Production and Utilization of Products from Commercial Seaweeds

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PREPARATION OF THIS DOCUMENT

This document was prepared and published under the FAO Technical Cooperation Programme as part of the background material for a Workshop on the Production and Utilization of Commercial Seaweeds which was held in Qingdao, People's Republic of China from 25 May to 15 June 1987. The Workshop was funded jointly by FAO, the Academia Sinica and the UNDP.

It was decided to publish it as an FAO Fisheries Technical Paper in order to fill a gap in the available literature on commercial extraction processes of the most important phyco-colloids. The publication is also a companion to FAO Fisheries Technical Paper (281) Case studies of seven commercial seaweed resources, edited by M.S. Doty, J.F. Caddy and B. Santelices.

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ABSTRACT

The publication describes the production, properties and main applications of the three major phyco-colloids extracted from seaweed: agar, alginate and carrageenan. There is also a supplementary chapter on the preparation and marketing of seaweeds as food. Although this is based mainly as Japanese experience it is included in order to encourage increased consumption of seaweeds as human food.

The authors of the three phyco-colloid chapters have considered raw material sources, post-harvest treatment, methods of extraction, chemical composition of the colloids, evaluation of quality, and uses, with some details of economics and marketing.

CHAPTER 1 - PRODUCTION, PROPERTIES AND USES OF AGAR

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According to the FAO thesaurus, agar can be defined as a hydrophilic colloid extracted from certain seaweeds of the Rhodophyceae class. It is insoluble in cold water but soluble in boiling water. A 1.5% solution is clear and when it is cooled it forms a firm gel which melts at temperatures between 85 and 95°C. It is used as a culture medium for microorganisms, as a laxative, as a thickener in food products, as a binder in pharmaceuticals and as a gelling agent in cosmetics.

Agar is the dried product of water extracts from red algae, such as species of the genera Gelidium and Gracilaria. Gelidium is the most important source of agar. Gelidium is a genus of red algae which grows in the form of a bush. Agar is the dried product of water extracts from red algae, such as species of the genera Gelidium and Gracilaria. Gelidium is the most important source of agar. Gelidium is a genus of red algae which grows in the form of a bush.

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A Japanese legend is told about the first preparation of agar:

> Some fishermen had left their boiled seaweed jelly outside the mountain during a snow storm and arrived in a small inn, where unexpectedly housed by the innkeeper who offered them a meal made of pickled cucumber, boiled beans and a dish of the jelly they had left outside the snow and which now was a pleasant jelly, cool, firm, and delicious. The innkeeper was astonished to see the jelly disappear into the fishermen's pockets and they explained that it would be a good dish for their master.

Agar production by modern methods of industrial scale harvesting was started in California by Minoru Yamanouchi in 1920 and spread to Japan in 1922 and 1923 to the Canary Islands, particularly under the leadership of Minoru Yamanouchi and Kenzo Okazaki, who established the first factory in Las Palmas, Canary Islands, in 1923. Young, 1966. This work was supported by the Japanese Government and by the Japanese Agar Association.

Agar from the above Gelidium production, particularly the early production of this product and World War II was the Japanese industry which was a very sophisticated industrial structure based on numerous small factories (about 400 Japanese factories) and supported by a very sophisticated research and development structure. Agar was used for many food products and was used in very large quantities for the production of bacteriological media for the Japanese Army during the Second World War.

During this second world war the shortage of supplies of agar meant an opportunity for those scientists with a sound knowledge of agar production, which is very similar to the Gelidium production and by the Japanese industry, to the Portuguese Laminaria industry and to the Chilean Gelidium industry. Agar production in Chile was started by Japanese scientists who had left the Canary Islands because of the Japanese occupation of the Canary Islands during the Second World War.

SOURCE OF AGAR

Agar is a phycocolloid and the raw material to agar production lies in seaweeds with differences in their biochemistry, although they can all be included in the general definition of agar. For the purpose of this report, when agar is mentioned, it is necessary to specify the seaweed from which the agar is produced, because the properties of agar from different seaweeds are different and the uses of agar are dependent on these differences. Agar is a phycocolloid and the raw material to agar production lies in seaweeds with differences in their biochemistry, although they can all be included in the general definition of agar. For the purpose of this report, when agar is mentioned, it is necessary to specify the seaweed from which the agar is produced, because the properties of agar from different seaweeds are different and the uses of agar are dependent on these differences.

Hydrophilic colloids are considered when the seaweed is a gelatinous group, or jelly-like, and the gelatinous group is considered to be a colloid. Although there appear to be many species of gelatinous seaweed, there are only a relatively small number of species which are used for the production of hydrophilic colloids. The production of hydrophilic colloids from seaweeds is a very specialized industry and there are only a few species of seaweed which are used for the production of hydrophilic colloids. Although there appear to be many species of gelatinous seaweed, there are only a relatively small number of species which are used for the production of hydrophilic colloids.

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The Japanese Government and the Japanese Agar Association were very active in promoting the production of agar from the seaweed Gelidium and the production of agar from the seaweed Gelidium was a very sophisticated industry based on numerous small factories (about 400 Japanese factories) and supported by a very sophisticated research and development structure. Agar was used for many food products and was used in very large quantities for the production of bacteriological media for the Japanese Army during the Second World War.

The Japanese discovery of the strong jelly-like nature of Gelidium was the Japanese interest in "Mamalaiching Pancake" (cream or dessert of the Gelidium agar jelly) brought into the international of seaweeds imported from Mexico to Japan, Gelidium corneum, Gelidium cartilagineum and Gelidium sesquipedale.

Seaweeds that are used for agar production are:

- Gelidium species of Spanish Seaweeds mainly in Spain, Portugal, Morocco, Algeria, Morocco, Tunisia, USA, Peoples Republic of China, Chile and Mexico.
- Gelidium species of Japanese Seaweeds mainly in Japan, Korea, Taiwan, Peoples Republic of China, Portugal, Morocco, Spain, Portugal, Morocco, Tunisia, USA, Peoples Republic of China, Chile and Mexico.
- Gelidium species of Chilean Seaweeds mainly in Chile.
- Gelidium species of Portuguese Seaweeds mainly in Portugal and Morocco.
- Gelidium species of Mexican Seaweeds mainly in Mexico.

Industrial harvesting techniques for agar production vary, depending on circumstances, but they can be classified as follows:

- (1) Harvesting of seaweed by hand.
- (2) gathering seaweed by cutting or mining them out from their beds.
- (3) combination.

Figure 1: Agar production in different countries

Figure 1a: Agar production in different countries (indicating the seaweed used)

COUNTRY	SEAWEED USED FOR AGAR	YEARS OF USE	TOTAL
Japan	Gelidium	1923 to date	1,000
Canary Islands	Gelidium	1923 to 1960	37
Portugal	Gelidium	1960 to date	40
Morocco	Gelidium	1960 to date	40
Morocco	Gelidium	1960 to date	40
Tunisia	Gelidium	1960 to date	40
USA	Gelidium	1960 to date	40
Peoples Republic of China	Gelidium	1960 to date	40
Chile	Gelidium	1960 to date	40
Mexico

In smaller quantities, agar is used to increase the viscosity of some alcoholic liquers.

The important gel-forming properties of agar have permitted the expansion of its use to applications other than the human food industry. To prepare casting moulds, an aqueous solution of high concentration (8% or more) is used with the addition of glycerin or glycols, as well as a preservative to avoid gel surface contamination by moulds; bacterial contamination is impossible because a gel with such a high concentration has very little free water left where bacteria can grow (it has a very low A_W). These kinds of gels are also used in sculpture, archaeology, and in other works in which a perfect or precise reproduction is essential. For this reason it is also used in dental moulds as it is possible to make better and more precise reproductions, in spite of the fact that casting moulds prepared with agar are more expensive than those prepared with alginate paste. The purpose of adding glycerin in these uses is to avoid cast dehydration since a balance with the outside humidity can be achieved and therefore stable gels can also be obtained which do not appreciably change the gelling and melting points. Glycerin also expedites heat transfer permitting a faster gel melting in a boiling water-bath. The perfect reversibility of an agar gel permits it to be repeatedly used in this application and its low gel point makes it possible to be used as a dental mould.

Another rare application is the preparation of food to feed insects during their larval stages. The breeding of certain insects on a large scale, such as the Mediterranean fruit fly that attacks fruit trees or Pazzinopora glusipsii that attacks cotton plantations, has made plague control possible through a type of biological warfare. Large numbers of insects are grown and sexually sterilized by gamma rays. When released they drastically reduce the reproduction of the overall population.

The application of agar in pharmacy as a smooth laxative is well known. Lately it has been used as an excipient in pharmaceutical preparations. In some Western countries agar is used as an antirheumatic since a prolonged treatment has permitted important improvements in patients' health. Agar has been used to stabilize cholesterol solutions.

Due to its low tendency to precipitate in alcoholic media, it is possible to prepare agar gels with alcohol concentrations that will burn when a match is applied to them.

Agar has been used in orchid nurseries for a long time. Improvement in cellular cultivation know-how has brought another important application of agar mainly in the techniques that, starting from meristems, produce perfect and virus-free clones of plants. Agar for these more refined agricultural applications must be especially prepared and strictly controlled to guarantee that the absence of inhibitors that prevent cellular cultivation, or make it difficult. This use is increasing since cellular cultivation media for vegetables is being used in industrial quantities because of the current application of these techniques in agriculture.

The 10 basic points previously mentioned are very important as far as Bacteriological Agar and Agarose applications are concerned, as well as those properties essential for the applications of both products. Agarose is produced from both Gelidium and Gracilaria and these two raw materials can give agaroses with different properties which are useful in various applications. Agarose is employed in biochemical technology for protein separation, mainly in analytical laboratories, but has started to appear in industrial applications due to the genetic engineering industry that produces proteins such as interferon, interleukin and insulin which are sometimes separated with beads made of agarose. Microbiologists employ it in tissue culture as well as in other very sophisticated techniques. Renn (1984) has described some of the applications of agarose.

The uses of agarose can be grouped in the following broad categories.

1. Immunodiffusion and diffusion techniques

2. Electrophoresis of particles carrying electrical charges with direct application for proteins, nucleic acids, polysaccharides that necessarily are charged in conventional electrophoresis as well as reverse electrophoresis, immunoelectrophoresis or electrofocusing.

3. Chromatographic techniques in gel chromatography, ion exchange chromatography (for which the required polar groups will be fixed in the agarose), affinity chromatography or chromatofocusing.

4. In bioengineering as a raw material for beads used in chromatographic columns for separations of proteins, as well as cross-linked beads to which active molecules can be attached which can be recovered afterwards.

5. In microbiology as an excellent base for growing very special cultures, in many cases related to oncological research.

It can be seen that agarose uses are developing as biochemistry and especially bioengineering advance. It constitutes an inert support of natural origin, modifiable by organic synthesis, with the highest known gelling power among natural colloids. Moreover it is of such a great stability that no reagents are needed to preserve it indefinitely, thus avoiding foreign interference with the products meant to be separated.

MARKETING

Agar is marketed pure, without adding mineral salts, other gums or products destined to standardize its properties as is done with carrageenans and some alginates. For that reason, it is very important to know the different techniques of gel strength measurement since the industry produces agars of different gel strengths. The use of agar combinations with other gums for several applications, to solve different rheological problems, makes it necessary to explain here its behaviour when mixed with substances to obtain certain textures. In some applications, agar by itself gives a brittle texture and to improve its elasticity, it is mixed with locust bean gum (also called carob gum) to obtain more elastic gels. In this case Gelidium agar behaves differently from Gracilaria agar as shown in Figure 14 which illustrates Nikan-Sui gel strength of solutions of agar-carob gum mixtures of 1.5% total colloid concentration. It can be seen that for Gelidium agar, the gel strength increased when substituting part of the agar by carob gum, reaching its maximum strength at an approximate concentration of 1.33% of agar and 0.17% of carob gum. Any further increase of carob gum produces a drop in the gel strength. In the case of Gracilaria agar, the addition of carob gum produces a drop in the gel strength. On the other hand Gracilaria agar used in high sugar concentration solutions (above 50%) increases its gel strength much more than Gelidium agar does.

The data for all these applications refers to industrial agars that are sold worldwide in powder form with different meshes, generally included between 60-100 mesh, ASTM standards, in the Orient there is a considerable household consumption of natural agar with much lower gel strengths, in the range 150-400 g/cm², with which daily food is prepared at home. This agar is marketed in "strips" or "square" (the appearance is string-like or bar-like respectively, Figure 15) produced always by freezing, thawing, draining, and drying without breaking the strips or squares, that are prepared at the gel stage. This popular method of presentation helps the housewife with her measurements. Such agar, produced basically in Japan, Korea, People's Republic of China and its Taiwan Province, is consumed locally and exported mainly to neighbouring countries with some quantities being sold in Western countries, mainly in health food stores. In Japan the sale of industrial agar for these uses is successfully presented in a pill form of the same content as a bar, to help the housewife with her measurement of it for cooking purposes.

Marketing of industrial agar, food grade, is generally made through trading companies operating from Japan, or in Europe (where the more important commercial centres are located in Hamburg or London), or in the United States where the most important trading companies are located in the areas close to New York.

It is difficult to give an idea of the prices of commercial agar because the usual trade statistics list in the same table, agars with different specifications and applications and therefore with different prices. However taking as a reference the Japanese statistics (since this country produces, Imports, and exports a large quantity of the world agar production) we can see in Figure 16 the export/import prices for 1984-86.

From Figure 16 the average prices for 1984 and 1986 were as follows.

Export	1984	1986
Agar, natural, strip	US$ 16.17 per kg	US$ 21.07 per kg
Agar, natural, square	US$ 28.76	US$ 45.61
Agar, industrial, powder	US$ 12.76	US$ 17.30
Import		
Agar, natural, strip	US$ 10.12	US$ 13.38
Agar, industrial, powder	US$ 12.74	US$ 21.40
Exchange.rate	Yen 246.07/$US	Yen 154.23/$US

Due to the large quantities of agar traded by Japan, this data is reasonably representative of the agar world market although the 1986 figures would represent the top market values. This is because the recent strengthening of the yen against most of the major world currencies has allowed some other countries to sell more cheaply.

Part of the industrial agar marketing is handled by companies that trade with food additives as pure products (like agar) or by the preparation of mixtures exclusively formulated for each application.

Figure 14 Agar gel solutions of agar/carob gum

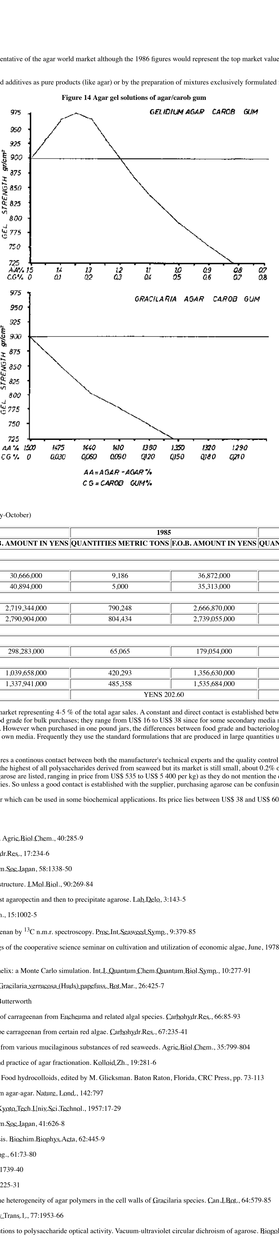

Figure 15 Agar in powder, strip and square forms

Figure 16 Agar imported and exported by Japan in 1984, 1985 and 1986 (January-October)

			1984		1985		1986 (JAN./OCT.)	
			QUANTITIES METRIC TONS	F.O.B. AMOUNT IN YENS	QUANTITIES METRIC TONS	F.O.B. AMOUNT IN YENS	QUANTITIES METRIC TONS	F.O.B. AMOUNT IN YENS
EXPORTS								
I	NATURAL AGAR							
	Strip		7,705	30,666,000	9,186	36,872,000	6,664	21,651,000
	Square		5,779	40,894,000	5,000	35,313,000	3,430	24,127,000
II	INDUSTRIAL AGAR							
	Powder		866,069	2,719,344,000	790,248	2,666,870,000	447,559	1,194,436,000
		TOTALS	879,553	2,790,904,000	804,434	2,739,055,000	457,653	1,240,214,000
IMPORTS								
I	NATURAL AGAR							
	Strip		119,674	298,283,000	65,065	179,054,000	103,078	212,693,000
II	INDUSTRIAL AGAR							
	Powder		331,386	1,039,658,000	420,293	1,356,630,000	227,231	750,114,000
		TOTALS	451,060	1,337,941,000	485,358	1,535,684,000	330,309	962,807,000
EXCHANGE RATE:		U US DOLLAR	YENS 246.07		YENS 202.60		YENS 154.23	

The world market for bacteriological agar is small in relation to the food grade market representing 4-5 % of the total agar sales. A constant and direct contact is established between the technical departments of both manufacturer and consumer, who is in general the manufacturer of dehydrated culture media. Prices are higher than food grade for bulk purchases; they range from US$ 16 to US$ 38 since for some secondary media manufacturing companies a very good grade agar is acceptable but for others with higher standards an agar with distinct specifications is absolutely necessary. However when purchased in one pound jars, the differences between food grade and bacteriological grade become very large since marketing and distribution costs have been added. Researchers buy from this source when they have to formulate their own media. Frequently they use the standard formulations that are produced in large quantities under strict controls by culture media manufacturers, in dehydrated or in ready-to use form, in bottles, tubes or Petri dishes.

A similar situation exists for agarose, the increasing development of which requires a continous contact between both the manufacturer's technical experts and the quality control experts of those companies that distribute biochemical reagents, as well as with the researchers who use agarose in very specialized techniques. Its price is the highest of all polysaccharides derived from seaweed but its market is still small, about 0.2% of the agar market. Prices recorded in commercial catalogues are difficult to compare (for example see Sigma Catalogue for 1987 where thirteen grades of agarose are listed, ranging in price from US$ 535 to US$ 5 400 per kg) as they do not mention the degree to which the corresponding agarose has been modified by synthesis and therefore a range of different products are listed under similar prices categories. So unless a good contact is established with the supplier, purchasing agarose can be confusing for the end user.

There is a small demand for Purified Agar, a special grade of bacteriological agar which can be used in some biochemical applications. Its price lies between US$ 38 and US$ 60/kg, the range being explained by the differences of quality in purified, noble or deionized agars present in the market.

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CHAPTER 2 - PRODUCTION, PROPERTIES AND USES OF ALGINATES

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1. INTRODUCTION

Alginates are the most economically important of the seaweed extracts of algae. The production of the alginate values from algae is confined to the choice of which seaweed species is chosen to meet the availability of particular species and the requirements of the alginate that they contain. The main commercial sources are species of Ascophyllum, Macrocystis, Laminaria, Lessonia, Ecklonia, Durvillaea, Sargassum, Turbinaria and Ulva. Alginates are used in Germany, Massachusetts and Washington.

Alginates are used in food products, in the textile industry, in the paper industry, in the welding industry, in the pharmaceutical industry, in the cosmetic industry, in the ceramic industry, in the paint industry, in the dental industry, in the medical industry, in the photographic industry, in the explosives industry, in the rubber industry, in the plastics industry, in the pesticide industry, in the fire fighting industry, in the ink industry, in the adhesive industry, in the glass industry, in the fertilizer industry, in the soil conditioning industry, in the fuel industry, in the water treatment industry, in the sewage treatment industry, in the mining industry, in the refractory industry, in the ceramic industry, in the cement industry, in the wood industry, in the fire fighting industry, in the insecticide industry, in the fungicide industry, in the herbicide industry, in the seed industry, in the plant growth industry, in the plant protection industry, in the veterinary industry, in the aquaculture industry, in the pharmaceutical industry, in the medical industry, in the dental industry, in the cosmetic industry, in the food industry, in the beverage industry, in the brewing industry, in the wine industry, in the canning industry, in the meat industry, in the poultry industry, in the fish industry, in the shellfish industry, in the seafood industry, in the dairy industry, in the ice cream industry, in the confectionery industry, in the bakery industry, in the pastry industry, in the cake industry, in the biscuit industry, in the cereal industry, in the pasta industry, in the noodle industry, in the rice industry, in the sauce industry, in the condiment industry, in the spice industry, in the flavouring industry, in the fragrance industry, in the perfumery industry, in the aromatherapy

FILAMENT FORMATION

If a solution of sodium alginate is forced through fine holes into a solution of a calcium salt, filaments of calcium alginate will be formed. Much research went into the development of alginate rayon (Tencel and Lilyflax) 1934; Mauro, 1939; but they were not commercially successful. Calcium alginate fibers are insoluble in water, but they can be converted into sodium alginate fibers by treatment with sodium carbonate solution. Calcium alginate fibers are used in medical dressings because they can be easily removed from wounds. When it comes into contact with sodium salts in the body fluids, some of the calcium ions are exchanged for sodium ions so that a thin soft gel forms at the interface of the dressing and the wound and the dressing never sticks to the wound.

SAFETY IN FIBER FORMS

General colloidal properties in the term used to explain why fibers occasioned in some applications where the monomer are not fully understood and where the alginate has been chosen on an empirical basis. These applications have been discussed by Mackie and Mullan (1968) Mackie 1968 The use of sodium alginate, as a flocculant, as a suspending agent, and as a stabilizer in ice cream; propylene glycol alginate (E 405) Ice cream 1% Stabilizer 0.5% Sugar 15% 10 minutes which prevented alginate salts or as a binder; at first sputtering contained the fibers and but approved the process. Fibers of calcium alginate, Fibers of calcium alginate, Fibers of calcium alginate,

CHAPTER 3 - PRODUCTION, PROPERTIES AND USES OF CARRAGEENAN

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CARRAGEENAN

INTRODUCTION

Carrageenans are commercially important hydrophilic colloids (water-soluble gums) which occur in many marine seaweed or seaweed species of red seaweeds (Rhodophyceae) where they are a structural function analogous to that of cellulose in land plants. Chemically they are highly sulfated polysaccharides. Due to their half ester sulfate moieties they are strongly anionic. Because of their high molecular weight and sulfate content they have a variety of commercially exploited rheological properties. Commercially, carrageenans are used as thickeners, gelling agents, and stabilizers in food, pharmaceutical, and other industrial applications. Because of their rheological properties and their ability to react with milk protein and cocoanut by-products, carrageenans are used in milk and cocoa mixes and cocoanut by-products, carrageenans are used in milk and cocoa mixes and cocoanut by-products, carrageenans are used in milk and cocoa mixes

CHAPTER 4 - PREPARATION AND MARKETING OF SEAWEEDS AS FOODS

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This chapter covers the preparation of seaweeds from raw material into forms, and marketed in the major foreign markets. It lists the Korean Seaweeds and Japan. In Japan, consists of marine algae, which are eaten as vegetables, differ from those of the other countries. Seaweeds are used in Japan for a variety of purposes, including as a food, as a medicine, as a fertilizer, and as a feed. It has been basically, seaweed that the Natural Japanese consumed which had been foraged in the beginning of the Jomon period, and the substitutes grain were being cultivated. Seaweeds are used in Japan for a variety of purposes, including as a food, as a medicine, as a fertilizer, and as a feed

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