

the traditional freeze-thaw process. Ninety percent of production is in the form of agar strip, with the remaining ten percent in powder form. In 1981, the country exported 594 tons of agar strip (average price US\$13.80 per kg) and 50 tons of powdered agar (US\$12.80 per kg). This accounts for about half of the total production. The bulk of exports went to Singapore (255 tons), Japan (180 tons), and Hong Kong (100 tons).

(b) Carrageenan

At present, there is only one carrageenan producer (100 tons per annum), but a new joint-venture with a Japanese company is planned (to manufacture 200 tons per annum). Production is based on *Chondrus ocellatus* and *Gigartina tenella*. The product is exported to industrialized countries.

(c) Alginates

Naylor (1975) reported exports of 105 tons per year to Japan from 1971-73, but it is doubtful that production has continued. In 1979, imports of alginates were 153 tons, followed by 235 tons in 1980; exports in 1980 were only three tons.

3. Potential for development

(a) Seaweeds

The Republic of Korea can fill current levels of demand for its brown seaweeds, both domestic and overseas. Prime interest, however, is in edible seaweeds, which are in high demand within the country, produce considerable export income, and yield much higher return to the producer than industrial seaweeds for colloid manufacture. The only area of potential growth appears to be the mariculture of *Gelidium amansii* for agar production. This species gives an agar of excellent gel strength, and any surplus production could readily be exported.

(b) Seaweed products

Agar. Agar production could be expanded if the mariculture of *Gelidium* succeeds. There is a good demand for agar strip domestically and in surrounding Asian countries. Demand might also increase if prices decline.

Carrageenan. Production of carrageenan is about to increase as the result of a joint-venture with a Japanese company. The large quantities of seaweed formerly exported should provide a good basis for expansion of the industry, and the joint-venture arrangement may ensure a market for the product. Given the current world demand and supply situation for carrageenan, any further expansion in Korea should be preceded by careful market appraisal.

E. Philippines

1. Seaweeds

(a) Red seaweeds

The mariculture of *Eucheuma* was pioneered and developed in the Philippines. Production has grown from 300 tons of wild seaweed in 1970 to an annual average of

13 500 tons over the years 1978-1980, valued at approximately US\$7 million per year. The principal species grown is *Eucheuma cottonii*, with smaller and irregular amounts of *Eucheuma spinosum*. The bulk of the seaweed is farmed in the Tawi-Tawi region of the Sulu Archipelago. Recently, *E. spinosum* has been farmed in Bohol Province. The seaweeds are exported to carrageenan producers, although some partial processing has recently been undertaken in Cebu.

The current average prices in Cebu are 2.60 pesos per kg for *E. cottonii*, and 3.20 pesos per kg for *E. spinosum*. However, the market for *Eucheuma* in the Philippines is notorious for its cyclical price fluctuations, a feature of the marketing system which is counter-productive and costly to both farmers and buyers. Prices fluctuate because buyers — assembler/wholesalers and agents — move quickly to obtain their annual needs from farmers only early in the year, pushing up prices during that period. Buyers then often abruptly withdraw from the market once their annual targets are filled. Early-year high prices frequently lead farmers to increase their production, but by the time new crops are available, prices have usually fallen, disillusioning farmers. They are forced to devote more time to other subsistence activities, neglecting seaweed farming activities. This leads to lower output and often a poorer quality product because epiphytes and grazers have invaded crops. This fall in supply forces buyers to again offer better prices, and the cycle starts again. This market behaviour was experienced in 1974-76 in Tawi-Tawi and in the Central Visayas (including Bohol) in 1979-80. No action has been taken to prevent its repetition.

The buyers are assembler/wholesalers and agents. Assembler/wholesalers sell either to agents, or direct to exporters. Agents sell to exporters and processor/exporters. Marketing costs incurred by middlemen include labour and investment costs, and operating costs (such as transport, and sometimes costs associated with further drying and sorting). Exporters are starting to insist on improved product quality, which requires higher standards of post-harvest handling and drying. The geographic flow of *Eucheuma* in the distribution and marketing network is from producing areas to Bungao in Tawi-Tawi, to Jolo in Sulu, and then from these areas to Zamboanga City, Cebu City and Metro Manila. Product from Bohol goes to Cebu City. Both Metro Manila and Cebu City are exporting centres.

Gracilaria culture has been tried on a trial basis at Bacoar (in the south of Manila Bay), by the Bureau of Fisheries and Aquatic Resources (BFAR). Initial results showed production can be significantly improved (doubled) by placing a solid substratum (such as cement blocks, adobe blocks or shells) on the sea floor. Production was highly seasonal and there were problems of predation, foreign weeds and losses due to waves. Collectors of naturally-growing *Gracilaria* sell to fishpond operators (milkfish feed), or dry it for sale to agar processors. *Gracilaria* production is reported to be nearly 1 500 tons per year, and in 1980 Japan imported 1 200 tons of dried "seaweed used for manufacturing agar" — thought to be *Gracilaria* — from the Philippines.

(b) Brown seaweeds

Sargassum species are being collected to the north of Cebu, sun-dried, and shipped to Japan through an exporter in Cebu City. It is used mainly as a fertilizer, replacing more expensive, artificially dried material formerly supplied by European countries and Japanese domestic production. The high cost of oil has made the artificial drying of seaweed too expensive (in Europe) for a low-priced product such as seaweed meal.

(c) Green seaweeds

Caulerpa racemosa has been cultured in ponds in Mactan, Cebu for several years. It is usually sold in fresh form for use as a salad-type food. Methods of packing so that it will remain fresh for several days have been devised. There is strong demand for this product in local markets and prices have increased. A brine-cured product is exported to Japan. There is no published information as to how Mactan farmers operate. A pilot study of the culture of *Caulerpa lentillifera* is being conducted at Calatagan (Batangas) by the University of the Philippines.

2. Seaweed products

(a) Carrageenan

The partial processing of *Eucheuma cottonii* to produce a "semi-refined" carrageenan has developed over the past four years, and about 700 tons of this product is now manufactured annually. Marine Colloids, Inc. of the United States is the main processor, but significant quantities are also being produced by Shemberg Marketing Corp, Cebu City. Genu Philippines (Copenhagen Pectin Ltd.) plan to start processing soon. The semi-refined product still contains some insoluble cellulose; it forms quite firm gels, but they are not clear. Part of the Marine Colloids Inc. production is shipped to the United States for further processing, which yields refined, or normal, carrageenan. Because the semi-refined material is one-third the weight of dried seaweed, there is a large saving in shipping costs. The rest of the Marine Colloids semi-refined production is sold to Australia, the United Kingdom and other countries for use without further processing.

(b) Agar

Small quantities of agar are made from *Gracilaria* for local consumption in food. About ten tons of bacteriological grade agar are imported annually.

3. Potential for development

(a) Seaweed

The Philippines has successfully pioneered the development of *Eucheuma* mariculture, but the accrued benefits, and the Philippines' premier position in the supply of carrageenan raw material, could be lost if steps are not taken to reorganize the marketing structure.

Should one of the neighbouring countries, such as Indonesia, Malaysia, etc. embark on *Eucheuma* mariculture and establish a marketing system which is more equitable to the producer, and thus offer a more consistent (in quality, quan-

tity and price) product to buyers, then carrageenan producers may prefer such a supply to the erratic pattern which has persisted in the Philippines since 1974. The Fishery Industry Development Council (FIDC) and BFAR have documented the situation, but no solution has been found. The present marketing system, with its variable price, product quality and output, offers little inducement to a carrageenan manufacturer to invest heavily in a processing plant in the Philippines. There is consequently a very high potential for loss of recent and potential gains unless corrective steps are taken.

Eucheuma spinosum mariculture is not well established as yet. Promising results have been obtained in Bohol Province, but more time is required before it can be said that its growth-behaviour is no longer erratic. This species is important because it yields iota-carrageenan, for which there is expanding demand. Additional work on the mariculture of this species could thus be beneficial and profitable.

Expansion of *Gracilaria* production by mariculture could yield sufficient raw material for an agar industry. A collaborative project between the University of the Philippines and the Southeast Asian Fisheries Development Centre (SEAFDEC) has recently commenced; it aims to study the conditions necessary for mariculture of *Gracilaria* in the Central Philippines.

Caulerpa lentillifera offers a good potential, with a strong domestic market as a fresh food, particularly in Metro Manila. Further study of its pond culture potential should be encouraged.

Seaweed industry development efforts, however, do not receive substantial support from the government because it is given relatively low priority, in view of the limited resources available for fishery development.

(b) Seaweed products

Carrageenan. The production of the new "semi-refined" carrageenan may be undertaken by small processors with comparatively little capital outlay. The product may be sold as a raw material to the major carrageenan manufacturers instead of dried *Eucheuma*, with a saving of shipping costs and some processing time accruing to manufacturers. It can also be sold direct to users who are content with a non-transparent gel (e.g. for petfood). The former market appears to have good potential, except for sales to those manufacturers which establish plants of their own in the Philippines. The latter market is very competitive and not easy to penetrate unless product consistency can be demonstrated. Joint-ventures with carrageenan producers in France, Spain or Portugal could be feasible, particularly because of the saving in shipping costs to these countries. There is also a saving in time and money in another way: any quality problems in the shipment of dried seaweed are not usually detected until arrival in the importing nation; this can raise problems — is it to be returned to the exporter, or accepted at a lower price in hopes that any processing difficulties or losses can be absorbed. It is much quicker and easier to deal with such quality

problems when the seaweed is processed in the country of origin. In view of the potential competition from *Eucheuma* mariculture in other countries, the establishment of any kind of processing industry, be it for semi-refined or refined carrageenan, must be seen as a positive step towards maintaining demand for Philippine *Eucheuma*.

Production of refined carrageenan is a more difficult undertaking and would best be approached through joint-ventures with partners who already possess the necessary technology, and who are already established in the market. This would help ensure a return on invested capital within a reasonable time. It would be possible to devise a production process with no previous experience, but such an effort must begin on a small, trial scale, and later be scaled-up in moderate steps. An entrepreneur undertaking this effort must be prepared to accept a low return on investment in the first two to three years. Then, having overcome the problems of manufacture, he would still be faced with those of marketing, as outlined in Section II. (B.I.d.). Since little carrageenan is in demand domestically, most of the production would have to be exported.

Because of the secrecy enforced in the production of technology and the marketing expertise required for seaweed colloids by the few established producers, an established manufacturer would need a strong incentive to enter into a joint-venture. Assured supplies of raw material seaweed, reduced operational costs, and lower shipping costs are some of the bargaining tools which can be utilized by an entrepreneur in negotiations with a potential foreign partner. The larger manufacturers have already invested heavily in domestic processing facilities. A more suitable partner might be a smaller manufacturer that wishes to expand his facilities and sales, and thus be receptive to proposals involving additional capital investment. The principal smaller manufacturers are found in Spain, Portugal, Japan and the Republic of Korea.

A process for the manufacture of carrageenan has been evolved on a pilot-plant scale by a group at the University of the Philippines with financial support from the Ministry of Natural Resources. It is not clear whether the process is for semi-refined or refined carrageenan. As no details of the process are available, its feasibility cannot be judged.

Alginate. The same group at the University of the Philippines is now working on a process for the production of alginate from brown seaweeds, particularly *Sargassum*, which is said to be abundant throughout the Philippines. The production of good quality alginate is even more difficult than for carrageenan; thus all the problems previously mentioned for carrageenan apply even more strongly here. Like carrageenan, the market in the Philippines for this colloid is negligible, thus any production must be exported, with the associated problems of market penetration.

The current picture in the world manufacture of alginate (two-thirds of the world production by one company and its subsidiaries) does not offer good prospects for finding joint-

venture partners. However, one of the smaller producers, say in Japan or France, might be interested in obtaining a different type of alginate from the ones they now manufacture. If the alginate from *Sargassum* had different and useful properties from those alginates made by such a producer, then there might be good arguments for a joint-venture. More information about the quality of *Sargassum* available and the properties of its derivative alginate would probably be required by any prospective partner. If the current 1 500 tons of *Sargassum*, currently exported to Japan for fertilizer at about US\$200 per ton, were used to produce alginate, the product would have an export value of about US\$1 200 000.

Seaweed meal and liquid fertilizers. A more immediate and less troublesome, but perhaps less profitable potential for *Sargassum* lies in further development of markets for the dried, ground seaweed meal currently being sold to Japan. Liquid fertilizers based on brown seaweed, and concentrates made from them, have found a market in some countries and could be another use for brown seaweeds such as *Sargassum*, both within and outside the Philippines.

F. Sri Lanka

1. Seaweeds

The only seaweed that has been of any commercial importance in Sri Lanka is the red seaweed *Gracilaria lichenoides* (syn. *G. edulis*), natural stands of which have been harvested on the northwest and the northeast coasts. It was collected by hand in shallow water, dried, and mostly exported to Japan for agar manufacture. Some is used by fishermen in soups and to form jellies. Exports to Japan reached a peak of 218 tons in 1973, but thereafter declined to 22 tons in 1978. The price of "Ceylon moss" on the Japanese market was always much lower than that for comparable seaweeds from other countries. For example in 1978, South American and South African *Gracilaria* sold for 200-220 yen per kg, but Sri Lankan material for only 100 yen. It is not clear whether this was due to poor quality or poor marketing. Amandakoon (1981) reports that due to poor trade practices, the export trade has been terminated.

The brown seaweed *Sargassum* grows on dead coral reefs along the southwest coast and in shallow waters in the north.

2. Potential for development

It may be possible to revive the export of wild *Gracilaria* if its collection and marketing can be effectively organized. However, the mariculture of the same species of *Gracilaria*, using vegetative pieces as seed, has been developed by India, so Sri Lanka might be able to do this, with advice from India. In fact, Sri Lanka ran a successful pilot trial using *Gracilaria lichenoides* in 1975, but no further action has been reported.

The preparation of seaweed meal, for domestic use or export as a fertilizer and feed additive, may be feasible using the natural stands of *Sargassum* and *Turbinaria* in the north, since the climate should permit adequate natural drying.

G. Thailand

The west coast has little seaweed of any commercial potential. The seaweed that exists there grows poorly, probably because of the changes in salinity after monsoons, the calm water which gets little aeration, silting, and perhaps grazing by predators. Growth is better on the east coast, but very little classification or survey work has been done on Thai seaweeds. *Caulerpa* and *Gracilaria* are sold in Phuket market (west coast) for use in spicy sauces. Import statistics for 1980 show that about 11 tons of "seaweed" were imported mainly from China with some from Japan and the Republic

of Korea—presumably for use in foods. In the same year, 19 tons of "seaweed used for manufacturing agar" (probably *Gracilaria*) was imported by Japan from Thailand.

Because much of the Thai coastline is mangrove, sandy, or mud, Doty (1977) suggested that seaweed for agar based on the farming of *Gracilaria* on unconsolidated bottoms offers the best opportunity for development. A large quantity of "agar-agar" was imported in 1980—208 tons with a value of about \$2.7 million—indicating a good market exists in Thailand.

INDEX TO TECHNICAL TERMS

TERM	SEE PAGE
Agar	2. 5. 27
Alginate	2. 11. 27
<i>Ascophyllum</i>	1. 2. 28
Brown seaweeds	1. 2
Carrageenan	2. 8. 28
<i>Caulerpa</i>	1. 2
<i>Chondrus</i>	1. 2. 28
Colloid	3
<i>Durvillea</i>	1. 2. 28
<i>Ecklonia</i>	1. 2. 28
<i>Enteromorpha</i>	1. 2
Epiphyte	6
<i>Eucheuma</i>	1. 2. 29
<i>Fucus</i>	1. 2
<i>Furcellaria</i>	1. 2
Furcellaran	2. 8
<i>Gelidiella</i>	1. 2
<i>Gelidium</i>	1. 2. 27
<i>Gigartina</i>	1. 2. 28
<i>Gracilaria</i>	1. 2. 27

TERM	SEE PAGE
Green seaweeds	1. 2
<i>Hizikia</i>	1. 2
<i>Hypnea</i>	1. 2. 28
Iota-carrageenan	8. 28
<i>Iridaea</i>	1. 2. 29
Kappa-carrageenan	8. 29
Lambda-carrageenan	8. 29
<i>Laminaria</i>	1. 2. 28
<i>Macrocystis</i>	1. 2. 28
<i>Nerocystis</i>	1. 2.
<i>Phyllophora</i>	1. 2
Polysaccharide	5
<i>Porphyra</i>	1. 2
<i>Pterocladia</i>	1. 2. 27
Red seaweeds	1. 2
<i>Sargassum</i>	1. 2. 28
Seaweed colloid	3
Semi-refined carrageenan	8
<i>Turbinaria</i>	1. 2
<i>Ulva</i>	1. 2
<i>Undaria</i>	1. 2

Appendix I
AVERAGE PRICES OF SELECTED SEAWEEDS AND SEAWEED PRODUCTS

Some of the prices mentioned in this report are collected here so that comparisons can be made more readily.

	Year	Country	US\$/ton
1. BROWN SEAWEEDS			
(a) Edible			
<i>Undaria</i> (wakame)	1981	Korea	1 200
	1981	Japan	1 120
Kelp tangles	1981	Korea	6 300
	1981	Japan	5 700
<i>Hizikia</i>	1981	Korea	5 350
(b) Industrial (for colloid manufacture)			
Brown	1980	average	250
<i>Laminaria</i>	1979	UK	100
<i>Ascophyllum</i>	1979	UK	100
<i>Durvillea</i>	1979	Chile	230
<i>Sargassum</i>	1981	Phil.	110
	1981	India	130
2. RED SEAWEEDS			
(a) Edible			
<i>Porphyra</i> (laver)	1981	Korea	8 300
(b) Industrial (for colloid manufacture)			
Agar-types	1980	average	890
Agar-types	1981	Korea	1 460
Carrageenan-types	1980	average	400
<i>Eucheuma cottonii</i>	1980	Phil.	560
	1982	Phil.	310
<i>Eucheuma spinosum</i>	1980	Phil.	1 120
	1982	Phil.	380
<i>Gracilaria</i>	1978	Chile	760
	1979	Japan	980
<i>Gelidium</i>	1978	Japan	1 100
	1978	Chile	1 100
3. SEAWEED MEAL			
	1980	Norway	210
	1981	Korea	275
4. SEAWEED COLLOIDS			

Current price levels of seaweed colloids are not easily obtained, in that most of the production is confined to a few companies. Comparison of prices between countries is also aggravated by different currency exchange rates and the way in which they fluctuate relative to the US Dollar. In any

particular country, the price will be a reflection of such factors as the currency exchange rates, the shipping distance and time (not always related), and the price of competing colloids. The most useful comparison for any buyer will be c.i.f. prices for the relevant colloids in his own country. INFOFISH may be contacted for most recent price quotations.

Appendix 2
THE PROCESSING OF SEAWEEDS — A BRIEF
DESCRIPTION OF THE MANUFACTURING TECHNOLOGY FOR SEAWEED COLLOIDS

Reprinted from pilot study of the World Trade Centre UNCTAD/GATT, Geneva, Switzerland.

1. The manufacture of agar

Frozen agar gel liberates water as it thaws, through a process called syneresis. Basically, it is this property that is exploited by traditional methods to remove most of the water from the liquid extracted from agar-bearing seaweeds. These methods rely on the right climatic conditions: agar manufacturing is still essentially a winter occupation for farmers in the mountainous areas of Japan, as it was over 350 years ago when this gum was first manufactured.

The small Japanese production units work mainly with *Gelidium spp* and with varying amounts of *Gracilaria* and *Ceramium spp*¹. About 100 kg of mixed seaweed is boiled with 4 500 l of water and with 200 ml of sulphuric acid for about four hours. The hot suspension is then filtered and allowed to set in about 300 wooden boxes each measuring about 45 x 30 x 5 cm. The gel is removed from the boxes, sliced into strips, spread on bamboo mats and exposed to the weather for several days. When most of the water has been removed by alternate freezing and thawing, which also removes most of the colour and impurities, the drying process is completed indoors, e.g. in barns or other farm buildings².

The process is essentially crude and imposes no scientific control over the ingredients, the process or the product. Although it remains economically important in some areas, Japan's production of agar by this means fell from 1 748 tons in 1970 to 964 tons in 1978³. It is interesting to note that until 1939, with the exception of the agar produced by the American Agar and Chemical Company, almost all the world's supply of agar was made in this manner.

The above-mentioned company introduced mechanical freezing to the industry. The method was subsequently widely used in Spain and in other countries during the Second World War. It was not used in Japan until 1946; today 17 factories in this country extract agar by mechanical freezing, often while processing fish and other food items to exploit refrigeration facilities to the full. Production in Japan by this process reached 1 099 tons in 1978⁴.

Mechanical freezing, essentially a refinement of the old process, uses more sophisticated equipment and freezes extracted gel with brine from a refrigeration plant. It offers the advantage of laboratory control over the raw seaweed,

the process and the final product. The process has been described by Hayashi and Nagata⁵ and, more recently, by Okazaki⁶.

The main seaweeds used in the production of agar are *Gelidium*, *Gracilaria*, *Acanthopeltis* and *Pterocladia*. The first two account for over 70 percent of production in Japan. The United States industry relies on *Gelidium robustum*; Spain uses both *Gelidium* and *Gracilaria spp*; New Zealand and Portugal depend on *Pterocladia spp*; USSR producers rely mainly on *Ahnfeltia-plicata* and *Phyllophora rubens*⁷. Agar is made in Morocco from local *Gelidium*⁸.

Different types of seaweeds produce different types of agar; only a few of them, for example, produce bacteriological grade agar.

2. The manufacture of alginates

Alginates were first manufactured in Scotland in 1881. In the early years of the twentieth century, attempts were made in the United Kingdom to commercialize the use of alginates binder in the production of briquettes from anthracite dust. However, the first successful commercial production of sodium alginate was launched only in 1929 in the United States by Kelco, which still remains among the leaders of the industry. The last 40 years have seen the entry of several other manufacturers but four producers control over 80 percent of current world production.

The methods used by various companies for the extraction of the alginic acid from seaweeds vary somewhat. For instance, only Kelco is able to use wet seaweeds, which renders the extraction process less expensive, as it takes place close to the harvesting area. Most other major producers have to depend on dried seaweeds because the transport of wet seaweeds over great distances is technically and economically unfeasible.

The very limited information available on the manufacture of sodium alginate is contained in patents taken out by Kelco and the Algin Corporation of America in the 1930s^{9, 10}. These documents describe the production of alginic acid but carefully omit information on the conversion of the acid to its sodium salt. The missing information is vitally important because it is at this processing stage that it becomes rather difficult to avoid degradation of the product.

¹JETRO, "Raw Materials for Agar-Agar", *Access to Japan's Import Market*, No. 23 (Tokyo, 1980).

²A. O. Kazaki, *Seaweeds and Their Uses in Japan* (Tokyo University Press, 1971).

³JETRO, *op.cit.*

⁴*Ibid.*

⁵K. Hayashi and Y. Nagata, *Nippon Shokuhin Gakkaiski*, 14, 450 (1967).

⁶A. Okazaki, *op.cit.*

⁷V.J. Chapman, *Seaweeds and Their Uses* (London, Methuen, 1970).

⁸*Ibid.*

⁹H.C. Green, *US Pat.*, 2 (036), 934 (1936).

¹⁰D.E. Clark and H.C. Green, *US Pat.*, 2 (036) 992 (1936).

Degradation also occurs when the sodium salt is not dried with care. In some cases, sodium alginate is dehydrated with isopropanol but this is used commercially only for the production of products with high viscosity. These products have a very small share of the market.

In general, alginates are manufactured in five basic operations:

- Removal of soluble matter (by washing with water) and reduction of the seaweeds to a size suitable for further processing;
- Extraction of alginate with sodium carbonate and filtration (the product may be bleached at this stage);
- Precipitation of the calcium salt by adding calcium chloride;
- Conversion of the calcium salt to alginic acid by treating it with hydrochloric acid;
- Conversion of alginic acid to its sodium salt by using a suitable alkali. The salt is then dried.

There are two major difficulties in the manufacture of alginate: the risk of decomposition during drying and the danger of obtaining it in fibrous form, which retains some water. Some seaweeds, e.g. *Laminaria digitata*, produce a long-fibred precipitate that is easy to handle. *Ascophyllum nodosum* tends to give a short-fibred calcium salt that is difficult to process; it is mainly for this reason that this seaweed is used only by three major producers despite the fact that abundant supplies of it are available.

All brown seaweeds contain alginic acid, but not all can be used for the manufacture of alginates on a commercial scale for technical reasons. For instance, of the abundant fucoids species only *Ascophyllum nodosum* is used commercially.

The major seaweeds used by the industry include *Laminaria digitata*, *L. hyperborea*, *Ecklonia maxima* and *Macrocystis pyrifera*. Of the rest of the large group of brown algae, only *Sargassum* spp, *Lessonia* spp and *Durvillaea potatorum* have any commercial significance although *L. longicruris*, from the Gulf of Saint Lawrence, was used by the Algin Corporation of America until the company ceased operations in 1956¹¹. *Laminaria digitata* is among the easiest algae to process. *Macrocystis pyrifera* is processed wet by Kelco.

3. The manufacture of carrageenan

The European carrageenan industry started in France in 1911 with the manufacture of the product "Coreine" for the treatment of constipation colitis and diarrhoea. This product is still available in France¹². The evidence of a United States patent on the use of isopropanol for an improved product suggests the existence of an American carrageenan manufacturing industry in the 1930s¹³. The industry came into its

own in post-war years and its growth has been rapid, especially since 1960, partly because of the decline in the Japanese agar industry.

World production of carrageenan, currently estimated at some 10 000 tons year, has so far remained in the hands of a few companies in industrialized countries. Over the years, they have developed processes to produce carrageenan from different seaweeds and for different end-uses. A detailed discussion is beyond the scope of this study, but it is desirable to present here some basic information on the subject.

Initially, all carrageenan was made from *Chondrus crispus* and from a very similar seaweed, *Gigartina stellata*, which grow under similar conditions and are collectively known as Irish moss. The industry now uses several other seaweeds to produce a wide variety of carrageenan.

The seaweed is first cleaned through various operations depending upon the impurities it contains. Before the extraction process, it may be soaked in sodium chloride, potassium chloride or calcium chloride according to the type of gel required. In general, treatment with sodium salts results in a viscous product with low gel strength; calcium salts give an elastic gel and potash salts produce a firm gel. The seaweed may be bleached at this stage; dilute sodium hypochlorite is commonly used as bleaching agent. It is essential to remove any residual hypochlorite with, for example, a slight excess of sodium bisulphite.

During the extraction process, the seaweed is stirred in water, at a concentration of approximately three percent, and it is normal practice to heat it at 90°C-95°C for two hours. The mixture often has a tendency to foam, which lowers the heating temperature. A filter aid is then added and the hot liquor is filtered as quickly as possible before it gels on cooling. The resulting clear solution contains about one percent of dissolved solids and it is concentrated to three to four percent in a vacuum evaporator. Gelling grades should be concentrated at around three percent but other grades may be concentrated at slightly more than four percent.

In the early days of the industry, carrageenan was isolated from the concentrate by drum-drying. This method is still used; however, a technically improved product is precipitated with isopropanol, using about equal volumes of concentrate and isopropanol. The mixture is then cooled and the separated carrageenan is dried and ground. The recovered isopropanol contains about 15 percent water and is re-usable. The still bottoms (residue) present an effluent problem, as they contain traces of isopropanol and a considerable quantity (approximately ten percent of the weight of the carrageenan produced) of dissolved solids with a high BOD (biological oxygen demand).

It is common commercial practice to add a small amount of soluble phosphate (about one kg/10 000 l) in the extraction stage, as this treatment appears to increase the carrageenan

¹¹E. Booth, in *Chemistry and Industry*, 528-34 (1977).

¹²E. Booth, in *Chemical Oceanography*, Vol. 4 (London, Academic Press, 1975).

¹³J. Pfister and J. Wolf & Co., *US Pat.*, 2, 231, 283.

yield (this practice has also been adopted in the manufacture of agar). In most cases, the extraction liquor is made slightly alkaline, at sat pH 7.2. Acidic conditions must be avoided throughout the process because carrageenan degrades rapidly in hot aqueous solutions.

There are many variations of this basic process, the most important being the modification of molecular structure under pressure with potassium hydroxide, a process which gives the product high gel strength. This method was introduced during the war to make an agar-like material from the carrageenan extracted from *Chondrus crispus*¹⁴ and it came into general use around 1960 when the shortage of agar created new outlets for strong gelling grades of carrageenan.

The best carrageenan is made from asexual plants of *Eucheuma* spp. which produce mainly the non-gelling lambda-carrageenan¹⁵. Several other seaweeds are used to make special types of carrageenan, e.g. *Iridaea*, *Polyiodes* spp and *Hypnea musciformis*. The extract from the last-mentioned seaweed gels unusually strongly in milk products, which is probably why it has been largely replaced by *E. cottonii* in these products.

The seaweed *E. cottonii* from the United Republic of Tanzania, which is usually called "thick Zan'ibar", and the thick, fleshy cakes of *E. platycladum* both produce strong,

gelling extracts. *E. spinosum*, generally known as "thin Zan'ibar", produces extracts that do not gel; the demand for this alga is low, as better-quality material is available from the Philippines. The strong gelling *Eucheuma* spp became important in the late 1950s and early 1960s because of the temporary shortage of agar. *Eucheuma* extracts replaced agar during that period, especially in the large market for canned petfoods.

It has long been known that *Chondrus crispus* contains a number of different types of carrageenan, including lambda-carrageenan which does not gel and kappa-carrageenan which gives a strong gel. These two gum types can be separated in the laboratory. On a commercial scale, the separation is not easy, often necessitating treatment of the extract under pressure with sodium or potassium hydroxide to obtain a good, strong gelling product.

Research in Nova Scotia (Canada) showed that it was possible to grow two different types of *C. crispus*, one containing lambda-carrageenan and the other kappa-carrageenan. Diploid plants (tetrasporophytes) yielded lambda-carrageenan while those grown from both male and female gametophytic plants produced kappa-carrageenan. This discovery is now being exploited but secrecy surrounds the actual progress some companies have made. Ceca S.A. is reported to be conducting trials on the matter in France¹⁶.

¹⁴J. C. M. Chen et al., *US Patent*, 3, 879, 890 (1975).

¹⁵K. Ramo Rao, *Botanica Marina*, 21, 257-9 (1978).

¹⁶J. P. Braud and R. Delepine in *Proceedings, International Seaweed Symposium*, Vol. X (Göteborg, Sweden, 1980), pp. 553-58 (hereinafter called *Proceedings*).

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