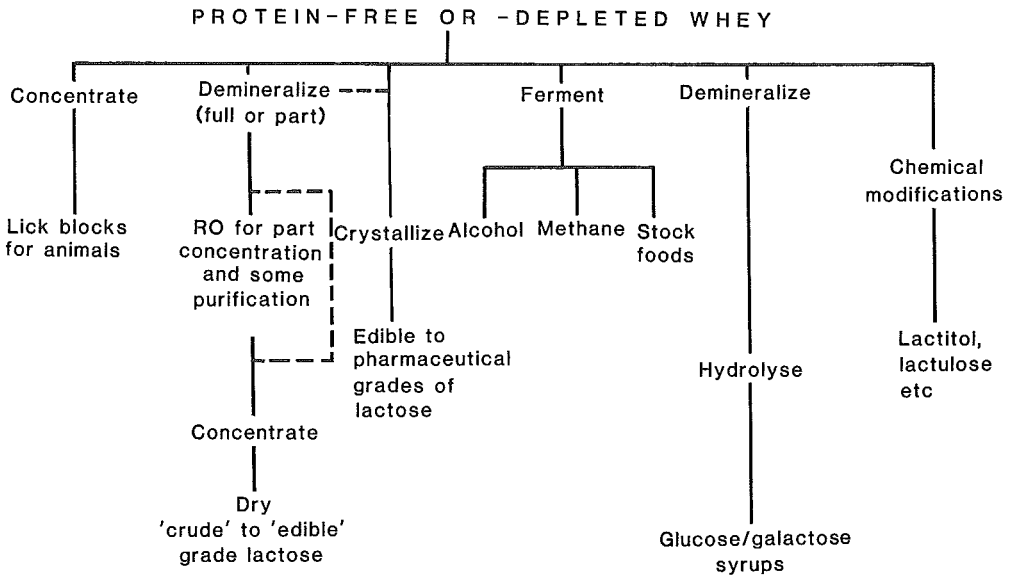

Fig. 4. Lactose products from protein-free or -depleted whey.

in Australia (Muller 1979*a*) and is evidently practised in Czechoslovakia (Dryàk 1976). MacBean (1979) refers to a commercial plant in the U.S.A. where cottage cheese whey is demineralized by ion exchange and concentrated. Some of the lactose is then crystallized out and separated by centrifugation. The residue is a protein-containing product of similar composition to that of skim milk. A 'crude' lactose product is being produced by partial demineralization of the permeate from the ultrafiltration of whey, followed by concentration and spray-drying. Higher purity can be obtained by 'full' demineralization, especially if RO is used to achieve part of the concentration. With somewhat open RO membranes, sufficient of the residual NPN and minerals will be removed with the water to increase purity from 95–96% to about 99% lactose.

It is considered likely that one or more of these processes will be adopted soon in Australia.

Even more likely to be applied soon are one or more of the processes for hydrolysis of lactose in whole whey (Fig. 2) or in protein-free or -depleted whey. MacBean (1979) gives details of the processes outlined in Fig. 5, in which partial demineralization is shown as preceding enzyme hydrolysis. This has been done to illustrate that full demineralization is not necessary when using enzymes as compared with the ion-exchange processes, particularly those where hydrolysis is achieved in the presence of cation-exchange resins. In this case the resin catalyst would require regeneration too frequently unless cations had previously been exchanged for hydrogen ions. Of course, if the end use of the product requires full demineralization, this is also possible, at extra cost, when using enzymes.

The market potential is being actively explored for whey products in which the lactose has been mainly hydrolyzed to glucose and galactose. Larger pilot plants have been in operation in Europe for some time using both the cation resin processes of Societé Applexion, France, and Portals Water Treatment, England, and a fixed enzyme process developed by Corning Glass Company (U.S.A.). Some progress findings on product quality, end-use applications and costs were given by MacBean (1979).

Market prospects — costs

Until recently, the depressing effect on world markets of EEC surpluses of skim milk powder, and the low prices for milk protein products and for sucrose and other sweeteners, all militated against the introduction to Australia of processes for

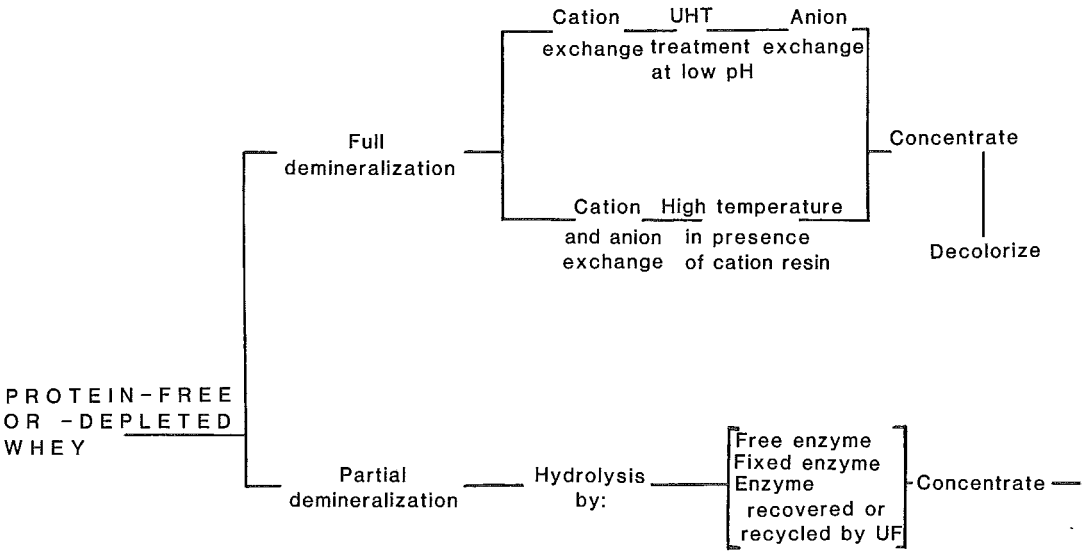

Fig. 5. Hydrolysis of lactose in protein-free or -depleted whey.

whey utilization. In the last year or two, this situation has changed in that more realistic prices for these products are now being obtained. The economic climate is therefore more favourable for decisions involving substantial capital investment. Spray-dried, non-hygroscopic cheese whey, as well as demineralized spray-dried whey, is already being made in Australia, and three ultrafiltration plants will soon be on stream. The next developments are likely to be in lactose products, especially those based on the hydrolysis of lactose. The total Australian market for sweeteners approaches 1 x 10^6 t per annum, so it is not difficult to envisage a 3–5% share for sweeteners derived from lactose. The dairy industry itself is a substantial user of sucrose and glucose for such products as ice cream.

Some observations on the economics of whey utilization were published recently (Muller 1979*b*). These were based on a case study in Western Australia where the quantities of whey were rather small. Even under these conditions, and at the lower prices applying at the time (early 1979), the prospects were reasonably encouraging. In that study, capital costs were treated very simply by allocating 25% per annum. A much more professional approach to costing was taken in a preliminary report on a cost analysis of alternative lactose hydrolysis systems (Ian A. Langdon, Deakin University, Preliminary Report to Whey Utilization Workshop, March, 1980). The report concluded that there is sufficient evidence to suggest that lactose hydrolysis by any of the main processes is commercially viable. The scale of operations, of course, has an important effect on costs. Many of the processes are too capital-intensive to be economically attractive to the small producer of whey. However, when the growing costs of waste disposal are taken into account the choice of process is wider, even for the small whey producer.

Energy balance — technological problems

The main energy-related problem in whey utilization is associated with its composition — it contains 93–95% water. Transport of unconcentrated whey and removal of the water by evaporation and spray-drying involve a substantial use of energy.* However, applications of ultrafiltration and reverse osmosis permit considerable reductions in the energy needed to remove water.

Although good progress has been made, there are still many technological problems

*This aspect will be discussed in a paper in *CSIRO Food Res. Q.* 41(3) by Dr K. R. Marshall.

requiring study. Most of the processes in Figs 2 and 4, for example, have been shown to be practical in pilot-scale studies. Choosing the best combination of the differing versions of the unit processes – demineralization and lactose hydrolysis – in relation to the identified requirements of particular markets, will require much work.

Conclusions

This paper has been confined to a summary of the current position with respect to research and development in the utilization of whey. However, the principles involved in attempting to make profits from this food waste can be applied broadly to other wastes. The first step in considering any food waste is to identify components which might have a good market value, either as the basis of new products or through recycling in the parent process. Having identified these components one can then consider which of the wide range of physico-chemical separation processes may be applicable.

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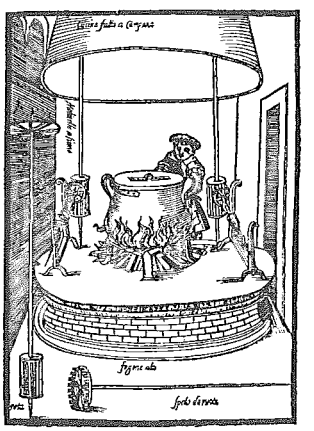

Acceptability of chilled and frozen ham

By R. L. McBride and K. C. Richardson
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In Australia there is a marked increase in the demand for ham around Christmas and, consequently, ham production is concentrated over a short period. However, if ham could be stored without any concomitant deterioration in quality, then the processor would be able to spread his production, thereby avoiding the pre-Christmas rush.

Perhaps the most convenient ways of extending the shelf life of food are chilling and freezing. It appears there have been no studies on the effect of chilling on the acceptability of ham and, unfortunately, the few studies on the effects of freezing (e.g. Jacquet *et al.* 1973; Zipser *et al.* 1964) have focused on physical and chemical aspects, ignoring the sensory properties which are of prime importance to the consumer.
We report an investigation into the effects of chilled and frozen storage on the sensory properties of ham and note the practical implications.

Product

Both leg ham cooked on the bone and boneless, pressed cooked ham were used in this study. All hams were produced by a major processor according to standard commercial practice.

The leg hams were pumped with a commercial curing solution, then immersed in the same solution for 48 h before being smoked and cooked overnight to an internal temperature of 72 °C. To investigate the effect of vacuum packing on shelf life, three of the leg hams were placed inside shrink-bags immediately after processing; these bags were then evacuated and heat shrunk. The remaining leg hams were loosely wrapped in polyethylene bags.

In the production of boneless ham, cured pieces of ham were mechanically massaged for 20 h then transferred to a press and cooked to an internal temperature of 72 °C. The hams were then vacuum-packed in PVDC film.

Sensory methods

On arrival at the Food Research Laboratory six leg hams (three vacuum- and three non-vacuum-packed) were chill stored at 5 °C. All remaining hams, both leg and boneless, were stored at either −15 ° or −30 °C.

The chilled leg hams were assessed 3 and 6 weeks after processing. Assessment was based on two replicate tasting sessions. The tasting panel comprised 32 experienced panellists from the Food Research Laboratory, all of whom liked ham. At each session panellists were presented with coded samples from the vacuum- and non-vacuum-packed hams and asked to rate them for appearance, flavour, texture and general acceptability on a 9-point hedonic scale; i.e. like extremely = 9, dislike extremely = 1.

All frozen samples were assessed after 7 weeks in storage. The hams were allowed to thaw in a domestic refrigerator at 5 °C for 2 days and the drip that was exuded during thawing was collected and measured. The leg and boneless hams were assessed on consecutive days. A panel of 29 assessed the leg ham at two replicate sessions, while 25 assessed the boneless ham at one session only. At each session panellists were presented with coded samples from the −15 ° and −30 °C storage treatments and asked to score them on the same response scale as used for the chilled ham.

Results and discussion

Mean response scores for the chilled and frozen ham are given in Tables 1 and 2 respectively.

Chilled ham

The scores in Table 1 indicate that 3 weeks after processing both vacuum- and non-vacuum-packed leg hams were still acceptable. Separate analyses of variance for appearance, flavour, texture and general acceptability revealed no significant difference ($F \leq 1.43$, df = 1,62). However, 6 weeks after processing, the pinker and wetter appearance of the vacuum-packed ham was found to be less attractive ($F = 26.22$, df = 1,62, $P < 0.001$), while the scores for flavour, texture and general acceptability were all significantly higher ($F \geq 16.85$, df = 1,62, $P < 0.001$). The additional 3 weeks of storage had clearly affected certain sensory properties, but in practical terms the effects were not drastic: all scores in Table 1 lie above the 'like slightly' mark on the hedonic scale.

There was to have been a further comparison 11 weeks after processing but this was precluded by the degree of microbiological spoilage on the surface of the non-vacuum-packed ham. Consequently, vacuum-packed ham alone was presented at this time and found to be still acceptable (e.g. mean general acceptability score = 7.0).

Frozen ham

Freezing had a deleterious effect on all products. The scores in Table 2 indicate that the leg ham frozen at −30 °C was least affected. The scores for this product were similar to those for the non-vacuum-packed ham chilled for 6 weeks (*cf.* Table 1). However, the scores for the leg ham frozen at −15 °C were significantly lower ($F \geq 13.72$, df = 1,56, $P < 0.001$). Except for flavour, which was just acceptable, the mean scores lie on the 'dislike' side of the hedonic scale. The same trend held for the boneless ham, with significantly lower scores (paired $t \geq 2.34$, df = 24, $P < 0.05$) for samples frozen at −15 °C.

Evidently it was the freezing process *per se* which damaged the sensory properties. Ice formation ruptured the ham structure causing the texture to become coarse and 'grainy', similar to that of corned-beef (see Fig. 1). The damage was more obvious in the sample frozen at −15 °C, presumably because of the slower freezing rate. Since the freezer temperatures in domestic refrigerators are closer to −15 °C than −30 °C, this same effect could be expected with ham frozen in the home.

Flavour also was seriously impaired. On thawing, a substantial amount of drip was recorded: approximately 1.6% of the initial frozen weight for the leg ham, 7.1% for the boneless ham. This loss of water

Table 1. Mean hedonic scores for vacuum and non-vacuum-packed leg ham stored at 5 °C

	Stored 3 weeks[A]		Stored 6 weeks		
	Non-vacuum	Vacuum	Non-vacuum	Vacuum	LSD[B]
Appearance	6.8	7.0	7.2	6.4	0.3
Flavour	6.8	6.8	6.3	7.2	0.4
Texture	6.9	6.6	6.3	7.1	0.4
General acceptability	6.9	6.8	6.2	7.0	0.4

[A] Differences non-significant.
[B] Least significant difference ($P < 0.05$).

Table 2. Mean hedonic scores for hams stored for 7 weeks at −15 °C or −30 °C

	Leg ham			Boneless ham		
	−15 °C	−30 °C	LSD[A]	−15 °C	−30 °C	LSD[A]
Appearance	4.8	6.9	0.4	4.2	6.5	0.7
Flavour	5.2	6.0	0.4	4.4	5.4	0.8
Texture	4.4	6.1	0.4	4.0	5.4	0.7
General acceptability	4.4	6.1	0.3	4.0	5.4	0.8

[A] Least significant difference ($P < 0.05$).

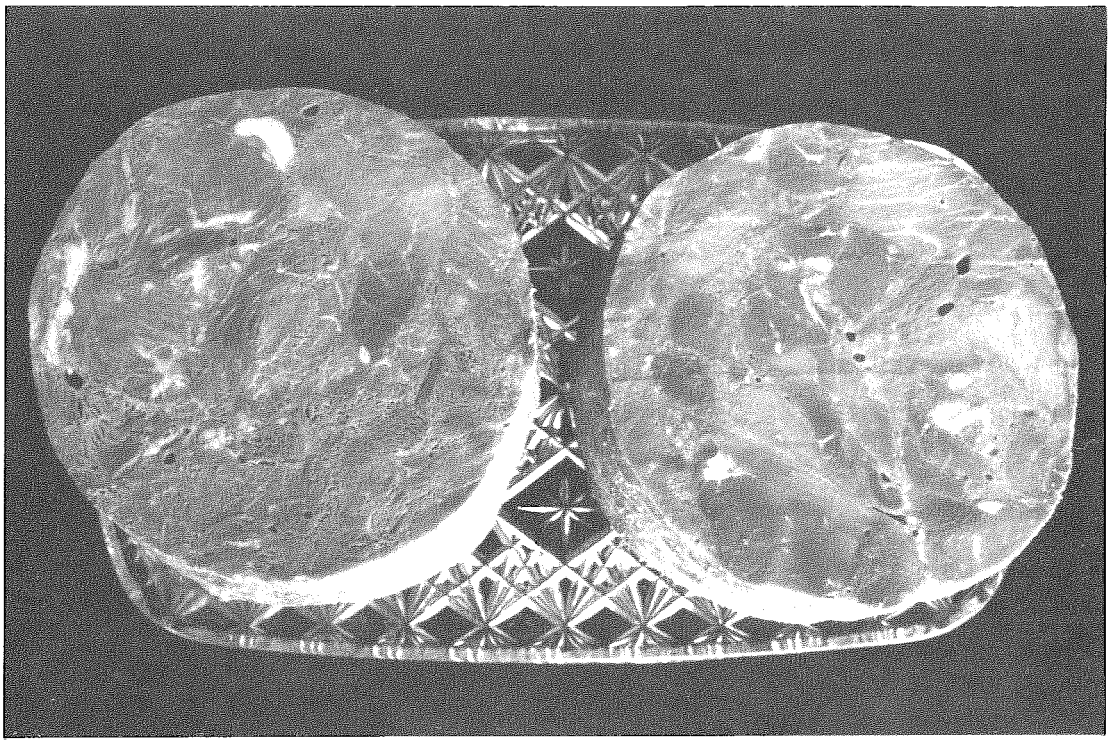

Fig. 1. The effect on ham of freezing at −15 °C (left hand side) and −30 °C. Note the coarse texture, especially in the sample stored at −15 °C.

effectively raised the salt concentration in the product, and in fact many panellists complained of excessive saltiness in the boneless ham.

This study was carried out on a small sample of product. Notwithstanding, the results were sufficiently conclusive to suggest the following guidelines:

- freezing of ham is not recommended
- unwrapped leg ham may be successfully kept at 5 °C for up to 3 weeks after processing
- vacuum-packed leg ham will keep well at 5 °C for at least 11 weeks after processing, but its appearance on serving may be less acceptable than that of unwrapped ham.

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New methods of measuring permeabilities of packaging films

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Introduction

The shelf life of many foods is determined by the permeability to oxygen and water vapour of the flexible films and film containers used in packaging. If possible, the packaging material should act as a barrier to all vapours and thus prevent the loss of desirable food odours or the entry of undesirable taints. A simple, routine procedure capable of measuring the permeabilities of films to water vapour and oxygen, and possibly to other vapours and gases, would be most desirable, especially since the barrier properties of laminated or coated films are difficult to predict.

Traditional methods

Ideally, the permeability of a homogeneous film is defined in terms of a permeability constant $P = (ql)/(At\,\Delta p)$ (1), where q is the quantity of gas or vapour diffusing through a film of area A and thickness l in time t, and Δp is the partial pressure difference of the gas or vapour across the film. For hydrophilic films the water vapour permeabilities may vary with moisture content; hence the humidity and temperature need to be specified. Since the permeability of a laminate is not proportional to total thickness, gas or vapour transmission rates are used, i.e. the quantities of gas or vapour transmitted per unit area in unit time.

Permeability measurement techniques used in this laboratory for gases or vapours have been described by Davis (1965) — water vapour, Davis *et al.* (1975) — sulphur dioxide, and Davis and Huntington (1977) — oxygen. For oxygen or sulphur dioxide the test film is sealed between two compartments of a cell with sampling ports in each compartment. The penetrant gas is introduced into one compartment at a known partial pressure and diffuses through the film into the second compartment. The gas composition in each compartment is measured by gas chromatographic analysis of samples from each port.

Other types of cells and detecting devices that have been described in the literature (Davis 1970) usually require expensive instrumentation, specialized cells and sophisticated gas measuring techniques, e.g. infra-red or electrochemical detectors.

For gravimetric measurements of water vapour permeability the test film is sealed across a shallow dish containing a desiccant. The whole system is then placed in a humidity cabinet (under controlled temperature and humidity conditions) and weighed at regular intervals over several days. Unfortunately, owing to the low sensitivity of the weight-increase method, this procedure is too slow for many quality control applications.

New methods

A new method for measuring permeabilities of packaging films, which requires little equipment and is both rapid and accurate, has been devised in these laboratories (Holland, *et al.* 1980). The basis of the method is a plastic detector film impregnated with a reagent that is sensitive to the gas being measured. The film, having an absorption spectrum that changes as the gas or vapour is absorbed, is thus suitable for spectrophotometric monitoring. The detector film is sealed between two pieces of test film in a simple cell so that the permeation rate of the penetrant gas or vapour can be readily measured.

The cell design used for measuring oxygen permeability has been described fully (Holland *et al.* 1980). The same cells have also been used for measuring the permeability to water vapour of several film and sheet materials. In Fig. 1 the various components of the cell are shown. Most of the dimensions are not critical and are related to the particular spectrophotometer (Varian 634) used in this work.

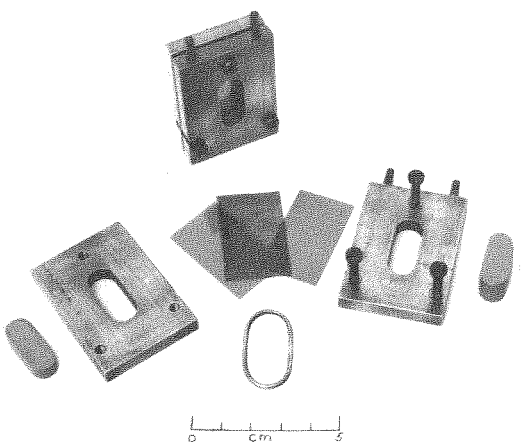

Fig. 1. Cell components and films together with an assembled cell.

The cell consists of two identical brass plates (about 6 x 4 x 0.6 cm) with central apertures and a copper wire gasket which is slightly larger than the apertures and provides a pressure seal when the plates (with films) are screwed together with three triangularly disposed screws. Detector film is sandwiched between two samples of test film (slightly larger than the gasket). The film 'sandwich' and the gasket are placed between the two plates which are then screwed together until a firm seal is obtained. The cell has positioning dowels for accurate placement in the spectrophotometer. For very permeable films an impermeable backing film may be used to reduce the test area, and for very impermeable films the detector area may be reduced to provide extra sensitivity.

Permeability to oxygen

Detector film. The oxygen detector consists of a cast film of ethyl cellulose 10–30 μm thick containing about 0.3 M dimethylanthracene (DMA) and about 5 x 10^{-3} M erythrosine. Casting of the film (on a Camag film spreader) must be done in red light or in subdued lighting because the film is sensitive to light.

A solution having ideal viscosity for spreading is given by 11.7% v/v ethyl cellulose/ethyl acetate. DMA and erythrosine are added as concentrated solutions before making up to the required value. The spreader gap is determined by multiplying the desired film thickness by a factor of 100/11.7. About 20 ml of polymer solution can be cast on the glass plate – area about 50 x 20 cm. Adhesion to the glass may be prevented by stretching polyester film over the plate before casting. The DMA in the film is stable in the absence of either light or oxygen, but it is oxidized within seconds in air in the presence of intense light. This dye-sensitized reaction was chosen because it is extremely fast in solution and is likely to be limited only by the rate of diffusion of oxygen through the plastic matrix. On absorbing blue light, the erythrosine can activate oxygen dissolved in the ethyl cellulose to form a reactive form of oxygen – singlet oxygen. Singlet oxygen has a life time of only a few microseconds in the film, but if in that time it diffuses to a neighbouring DMA molecule it reacts with that molecule. Consequently, the disappearance of DMA, monitored in the u.v., is a measure of the oxygen consumed. Since the ethyl cellulose detector is highly permeable to oxygen, it is capable of measuring very high rates of oxygen permeation.

Another sensitive reagent for singlet oxygen is 1,3-diphenylisobenzofuran which has the advantage of giving a visible colour change (from orange to red) in the presence of erythrosine, thus permitting visual assessment of the permeability of films.

The amount of oxygen consumed, q, may be expressed in terms of spectrophotometric quantities and used in the equation for the permeability constant, i.e. $q = (A_0 \Delta\alpha)/\varepsilon$ where A_0 is the area of the detector film, α is the absorbance, and ε is the molar absorption coefficient of the detector material. As an example, if $A_0 = 1$ cm^2, and $\varepsilon = 20\,000$ for a typical detector concentration of 0.1 M in a film of 10 μm thickness, an absorbance decrease of 0.02 corresponds to a 10^{-3} M change in the detector concentration, or 10^{-9} moles (or 22 nanolitres) of oxygen consumed (assuming a stoichiometry of 1 : 1). Smaller

quantities of oxygen could be measured if smaller areas of detector film were used. The detector film has other applications, e.g. as a barrier film, or for oxygen scavenging purposes (Rooney and Holland 1979; Rooney *et al.* 1981).

Measurement. The detector film can measure much less than the minimum detectable quantity of oxygen determined by most other methods, and therefore permits the use of either smaller film samples or more rapid permeability determinations.

Response is rapid because the distance between the detector and the test film is very small, and because the total volume of gas inside the film envelope is also extremely small. However, even this small volume of air, trapped inside the envelope while assembling the test cell, can result in the removal of a large proportion of the detector material at the initial illumination. Plastic inserts (see Fig. 1), the same size as the aperture in the cell, are used to squeeze out as much air as possible from the film package before the cell is sealed. Providing a slight excess of detector material is incorporated in the film, the remaining oxygen can be scavenged in a few minutes by exposure to light. The absorption of the detector after scavenging can be taken as the starting value for the permeation run.

To carry out a measurement, the assembled cell may be kept, for example, on a 32-W diffused light viewing box for a short time (say 5 min). Any uniform light source can be used. For very rapid measurement of permeability a brief exposure to a projector light beam is satisfactory. It is not advisable to expose the detector film to too much light if the oxygen level is extremely low, as the dye may be photobleached.

After the initial, timed exposure, the change in absorbance is measured spectrophotometrically. This change is a measure of the decrease in detector concentration, and hence the amount of oxygen consumed. The permeability to oxygen of the test film can be determined from equation 1. If an appreciable absorbance change is measured, the cell can be placed back on the viewing box and a reading taken at similar intervals until a satisfactory linear plot is obtained. If little or no change is measured, readings can be taken at longer intervals as required. If the absorbance change is too small to measure within a few hours, the cell should be stored in the dark for daily periods and exposed to light for a few minutes before each reading. Duplicate runs may be performed to check for leaks or pinholes.

After exposure to light, the oxygen partial pressure difference, Δp, at standard atmospheric pressure is 21 kPa. For accurate work, a controlled temperature and humidity room should be used when the permeability of the film varies with water content or temperature. In Fig. 2 the absorbance change of the film, measured by the spectrophotometric method, and the equivalent quantity of oxygen absorbed are plotted against time. Whereas the gas

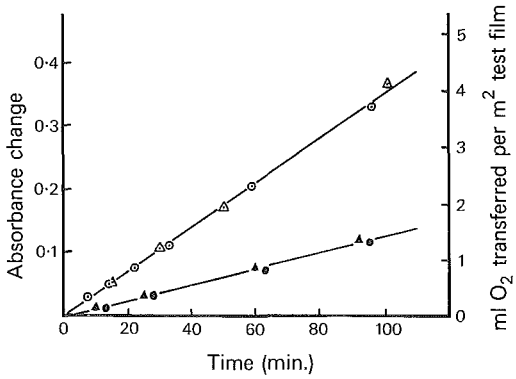

Fig. 2. Duplicate plots of oxygen permeability of 25 °C (⊙▲, 40 μm Nylon 11 film; ●▲, 13 μm Mylar A/25 μm low density polyethylene laminate.)

chromatographic method (Davis and Huntington 1977) uses a test permeation area of 280 cm^2 of film, the new method uses a test area of about 8 cm^2 for similar sensitivity and accuracy (Holland *et al.* 1980). See Table 1 for a comparison of permeabilities of the same films measured by the two techniques. For heat sealable films a simpler technique may be used whereby a strip of detector film is (preferably) vacuum-sealed in a pouch. A similar technique to that described above is then used to scavenge and monitor the film.

Permeability to water vapour and other gases and vapours

A solution-based detector using the same principles as the film-based system is possible but the latter offers significant advantages of reproducibility and convenience. Another type of film detector (to be described more

Table 1. Permeability of films measured by the spectrophotometric [A] and gas chromatographic methods

Film	$10^4 \times$ oxygen permeability in (ml O_2 (S.T.P.) μm)/(m^2 s kPa)	
	Spectro-photometric	Gas chromato-graphic
Low density polyethylene (Union Carbide)	202	174
Cellulose acetate (Beseler)	68.0	50.8
Nylon 11 (Rilsan)	12.4	10.5
Mylar A/L.D.P.E. (Dupont/I.C.I.) (Thickness of barrier web used in calculation)	1.32	1.07

[A]Monitored at either 359 or 379 nm.

fully elsewhere) has been devised to measure rates of transmission of water vapour in test films in much the same way as the oxygen-detecting film. It consists of cellulose film which becomes bright blue when soaked in cobalt chloride solution and dried over calcium chloride but rapidly turns pink on exposure to high humidities. A humidity cabinet is used to provide the partial pressure gradient across the test film, which is sealed in the same way and in the same cell as used to measure oxygen permeability.

Similar detectors to those described above could, no doubt, be designed for carbon dioxide, sulphur dioxide, odour components and most other gases or vapours of interest using suitable solution-based chemical reactions.

Detectors for classes of materials such as acids, ketones, or even organic vapours are also possible. For permeability applications, a detector film that is highly permeable to the particular gas or vapour should be used otherwise the detection and measurement rates might be too slow to be useful. Polymeric materials appear to be effective solvents for detector substances whilst having a number of advantages over liquids with similar chemical characteristics. A wide choice of detector film materials that may be cast, or soaked in the required reagents, is available to make detector films for many applications.

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News from the Division

Honours and awards

Doctorates of Science have recently been awarded to three members of the Division:

Mr M. B. Smith, of FRL, received the degree of Doctor of Science from the University of New South Wales for published work on the topic 'Physico-chemical studies on proteins, with particular reference to the structure and stability of egg proteins'.

DRL's J. G. Zadow was awarded the degree of Doctor of Applied Science by the Victoria Institute of Colleges on the basis of his published work which was incorporated in a thesis entitled 'Milk and milk proteins'.

Dr W. G. Murrell, Leader of FRL's Food Safety and Nutritional Quality Group, was awarded the degree of Doctor of Science in Agriculture by the University of Sydney for his published work on 'Bacterial spores'.

Food wastes workshop

To investigate suitable methods of treating food processing wastes, a Food Waste Materials Project has been established under the ASEAN-Australian Economic Cooperation Program. Biogas technology, the technology of converting wastes into methane for use as fuel, is of particular interest.

Dr Alan Lane and Mrs Kathy Adams of the Food Research Laboratory with Mr E. Halpert of CSR Limited were invited to organize a workshop on biogas technology to pass on Australian knowledge and experience of the latest developments and possible adaptations needed for conditions in ASEAN countries. The workshop also provided an opportunity for discussion of problems faced by individual countries.

The workshop was held in Manila from (16–21 March 1981) and mini workshops (2 days) were held in Kuala Lumpur and Bandung for those people unable to go to Manila. The workshops were funded as part of the Australian Government's ASEAN Aid Program, administered by the Australian Development Assistance Bureau (ADAB).

Left to right: Dr Rahim Bidin, SIRIM, Chairman Malaysian Working Group on Food Waste Materials, Mr Erik Halpert, CSR Research Laboratories, Dr Alan Lane, CSIRO Division of Food Research, Professor Ho Coy Choke, Professor of Microbiology, University of Malaysia, Mrs Kathy Adams, CSIRO Division of Food Research, and Dr R. A. Buchanan, Australian Scientific Liaison Officer, ASEAN-Australia Economic Cooperation Program.

Food allergens — new projects

A pilot investigation in the area of food allergy has been commenced recently by Mr D. Barnett and Dr R. W. Burley of FRL in collaboration with Macquarie University and a number of medical practitioners.

Adverse or abnormal reactions to particular foods are experienced by a considerable proportion of the population. Symptoms range from abdominal discomfort through hives, rhinitis, migraine, asthma and, in very rare cases, fatal anaphylactic shock. The present study is confined to discovering those proteins present in legumes, particularly peanuts, that can elicit severe, immediate hypersensitive reactions (IgE mediated) in certain sensitized persons. The aim is to gain insights into the structure of allergenic proteins and, in the long term, to provide basic information that will enable improved diagnosis and treatment of food allergies to be made.

Counter current extraction

Recent work by Dr D. J. Casimir of FRL has resulted in a patent being filed for the Counter Current Extraction equipment (see Fig. 1). Australian Patent No. PE 2383 entitled 'Screw Diffuser' was granted in July 1980. A licensing agreement has been entered into with Howden Equipment Services who will manufacture and market the equipment world-wide. Following successful trials during the 1980 apple season, a commercial unit with a throughput of 150 t per day has been built and will commence operation in New Zealand during the 1981 apple season.

Preliminary trials have indicated that the equipment has potential application in the grape juice and fermented grape juice industry, in the citrus industry, and in the extraction of sugar from sugar-beet and cane, sweet sorghum, grape marc and sugar-containing residues. The recovery of soluble proteins and flavouring material or flavourful 'soup stocks' is also possible from edible-grade residues from the prawn, crayfish and fish industries.

Further engineering and product applications will continue during the three-year CSIRO-Howden licensing agreement.

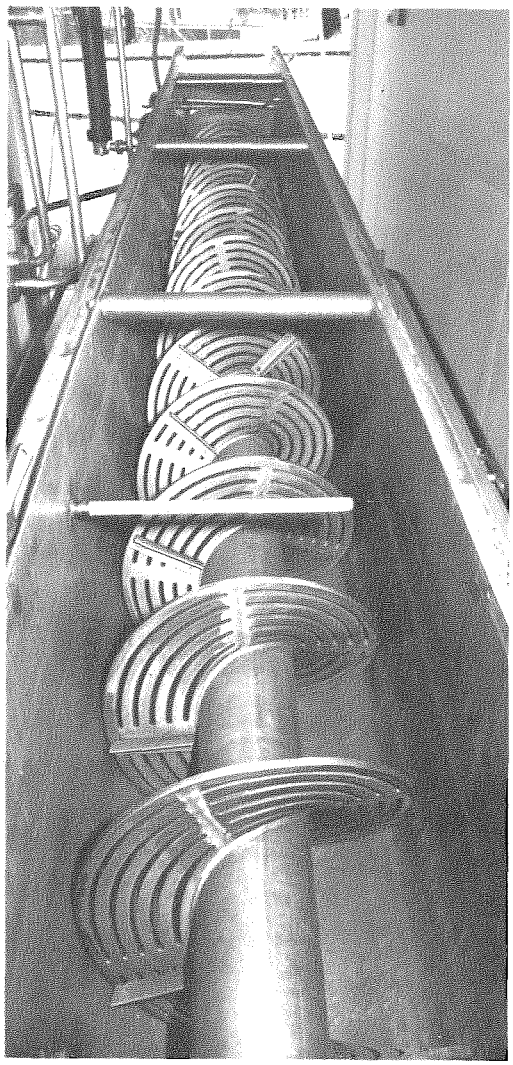

Fig. 1. The 'Screw Diffuser'.