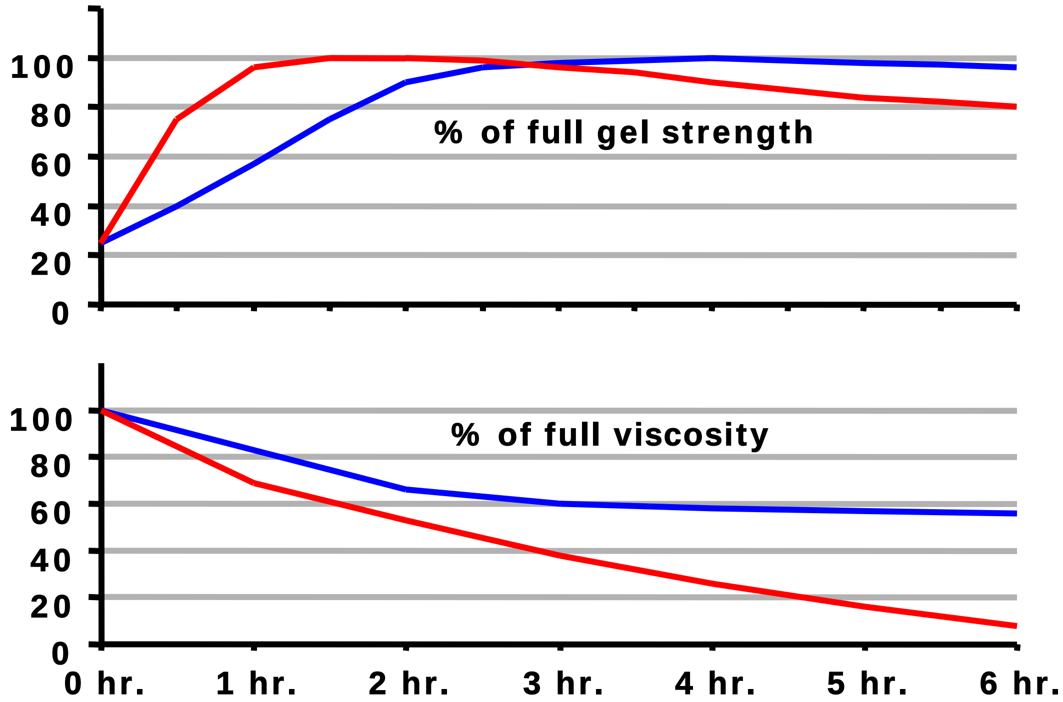
Basic manufacturing practices for
raw-dried seaweed and semi-refined carrageenan
from Eucheuma and Kappaphycus



by Iain C. Neish

SEAPlant.net Monograph no. SEAPlant.net Monograph no. HB2G 1008 V2 BMP

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GLOSSARY A-G

ADB - Asian Development Bank

Agar - Red algal galactan biopolymer produced by genera such as Gracilaria, Gelidium and Gelidiella.

Agronomics (marine) - The art or science of managing marine habitats for production of seaplant crops

Apical - Pertaining to the terminal segment or "tips" of fronds

ATC - Alkali-treated cottonii chips

AusAID - Australian Agency for International Development

Axenic - Uncontaminated and germ free (applied to cultures)

Basal - Pertaining to the oldest segment or "base" of fronds.

Biopolymer - Compound of high molecular weight synthesized by living organisms

BIMP-EAGA – Brunei, Indonesia, Malaysia Philippines East ASEAN Growth Area

Callus - Tissue that forms over cut parts of fronds

Carpospore - Diploid spores produced by carposporophytes that live parasitically on their mother plants

Carrageenan - Red algal galactan biopolymers produced by genera such as Kappaphycus, Eucheuma, Betaphycus, Gigartina, Chondrus and others.

Cisternae - Reservoirs or receptacles that hold fluid in the plant tissue

Clone - A group of organisms derived from a single individual

Conjugate - Fusion of two one celled organisms for reproduction where fertilization occurs

Coral Triangle – includes most of East Malaysia, Philippines, Indonesia, Timor Leste, Papua New Guinea and Solomon Islands

Cortex - The pigmented outer cell layer of a thallus or frond

Cottonii – Kappaphycus spp.

Cultivar – A clone derived from vegetative propagation originating from a single seaplant thallus.

DES - Dried Eucheuma Seaplants

Dioecious - Organisms that have male and female reproductive structures on different individual members of the species

Diploid - Having two similar complements of chromosomes

DKP - Dinas Kelautan dan Perikanan (Indonesian Department of Oceans and Fisheries)

EAI - East ASEAN Initiative of AusAID

ES - Eucheuma Seaplant (s)

End-user – an enterprise that utilizes as-is or further-processed ingredient building-blocks or ingredient solutions in goods that are purchased by wholesale and retail enterprises.

Eucheuma - “spinosum” of the trade; source of iota carrageenan.

Eucheuma seaplants – Betaphycus, Kappaphycus and Eucheuma

FAO – United Nations Food and Agricultural Organization

Frond - A branch of a thallus

Furcellaran - Red algal galactan biopolymer produced by Furcellaria spp.

Further processor – an enterprise that purchases -building blocks for further refinement.

Gamete - Mature haploid reproductive cell capable of fusion with another gamete to form a diploid nucleus

Gametophyte - Life cycle stage in many plants and algae; individual plant composed of haploid cells that produce gametes

GAP – Good Agronomic Practices

Germinate - To begin growing or developing

GMP - Good Manufacturing Practices

Golgi body - Golgi apparatus/body; a net-like mass of material in the plant cytoplasm that is a site of biopolymer synthesis

Gonimoblast - filaments extending from egg cell to carposporophytes

GTZ - Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ)

GLOSSARY H-Z

Habituate - To become used-to or adapted-to stimuli

Haploid - Having one complement of chromosomes

IBB - Ingredient building-blocks – products derived or extracted purely from one defined source of raw material and then sold to further-processors or solution providers.

IFC – AS - International Finance Corporation – Advisory Services

IFC-PENSA - IFC Small Business Development in Eastern Indonesia

IMTA - Integrated Multi-Trophic aquaculture

Indigenous – Originating in and characterizing a particular region or country.

JaSuDa – Jaringan Sumber Daya (Source Net), a program of SEAPlant.net.

Kappaphycus - "cottonii" of the trade; a seaplant source of kappa carrageenan

KITS - Knowledge + Information + Tools + Solutions

Macrophyte - Plants large enough to be readily seen by the naked eye

Macroalga - Non-vascular aquatic or marine plants of the phyla Chlorophyta, Rhodophyta and Phaeophyta; Large enough to be seen using the naked eye

Marinalg – World Association of Seaweed Processors (marinalg.org)

Medulla - The un-pigmented cell layer immediately below the cortex

Microalga - Non vascular aquatic or marine plants too small to be seen by using the naked eye

Monoecious - Organisms that have both male and female reproductive structures on the same individual

Morphology - Form and structure of the plant

Pericarp - The walls of a ripened fruiting body

Phenotype - A character or individual defined by its appearance and not by its genetic makeup

Phycocolloid - Complex polysaccharide biopolymers produced by algae (e.g. agar, alginates and carrageenan)

Propagule - A cutting or fragment of a seaplant thallus that is used for vegetative propagation of a crop

Protoplast - Actively metabolising membrane-bound part of a cell (as distinct from the cell wall)

RAGS – red algal galactan seaweeds (includes eucheuma seaplants)

RC - Refined Carrageenan

Rheology - Textural characteristics of a gel or solution.

Rhizoid - Root-like filaments by which a macroalga attaches to substrate; collectively may form a holdfast

Seaplant - Any photosynthesising organism that lives in seawater

Seaweed - Common name applied to most marine macroalgae

SFDM - Salt free dry matter

SGR - Specific growth rate expressed in percent per day

SIAP - Seaweed Industry Association of the Philippines

SPNF- Seaplant.net Foundation

Spinosum – Eucheuma spp.

SME - Small-medium enterprise

Sporophyll - Structure that produces reproductive cells called spores

Sporophyte - The life cycle stage in plants and algae that terminates in meiosis to produce spores

SRC – semi-refined carrageenan (a.k.a. processed eucheuma seaweed, PES or E407a)

Tetraspore - one of four asexual spores produced in a tetrasporangium

Thallus - The entire physical entity of a propagule or a whole plant

Uniseriate - Occurring in a single series

USD - United States dollar

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PREAMBLE

This monograph and its companion monographs in the HB2 series supersede and expand upon *The Eucheuma Seaplant Handbook Volume I : Agronomics, Biology and Crop Systems* (SEAPlantNet Technical Monograph No. 0505- 10A; ISBN 979 99558 0 7). Volume II of the Eucheuma Seaplant Handbook was never completed. Material that was to be included in that have been written up as other monographs in this HB2 series.

SEAPlant.net Foundation (SPNF) began as an initiative of IFC – Advisory Services under the PENSA I program that ended its five year term in June, 2008. During jointly funded work involving the PENSA program and GTZ (Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH.) it became clear that an integrated, ongoing and readily accessible body of information was necessary to facilitate and catalyse the development of seaweed farming as a component of integrated multi-trophic aquaculture (IMTA) in the BIMP-EAGA region in particular and in the Coral Triangle in general. GTZ therefore joined with SPNF to develop *A Practical Guide to Quality Assurance, Governance Systems and Good Practices for Tropical Seaweed-to-Carrageenan Value Chains with focus on developing harmonization and transparency in the BIMP-EAGA region of ASEAN in the Coral Triangle* (SEAPlant.net Monograph no. HB2D 1108 V1 GTZ). The practical guide is provided as a tool for negotiating the tangled web of rules, regulations, standards, tests and other requirements that increasingly make life complicated for industry stakeholders whether they be seaweed farmers, processors or end-users.

One of the objectives of the Practical Guide is to bring about the development of harmonized Good Manufacturing Practices (GMP) for seaweed farming within the region. The present document is a draft set of basic manufacturing practices that we hope will ultimately lead to GMP.

Regulations and standards for the aquaculture industry are at an early stage of development. Those for the specialty chemicals businesses are in a constant state of change and comprehensive standards for carrageenan and agar in the BIMP-EAGA region have yet to be adopted although draft standards are under development. Consequently this is a "living document" that is being updated periodically.

We heartily welcome suggestions and guidance from the users of the present monograph and the Practical Guide.

Iain C. Neish, October, 2008
Makassar, Sulawesi Selatan, Indonesia

BIBLIOGRAPHY FOR THIS MONOGRAPH: Please download: "*A Reference List for Commercially Cultivated Tropical Red Seaweeds.*" SEAPlant.net Monograph no. HB2G 1008 V3

Contact us at: Seaplant.net Foundation, Graha Pettarani Lt. V, Jl. Andi Pangerang Pettarani 47, Makassar, Sulawesi Selatan, Republic of Indonesia, Tel : (62 411) 425280 –84 Fax : (62 411) 425269, Email: contact@seaplant.net, URL: http://www.seaplant.net

1. Drying the crop

Eucheuma seaplant crops are generally dried before shipment to further-processing facilities. "industry standard" is about 38% moisture. Individual transactions may involve specifications as low as 30% or as high as the trading environment permits. Attempts at finding better and more cost effective all-season drying options are a persistent industry preoccupation.

Plate 1. Here the author (left), Tita Barriga Tomayao and Ruben Barraca puzzle over one of many systems tried over the years. (Cebu City, Philippines, 1979)

Depending on weather conditions and plant density eucheuma seaplants can typically be dried in 2-3 days under tropical conditions. Plants must be turned over frequently. Wet : dry ratios vary between species and locations but generally range from 6:1 to 9:1.

Figure 1. A typical drying curve for cottonii spread thinly on a cement slab or drying net under full tropical sunlight.

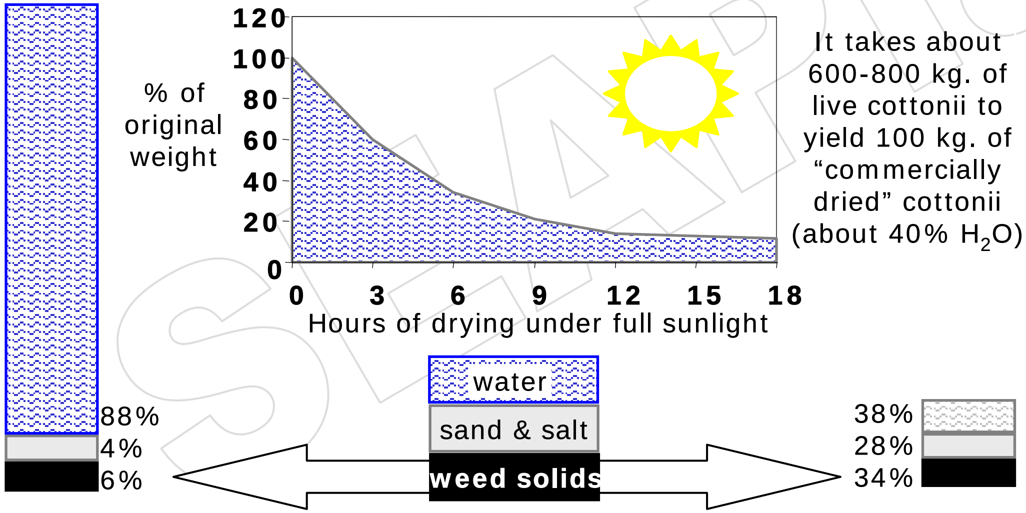

Plate 2. Basic equipment needed for eucheuma seaplant quality testing includes a good analytical balance (A) or top-loading balance (B) and a recirculating drying oven (C).

Table 1. Parameters tested during the assessment of dried eucheuma seaplant quality	
Water	Weight lost during desiccation in a drying oven is defined as being "moisture content".
Sand	Material that does not dissolve after thorough soaking and rinsing is defined as "sand".
Junk	Junk weed, tie-ties, debris and other foreign matter is simply removed and weighed.
Salt	Whatever disappears after thorough rinsing and drying is defined as being "salt".

Salt-free dry matter; which includes	
Carrageenan	Salt Free Dry Matter (SFDM) is also known as Clean Anhydrous Weed (CAW). It is left over after thorough rinsing and drying. It includes carrageenan, crude fiber (a.k.a. acid insoluble matter or AIM) and organic materials lost during cooking and washing.
Fiber	
Lost organics	

Download SEAPlant.net monograph HB2H 1008 V3 LTP for test procedures

2. Drying methods

Eucheuma seaplant crops are almost universally dried under the tropical sun before they are packed and shipped for further processing. The basic rules for producing a high quality of dry eucheuma seaplants are:

1. Clean the material as described on page 8.
2. Dry the material to below 38% moisture.
3. Do not salt the crop (page 10)
3. Do not play “trading games” (page 11)

These rules can be obeyed using a wide variety of drying surfaces and techniques. Some of the more common ones are illustrated in Plates 3 to 6.

Plate 3. Clean concrete slabs make an excellent drying surface especially if they have good drainage (left) but where farm houses are located over water wooden platforms are also effective (right).

Plate 4. Drying platforms (para-para in Bahasa Indonesia) can be made from bamboo strips with fine netting on top. This is an excellent drying technique.

Plate 5. Another excellent drying method is to hang the planting lines from frames; under a rain shelter if possible. The hanging method is commonly used in Central Sulawesi, Indonesia. In the situation below right the drying frames are located under a cliff overhang that shelters plants from rain.

Plate 6. Avoid drying the crop in places that are surrounded by dirt and debris as in the case below.

Avoid drying eucheuma seaplants on roadways and on the shoulder immediately adjacent to roads. This causes dirt and fumes to contaminate the crop and is thought to be a source of heavy metal contamination that can diminish crop value.

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3. Cleaning & re-drying

At certain times and in certain places dried eucheuma seaplants have come straight from the farms with no need for further cleaning and redrying. Unfortunately this is the exception rather than the rule nowadays.

Processors and traders must ensure that dried eucheuma seaplant quality is at specified levels before they can process or sell it. Typically they must bear the costs of removing and further-drying the dried eucheuma seaplant that they purchase and it is common for substantial "shrinkage" to occur.

A rule of thumb in the dried eucheuma seaplant trade is that moisture content and contamination goes up during sellers' markets and down during buyers' markets.

High moisture can be difficult for farmers to avoid during wet seasons and some contaminants are inadvertently added to the crop during harvesting and PHT. Unfortunately PHT "trading games" (page 11) can also be the source of high moisture and contamination.

During cleaning and re-drying there are some steps that are generally applicable and others that are optional.

1. **Raffia, rope and other materials** used during farming activities can cause process problems and product contamination so they should be removed.
2. **Junk weed, debris and other large "non-crop" items** should be removed as much as possible especially if they can have critical effects on quality (e.g. a spinosum + cottonii mix may be useless for processing).
3. **Sand and stones** cause equipment fouling, wear and tear so they must be removed.
4. **Mud, dirt and other particulate contaminants** should also be removed.
5. **Seaweed salt removal is optional**. The natural KCl in eucheuma seaplants has a role in processing and can be left in the crop.

Plate 7. Before they are packed dried eucheuma seaplant crops are usually sorted by hand to remove "junk weeds", raffia and other debris.

Plate 8. In some areas harvested, live seaplants are washed in seawater to remove silt, salt or other contaminants.

Plate 9. A. Well dried <u>Kappaphycus</u> has KCl salt crystals on the plant exterior and fronds have a stiff texture. **B.** Some processors flail the crop to remove external sand and salt.

4. Packing & shipping

Dried eucheuma seaplants are usually stuffed into sacks for domestic trade and are pressed into tightly compressed bales for export in twenty-foot containers to overseas processors. Woven plastic or jute sacks or wrapping materials are generally used. Sacks generally hold about 50-80 kg of dried eucheuma seaplants with moisture in the range of 35-45%. Sacks are useful for "break-bulk" shipping but their rounded shape leaves spaces that make full loading of a container impossible (usually 14-16 tons can be stuffed in).

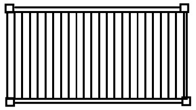
Bales are generally made at weights ranging from 50-110 kg and are proportioned so they snugly fill a 20-foot container to the full capacity of 20-22 tons. Bales may be wrapped in woven plastic and/or strapped but some buyers prefer to receive "naked bales" with no wrapping or strapping.

An interesting characteristic of well-dried dried eucheuma seaplants is that they spring back immediately after compression but will "relax" if compression is maintained over several minutes (an hour or more if possible). Once the dried eucheuma seaplants "relax" the bale maintains its shape fairly well and can be loaded as "naked bales".

Plate 10: Following sorting and cleaning the seaplants are tightly packed in sacks (below) or are compressed into bales (images opposite).

Figure 2. Bales are generally made at weights of about 50 to 110 kg. and permit full loading of 20 tons per 20-foot dry freight container.

20 foot dry freight container



<u>Interior Dimensions:</u>
Length: 19'5", 5.919 m
Width: 7'8", 2.340 m
Height: 7'9.5", 2.380 m
<u>Tare Weight:</u>
4,189 lbs, 1,900 kg
<u>Cubic Capacity:</u>
1,165 cubic ft., 33.0 cbm
<u>Payload:</u>
48,721 lbs, 22,100 kg

Plate 11. Bales may be wrapped and strapped for shipping but some customers prefer "naked bales" with no strapping material at all so they can dump entire container loads and treat them as single raw material lots.

Plate 12. Manual screw presses are still used but bales are usually compressed using hydraulic presses (right). A wide variety of designs is available.

Plate 13. Dried seaplants are commonly shipped within Southeast Asia in vessels such as the Filipino "kumpit" (below with 80 tons of cottonii aboard).

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5. Salting & alkali dips

"Salting" is a controversial practice that has arisen in some eucheuma seaplant production areas.

Salting impacts on quality preservation and extract quality are still being investigated. Meanwhile many processors avoid "salted weed".

Salting diminishes drying time but it introduces the "salt game" into transaction equations. Some processors also claim that salting diminishes extract yields, darkens crop color and/or causes excessive variability in extract yields and quality.

Dry-salting Zamboanga style...

Plate 14. During "dry-salting" freshly harvested cottonii is piled on tarpaulins and salt is broadcast at a rate of about one sack/1,000 kg (45 kg salt/sack; cost about 2.00 USD; image “A”). In good weather the pile is left overnight and the crop is spread on tarpaulins early on the next day (image “B”). Salted cottonii dries in one day under direct sunlight. About 80% of applied salt is consumed during salting or is mixed with the crop. The balance is recycled (see white piles of salt in image “C”).

Washing and treating eucheuma seaplant yields effluents high in color, odor, B.O.D., alkali or salts so they must be disposed of with care.

Wet-salting Madura style...

Plate 15. In Madura, Indonesia farmers employ a method that is similar to the salting of fish. It involves placement of live seaplants into cement vats (below). For every 1,000 kg. of fresh crop about 50 kg of sea salt is added. No water is added. After overnight soaking the crop is removed and sun dried (below). After the first salted batch a pungent, vermillion colored saline "soup" is left in the vat (B). 1,000 kg. of fresh crop and 25 kg. salt are added for a second batch. After that the “soup” is discarded.

Plate 16. NaCl wet-salting leads to dark crop color on drying (right).

OK

Value can be added by dipping fresh plants in weak alkali (about 0.1N) for several hours.

Alkaline stabilization removes color and effectively preserves crops if properly applied. It is not yet commonly applied to Kappaphycus but is a common practice for Eucheuma. If the correct combination of soaking and drying conditions is achieved the "alkali-stabilized spinosum" can be ground, blended and utilized as an iota-carrageenan form of "processed eucheuma seaweed" (PES; E407a).

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6. Trading games

Inadvertent problems with post-harvest treatment (PHT) and intentional "trading games" increase shipping and processing costs & diminish crop quality.

Most properly cultivated eucheuma seaplants are of good quality at harvest but much crop value can be lost by intentional or inadvertent PHT manipulations such as the following:

Water games...

Sellers love to get paid for water and buyers hate to buy it. Quality issues arise because wet crops can rot in storage. "Water games" add persistent “noise” to eucheuma seaplant value chains. The most common water games are:

1. **Under-drying the crop**; which enables sellers to get away with high moisture when there is a "seller's market".
2. **Adding moisture to well dried crops** is a trick employed by some "middlemen" to increase their margins.

Salting games...

Eucheuma seaplants naturally concentrate potassium chloride (KCl). KCl is useful in alkali treatment process steps but NaCl is not useful for that purpose. Salt-soaks usually utilize rock salt or sea salt (mostly sodium chloride) to reduce drying time and dilute the crop. Processors buy salted material only when they have no alternative or if it has a very low price.

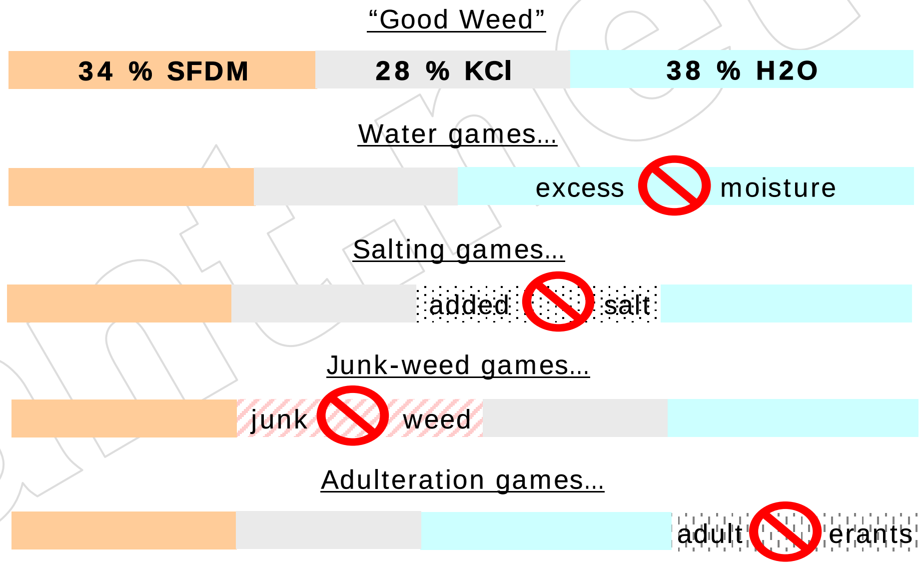
Junk-weed games...

Mixture of low-quality eucheuma seaplants or seaplants other than the one specified by buyers can lead to low yields, poor extract quality or shipments being sent to the garbage dump. Mixing spinosum with cottonii is an especially problematic practise.

Adulteration games...

Adulterants diminish crop value and add quality and/or processing problems. Raffia, dirt, salt, cement and other such diluents are nothing but trouble to processors and they will avoid suppliers who habitually adulterate the crop.

Figure 3. Processors of eucheuma seaplants want to buy "good weed" with high, un-decomposed salt-free dry matter (SFDM) and a minimum of salt or moisture. Quality and quantity of SFDM is reduced by the "trading games" listed below:



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A game with tighter rules but higher rewards... the "chips" game

Alkali "dips" for live spinosum have been a commercial practice since the early 1980s but the practice has not yet been commonly adopted in PHT of cottonii. There is, however, a growing tendency for dried cottonii to be subjected to alkaline modification, washing and chopping to yield a product variously known as "treated cottonii chips" (TCC) or "alkali-treated cottonii/chips" (ATC) or "PES chips". One of the main attractions of chips is that they minimize the scope for trading games. Most water, sand, salt and other non-essential materials are removed during processing so cheating is readily detected.

7. “Gel-mode” carrageenan processes

Over the years a variety of trade names has been used for the alkali-modified "gel-mode" products of eucheuma seaplants. The term “SRC” (semi-refined carrageenan) came into general use in the marketplace around 1978 and this is still commonly used in the trade. The term ”SPC” (Semi-Processed Cottonii) was briefly current but this term met resistance from petfood producers due to connotations of the Society for the Prevention of Cruelty. Other trade names have included AMF (alkali modified flour), alkali-treated cottonii (ATC), Philippine Natural Grade Carrageenan (PNG carrageenan), alternatively Processed Carrageenan (APC), treated seaweeds, treated cottonii chips (TCC), alkalized seaweeds, bleached cottonii and a variety of other names.

The term "Processed Eucheuma Seaweed" (PES) was adopted when European Union regulatory authorities added this product to their list of approved food additives in December, 1996 by Directive 96/83/EC. INS and E numbers designate food grade-PES as “407a”. INS and E number “407” applies to carrageenan extract.

The defining characteristic of PES is that it is reduced to final-product form without being dissolved in water; hence without having fiber (acid insoluble matter; a.k.a. AIM) removed. This type of process enables the product to be recovered using low-cost water-removal methods. The PES process is an attenuated version of processes used in the manufacture of some kinds of clarified agar and carrageenan extracts. It is one of a family of processes in which alkaline modification is done while the gum is in a gel (frozen) state rather than a sol (melted) state. The two types of processes are referred to here as "gel-mode" and "sol-mode" processes. The two types of process are compared and contrasted in the table opposite.

The simplest form of PES process is generally referred to as "alkaline stabilization" (A/S). By this process live seaweeds are sprinkled with soda ash or soaked in a weak solution (about 0.1 N) of NaOH or KOH. The seaplants may then be washed and dried or dried without washing. Iota PES is made by re-washing dried A/S spinosum, chopping it, re-drying it and milling it to a powder. Some of this product is used by the petfood industry. The method used for making PES cottonii is more involved.

PES is a product in its own right but it also finds increasing favour as raw material for the manufacture of clarified carrageenan (E407). Drivers for this trend include:

1. **Avoidance of PHT "trading games".**
2. **Minimization** of raw material variability.
3. **Lower net cost** of manufacture.
4. **Avoidance of effluent problems** at extraction plants.
5. **"Gel-mode" modification can be an attractive option** even when extraction is taking place near raw material sources.

Table 2. Comparison of process steps in the manufacture of PES (E407a); extract (E407) made from PES raw material; and extract (E407) made from whole DES (dried eucheuma seaplants).

			Extract from	
#	**Process step**	**PES**	**PES**	**DES**
1.	Treat and/or dry fresh seaplants	+	+	+
2.	Sort and sift dry seaplants	+	+	+
3.	Wash or soak dried seaplants	+	+	+
4.a.	Modify PES in a gel-mode... OR	+	+	-
4.b.	Paste and modify in sol mode	-	-	+
5.a.	Wash, neutralise PES... OR	+	+	-
5.b.	Neutralise & dilute sol-mode paste	-	-	+
6.a.	Recover wet PES... OR	+	-	-
6.b.	Paste, dilute & clarify PES... OR	-	+	-
6.c.	Clarify modified sol-mode paste	-	-	+
7.a.	Dry & sift PES chips... OR	+	-	-
7.b.	Recover gum from paste	-	+	+
8.	Mill, blend & pack dried powder	+	+	+

8. Process flow for making PES "chips" or "meal"

Figure 4. The process flow diagram at right shows a simple generalized version of the kappa PES process.

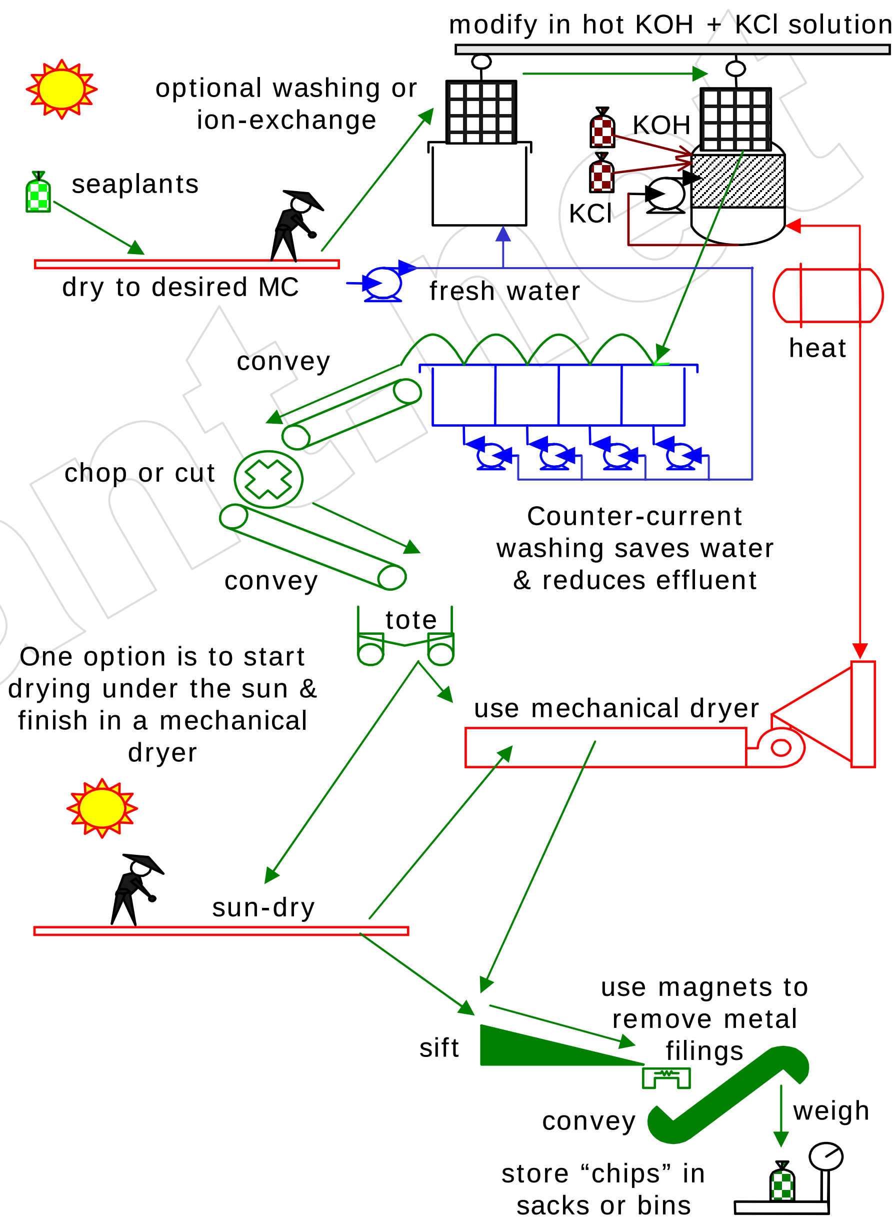
Plate 17. The end product is PES "chips" or "meal" as shown right ("Chips" left and "meal" right. (Coin 2.8 cm dia.). Meal has a finer grind and therefore has higher bulk-density and better flow properties.

Further details concerning each process step are compared and contrasted with reference to this process flow and in light of the steps shown in the table above. Processes flows and treatment regimes vary depending on the type of PES end-product desired. Some variations are shown opposite.

The manufacture of iota PES from spinosum involves very mild wet-processing compared to cottonii protocols. For spinosum alkaline modification can be accomplished during simple "alkaline stabilization" procedures. Such material can enter the process flow for manufacture of gel-press extract (E407) at the "washing" stage. Mild treatment is the rule with iota PES because iota carrageenan is readily degraded by harsh process protocols.

Some variations on the PES process include:

1. **"Slurry" washing** may occur after the "chop or cut" step.
2. **Neutralization,** sanitization or other chemical treatment may be done during the slurry wash.
3. **For food-grade PES sun-drying would be avoided** and rapid drying would occur in a mechanical dryer of some sort.
4. **For food-grade PES sanitization steps** such as ultra-violet light treatment, heat treatments, alcohol washes or chemical treatments may occur before, during or after the drying and milling steps.
5. **For food-grade PES special care must be taken** in packing and storing chips prior to final milling and blending.



9. Pre-modification processes

Treat and dry live seaplants (Step 1)

Most seaplant production sites are remote from processing facilities. Live seaplants are generally dried on nets or slabs under the sun. If the seaplants are spread thickly or there is cloudy weather drying can take several days. If the crop is to be immediately processed in a facility close to farms it need not be thoroughly dried. About one day under clear skies can be sufficient.

Except for a few strains bred for the human food market cottonii fresh from the sea has high potential to make strong petfood PES. Unfortunately the material is often degraded during poor drying and storage conditions.

There are also cases of intentional dilution or adulteration of material by farmers or traders. Most PES manufacturers would like to be able to buy and process live seaplants in order to get high quality material all year around and eliminate “trading games” that make seaplant pricing difficult. Some processors are therefore striving to develop means for directly buying live crops from farmers so they can gain control of post-harvest treatment themselves.

The use of dryers has been tried as a means of combating seasonality but most cottonii proceeds through trading networks as dried eucheuma seaplants (DES) originating directly from farms. Thus variable quality and irregular supplies remain as chronic industry problems. This situation is further aggravated when strain differences and salting cause erratic raw material quality from shipment to shipment. Locating process facilities close to seaplant farms is an effective means of addressing this issue.

If near-source processing is undertaken the processor has an opportunity to commence processing with "live weed" that has not been subjected to PHT problems introduced at the first value-chain stages. Material entering the process can be dried to optimal levels rather than being over-dried and PHT steps can be implemented that are appropriate for the manufacture of high-value products such as low-color, low-odor food grade PES.

Sorting and sifting (Step 2)

Hand-sorting is a standard method that is undertaken with raw seaplants entering the PES process. Sorting removes "junk-weed", debris and nylon that serve as contaminants and interfere with chopping or milling. Some processors also prefer to use sifting or flailing to reduce the amount of sand entering the process.

Removing sand is a good move but quite a bit of useful KCl is also removed by such processes so it may be economical to recover the KCL in aqueous solution for use during alkaline modification procedures.

Washing and soaking (Step 3)

Sand can be removed and KCl recovered if the dried seaplants are washed or soaked with fresh or salt water before modification. As an optional process step PES modification can be preceded by an ion-exchange pre-soak in which raw cottonii (complete with its natural KCl content) is soaked in a minimal volume of water for 0.5 or more hours at pH 6.5 - 8.5. The effectiveness of pre-soaking can be enhanced by adding NaCl or KCl and by following the initial soak with a series of KCl or NaCl soaks. Pre-soak solutions should have lowest possible contents of polyvalent cations such as magnesium (Mg^{++}) and calcium (Ca^{++}).

Ion-exchange pre-soaking can be a useful addition to the PES process in cases where it is necessary to:

1. **Remove** of unwanted dirt and water soluble compounds.
2. **Partially remove** of Mg^{++} and Ca^{++} that bind carrageenan in the acid-insoluble fraction of PES, form carbonates that "fizz" when PES is dissolved and form a variety of bases that dissolve slowly and cause a drifting pH.
3. **Hydrate** the raw material to affect the reaction chemicals-to-biomass balance.

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10. Alkaline modification

Cooking & alkaline modification (Step 4)

Raw eucheuma seaplants can form gels but alkaline modification is required before strong gels will form. It is the order of modification steps that differentiate the gel-mode and sol-mode processes. During gel-mode modification carrageenan remains in the seaplants' cell matrix and is alkali modified in a gelled state. Cation concentration is raised to a level where the gel melting point is above the cooking temperature (usually 75-90ºC). This is normally done using a mix of KOH and KCl. NaOH may be used in place of the KOH.

Typically gel-mode cooks are done at an alkalinity of 0.5-2.0 N and a K+ molarity of above 1.5 M. Cooking time for cottonii is normally 2-4 hours. During alkaline modification of kappa carrageenan 3, 6-anhydrogalactose is formed, some depolymerization of carrageenan occurs, and non-gum constituents of the seaplant undergo various reactions with bases and salts in the liquor. Alkaline modification relationships observed in the author's laboratory are shown in the figure opposite.

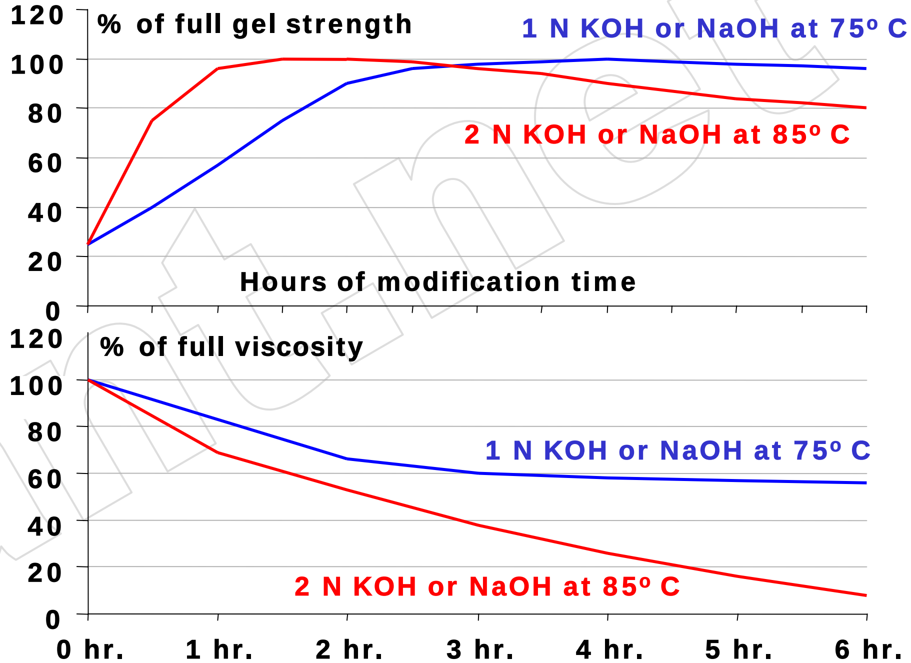
Salient points are:

1. **Gel strength develops fully** within a narrow range of conditions.
2. **During modification there are trade-offs** between cooking temperature, alkali level, cation level and cooking time.
3. **Severe reaction conditions** (i.e.: high temperature and high alkali) tend to reduce viscosity relative to gel strength.
4. **Intermediate conditions** yield intermediate response curves.

In the PES process the gum is still gelled and can easily be separated from cooking liquor.

Alkaline cooking liquor is reconstituted and recycled for the next batch to be cooked. Careful management of the cooking step is important if consistent quality is to be achieved. Savings result from maximization of the product yield from raw seaplants, optimizing product quality and minimizing the cost of chemicals. In particular savings can result through control of the ratios and levels of KOH, NaOH and KCl.

Figure 5. Typical Kappa PES alkaline modification curves.



If raw seaplants are subjected to sol-mode processing seaplant solids and treatment chemicals are dissolved in a "paste" that presents gum-separation challenges. If PES is pasted most alkali and salts from the modification step have already been removed before pasting. This facilitates further process steps.

During sol-mode processing cation levels are kept so low that the gel's melting point is below the cooking temperature of about 95 ºC. Alkali sources are generally lime and NaOH used singly or in combination. Cooking times for cottonii generally range from 12-20 hr. Pastes generally have a solids concentration of 1-2%.

Washing and neutralization (Step 5.a.)

PES washing generally involves a series of agitated washes with fresh-water-to-DES ratios of about 5:1-10:1 for each wash. For PES products requiring residual alkali below 0.8 meq/gm sulfuric or hydrochloric acid can be added to one or more washes at a level that keeps wash water pH above 7.0. Each wash normally has a duration of 10-20 minutes but neutralization washes may last for more than one hour. During washing the carrageenan is gelled and the cottonii looks intact. Chlorine may be added during washing to inhibit microbe growth and bleach the PES. The extent of washing and neutralization can be regulated to influence the content of KCl, alkali and cations in the PES. Calcium, sodium or potassium salts can be added during washing to adjust the cation content of the finished product.

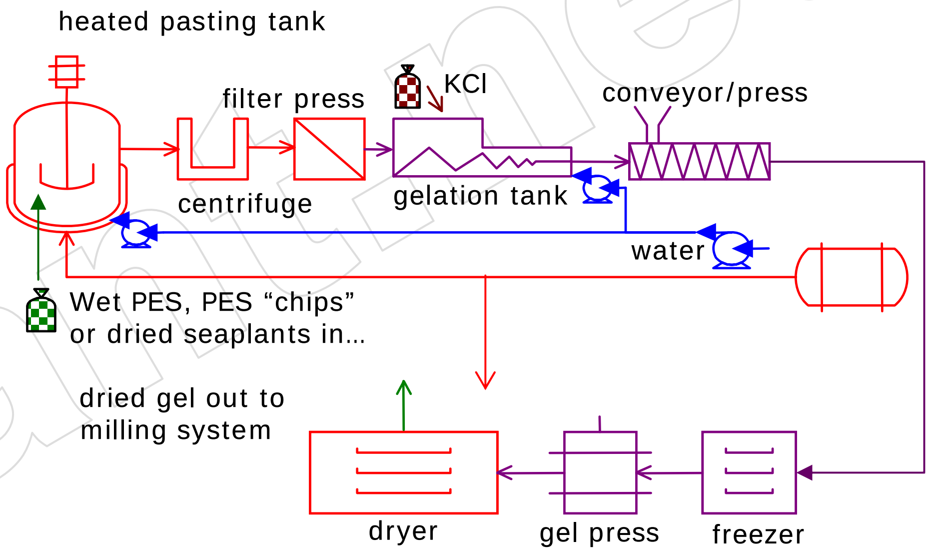
NB: Counter-current washing saves water & reduces pollution.

Dilution & clarification (Steps 5.b., 6.b. & 6.c.)

About 5-15% of PES comprises crude fiber (acid-insoluble matter) that makes PES gels cloudy and granular. fiber can be removed if dilute paste from gel- or sol- mode modification is subjected to screening, decanting or centrifugation. The resultant sludge can be washed or pasted further to maximize gum recovery. Polishing filtration (e.g.: in a plate-and-frame filter press) can be used to almost totally remove acid insoluble matter and provide a product that gives clear, smooth gels.

Clarification is associated with cost-adding process steps. These include heating, paste dilution, chemical depolymerization and filter-aid addition. Industry trends are therefore moving toward clarification to minimum standards required by a given application. "Crude" extracts with little or no clarification (now produced by some factories in China) are finding a niche in the market and may replace or pre-empt PES in some applications. The PES gel-mode modification method lends itself well to crude extract preparation because pasted PES has most salts and alkali removed. Its acid insolubles are present as large fluffy particles and there is no slurry of fine lime particles.

Figure 6. An example of a gel-press process for extracting and recovering clarified carrageenan that is dissolved in a “paste”. The example has a freeze/thaw step. It is possible to eliminate freeze/thaw or to go straight from freeze/thaw to drying and skip the pressing step but using both steps can lead to more efficient biopolymer recovery.



Gum recovery from sols (Step 7.b.)

PES "chips" (whether previously dried or undried) can be pasted, clarified to the desired extent then recovered by a variety of techniques including roll-drying, alcohol precipitation, KCl precipitation, gel press methods, spray drying and freeze-thaw procedures. Prior to precipitation the paste can be neutralized. Gel-press and freeze-thaw methods have been commercially applied to recovery of pasted PES in several countries; notably in China, the Philippines and Indonesia. Precipitated gum from paste is generally de-watered during precipitation, pressing and other gum-recovery steps so it has a lower water content than washed PES chips. Vacuum, belt, vibrating-screen and a variety of other drier types can be used for final drying of precipitated extracts. Once dried this "pre-gelatinized" recovered gum is generally easier to mill than PES.

12. Drying and sifting

Chopping, and drying of PES (Steps 6.a., 7.a.)

The 80-90% water content of washed PES can be reduced to about 70% by pressing but most water is removed by desiccation of chopped material under the sun or in indirectly heated forced-air dryers. If powder is to be made the most economic approach is generally to sun-dry the material to about 20% water content then dry to about 10% water content in a forced-air dryer prior to milling. In the early days of PES processing modified, washed material was dried under the sun in the "whole" state and was then chopped and pulverized to yield chips or powder. Whole fronds are difficult to handle and tough to mill. Chips are the way to go for ease of processing (Plate 19).

Plate 18. Whole-dried alkali-treated cottonii.

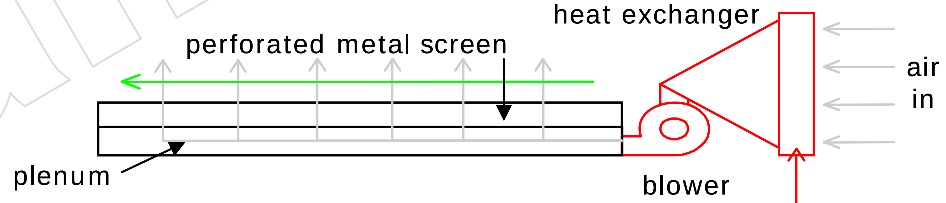
During the early days of PES manufacture in the late 1970s it was found that drying was greatly facilitated if treated seaplants were chopped into pieces with a maximum length of one-two cm. This made for more uniform particle size. The resultant "chips" could be handled somewhat like rice or maize kernels and were much easier to mill than tangles of wiry whole fronds.

Frequent problems with rainy weather created a need for mechanical drying if production was to remain consistent throughout the year. Almost all imaginable forms of dryer received consideration and many were tested. "Coffin" dryers and belt dryers have both been used successfully (Figure 7).

For food-grade PES rapid desiccation in mechanical dryers and/or in-process sanitization steps are required.

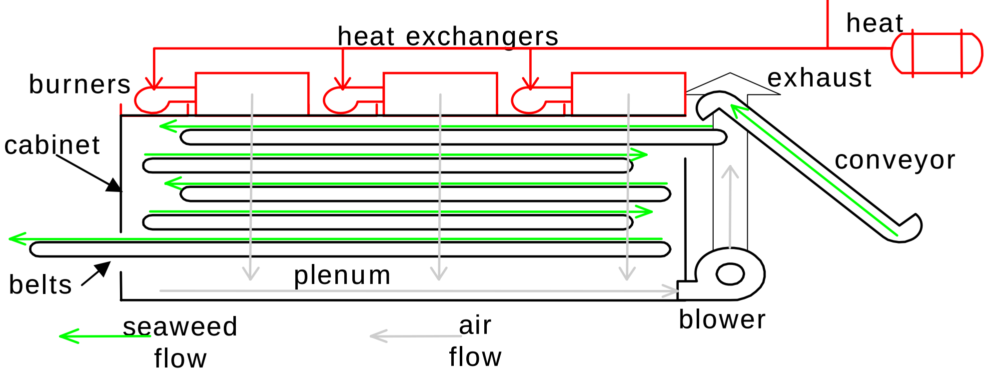
Plate 19. Sun drying chips on concrete slabs is energy efficient for non-food-grade material (Gan K.T. photo below).

Figure 7. The cheapness, simplicity and effectiveness of the "coffin-type" (also called "bin-type") of dryer has caused them to be used by many producers. This type of dryer does not look elegant and requires hand labor so there is always an urge to replace it with a belt dryer or some other complex mechanical device. Thus far such devices have not displaced coffin-dryers.



Above: "COFFIN" (BIN) DRYER side section

Below: BELT DRYER side section



13. Milling and blending

Milling and blending (Step 8)

During early stages of PES development German and Japanese milling systems predominated but several much cheaper alternatives are now on the market. For example China and India are both sources of reasonably priced, effective milling systems and several manufacturers in Indonesia, Malaysia and the Philippines have experience in making PES milling equipment. It is now feasible to design economically useful plants with a wide range of output levels. Most milling systems capable of producing high-quality PES are also capable of producing carrageenan extracts.

PES is harder to pulverize than clarified extract so with many types of mill throughput is low and the danger of charring is great. Attrition mills with high air flow and low operating temperature work best. For most efficient operation these should be connected to recirculating systems that include sieves and a bag-house.

PES made from a variety of raw material sources can be widely variable so batches must be mixed in "master blends" to yield product with uniform characteristics. During milling particles of the desired size range are separated using a vibrating sifter and oversized material is recycled back to the mill. "Pre-blend" batches of a size convenient for blending (usually 1-3 tons) are then blended and tested for desired rheological characteristics such as viscosity or gel break-force index against standard samples. Pre-blends are ultimately combined in a master blend of the desired size (e.g. 20 tons to provide one full container load).

By mixing "strong" and "weak" pre-blends master blends of fairly uniform quality can be reliably produced. This must be done carefully, however, because mixing very weak material with very strong material may give the same test performance as a blend of batches having similar strength but the resulting blends may perform differently in some applications. For example very weak material may be degraded to the point of depolymerizing during retorting and failed process batches can result. Likewise, the use of diluents and standardizing chemicals must be done with caution. Sometimes such chemicals may "fool" quality tests but fail in the application.

Figure 8. Schematic of milling, blending and packing lines for SRC.

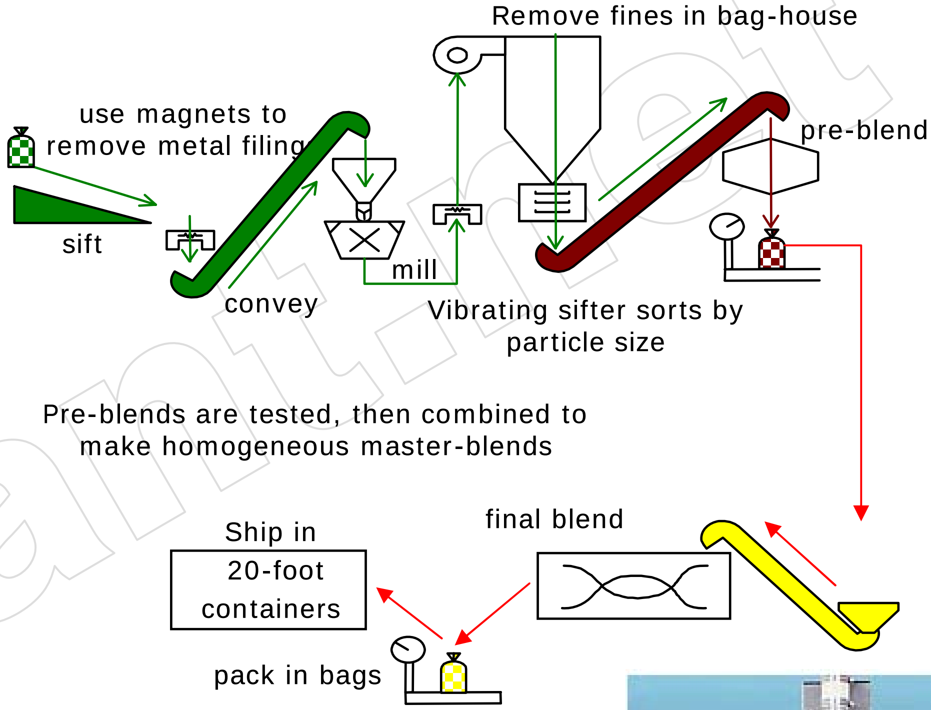


Plate 20. Alpine-Hosokawa were pioneers in grinding systems for PES and their UPZ series fine impact mills (e.g. type 160 shown in manufacturer's photo, right) remain as a top-of-the-line choice for making high quality product. These are versatile mills that can yield both fine and coarse grinds of PES and extract.

During fine-grinding some gel strength may be lost in any milling system – even the best.

14. Materials partitioning

Keeping track of materials and energy balances is a key to good process control. This requires effective testing and quality assurance programs. Materials flow runs in parallel to progress along the value chain. At each step there are inputs, functions, product outputs and waste outputs. In addition the utility and value of the eventual end product is maintained, enhanced or degraded.

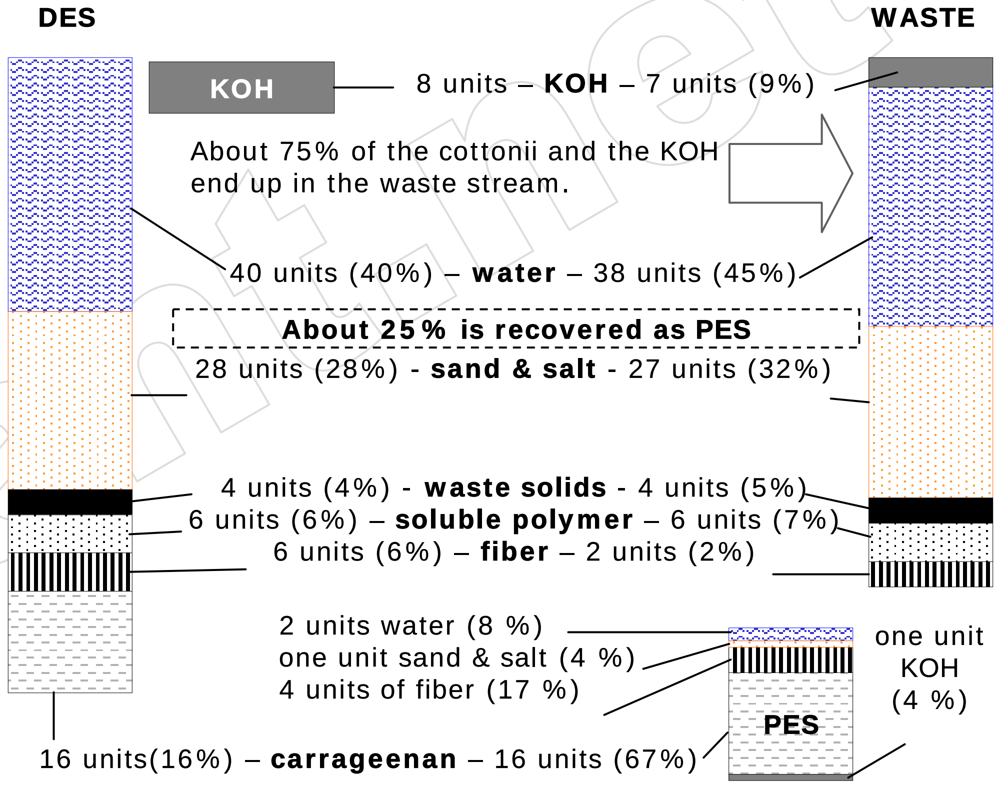
Seaplant raw material is usually the major contributor to production cost. Optimizing raw material use is an exercise in balancing process inputs and outputs. Typical partitioning of cottonii material during PES manufacture is illustrated opposite. In this case about 23% of the cottonii is recovered as PES and the balance is lost during processing. About 10-20% of the KOH added during processing is lost in-process and the actual PES yield in the illustrated case is 24% of the weight of cottonii used. Most of the moisture, sand, salt and solid waste (debris and "junk-weed") is removed as cottonii becomes PES. Some fiber is realized in PES as useable gum.

Some carrageenan is lost as soluble polymer. In good raw material soluble polymer losses are about 1% but with poor cottonii 10% or more may be lost during processing. This lost polymer is probably de-polymerized carrageenan resulting from degradation during drying and storage.

Soluble polymers can raise the viscosity of cooking liquor and cause unwanted pasting during PES processing. This can happen especially if spinosum or highly degraded cottonii enters the process. Dissolved polymers can act as "co-solutes" that induce pasting and result in process stoppages and material loss. Periodic addition of oxidising agents (e.g. chlorine) to the liquor can be used to prevent this.

PES and carrageenan plants in several countries have been forced to close temporarily or permanently because of actual (or alleged) violations of acceptable effluent-treatment or waste-disposal protocols. Processors must avoid this mistake.

Figure 9. An example of materials partitioning for PES made from DES. A proper materials balance would follow the distribution of such components through each process stage.



Examination of the figure above indicates the large shrinkage in weight and volume that occur as eucheuma seaplants move along the value- chain. It is this phenomenon that introduces complexities into trading dynamics and process economics and provides an incentive for ongoing innovation and optimization of value-chain structure. An examination of cost partitioning provides further insight into the drivers behind such developments.

15. Cost partitioning

PES manufacturing cost varies widely. Minimum costs as of 2007 were on the order of 1,800 USD/mt for chips and 2,500 USD/mt for blended powder. In 2008 costs were rapidly rising. Costs vary depending on raw material price/quality and the type of process used. Specialized food-grade products cost the most to make.

Table 3. Manufacturing costs for blended PES powders partition approximately as follows:

Item	Percentage
Cottonii	45-55
Chemicals	5-10
Other Variable Items	14-18
labor	9-12
Fixed + Semi-Fixed	14-18

Seaplant raw material generally comprises more than half of PES cost and has a profound effect on quality. "Bad weed" effectively raises raw material cost by limiting the supply of useful material and increasing inventories of off-specification product.

Transportation costs and a proliferation of collecting or trading links can boost DES cost significantly. At current prices shipping baled DES at 20 tons per 20-foot container costs on the order of 50 USD/mt from SEAsia ports to South China and about twice that amount to Europe. Furthermore local shipping within major producing countries such as the Philippines and Indonesia can add substantially to DES cost. Moving DES from feeder hubs to major hubs can cost more than shipping from major hubs to overseas destinations and with each step in the chain there is high risk of losses, shrinkage and "trading games". Furthermore some jurisdictions impose levies on DES transported through their ports or roads and unofficial "rent-seeking" activities by people with power can add appreciably to DES cost.

If effective technology and quality controls are in place economics favour the production of PES near eucheuma seaplant sources. The following comparative advantages of processing PES near eucheuma seaplant sources can amount to hundreds of USD/mt:

1. **Shortening supply lines** can save tens of USD/mt on all-in DES cost and this can easily translate to several hundred USD/mt in PES chips or powder cost.
2. **Near-source processors** can minimize "trading games".
3. **Seaplant sources are usually in areas with low-cost labor** and abundant sunlight that is useful for drying.
4. **Processing near sourc**es minimizes handling and process steps associated with drying and packing.

Several factors have inhibited the migration of processing toward eucheuma seaplant sources but times are changing... not only for PES production but also for production of more sophisticated biopolymer products. The era of the "Asian tigers" ended with the "economic correction" that occurred subsequent to 1998 but a new era of solid growth is underway and is especially evident in the hugely populous countries of China and India where eucheuma seaplant value chains have great scope for development. PES (E407a) and clarified extracts (E407) have separate but overlapping markets. E407 costs more to produce but the gap with E407a may narrow.

Factors that have made E407 more expensive include:

1. **Lower yields** due to removal of solids during filtration.
2. **High energy cost** of removing water from dilute pastes.
3. **High overheads** related to high-capital facilities located in high-operating-cost locations.
4. **High chemical, process-aid and waste-disposal costs.**

Low-energy processes effectively applied at locations close to eucheuma seaplant sources may significantly narrow the cost-gap between food-grade PES and clarified carrageenan.

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16. Interpreting test results

The basic tests necessary for process control and quality assurance in PES systems are outlined in the table right. See SEAPlant.net Monograph HB2H 1008 V3 LTP for test procedures. In using these tests one must take note of the following points:

1. **Component identities such as "sand", "salt", "moisture", and others are correct only as defined by specific tests and are not necessarily true in a chemically definitive sense.** These are component definitions that are adequate for practical commercial purposes.

2. **PES is not pure carrageenan.** Actual carrageenan may vary widely in both concentration and quantity. This, in turn, effects product performance in both rheological tests and applications.

3. **Proper use and interpretation of rheological tests (e.g. gel-strength and viscosity) is used not only for quality assurance (QA) but also for quality control (QC).** Process parameters can be adjusted to hit fixed rheological performance targets even if raw material is variable.

4. **Low gel-strength accompanied by high viscosity** indicates under-modification and/or "immature" raw material.

5. **Low gel-strength accompanied by low viscosity** indicates over-modification and/or degraded raw material.

6. **Gel-strength can be adjusted somewhat** by regulating the degree of washing - hence the salt content.

7. **High fiber** can indicate that gum is being locked into insoluble complexes by divalent cations (e.g. Ca++ and Mg++). This can be reduced by using an ion-exchange presoak and/or soft process water.

8. **Note that during blending it is dangerous to reach on-specification gel-strength by mixing very strong with very weak batches.** Such blends may pass gel-strength tests and still fail in applications. Strong and weak material respond differently to process conditions (e.g. the weak material depolymerising and "failing" in process).

Table 4. Interpreting test results.

Cottonii raw material tests...	
Water	Weight lost during desiccation in a drying oven is defined as being "moisture content".
Sand	Material that does not dissolve after thorough soaking and rinsing is defined as "sand".
Junk	Junk weed, tie-ties, debris and other foreign matter is simply removed and weighed.
Salt	Whatever disappears after thorough rinsing and drying is defined as being "salt".
Salt-free dry matter includes...	
Carrageenan **Fiber** **Lost organics**	Salt Free Dry Matter (SFDM) is also known as Clean Anhydrous Weed (CAW). It is left over after thorough rinsing and drying. It includes carrageenan, crude fiber (a.k.a. acid insoluble matter or AIM) and organic materials lost during cooking and washing.
PES tests...	
Water	Weight lost during desiccation in a drying oven is defined as being "moisture content".
Sand	Should be absent in PES.
Junk	Should be absent in PES.
Salt	Should be present at low concentration in PES. A high salt means poor washing.
Salt-free dry matter includes...	
Carrageenan	Quantitative measurement of carrageenan requires extraction of the gum from PES. Viscosity is a rough indicator of molecular weight and gel strength reflects the degree of modification, and carrageenan concentration.
Fiber	Fiber content is what differentiates E407 from E407a.
Alkali	A high level means poor washing.

17. Composition of carrageenan "master blends"

The chemical composition and rheological characteristics of PES and carrageenan "master blends" can vary substantially depending on the process methods used. This is true of both iota and kappa carrageenan products. Since the market for kappa carrageenan is by far the largest it is used in the example shown. The examples shown in the table opposite gives an approximate idea of how kappa carrageenan master blends vary. Further elaboration of differences follows:

1. **PES is distinguished by having a level of crude fiber** (acid insoluble matter) on the order of 10-15%. This makes PES gels grainy and cloudy.

2. **PES also tends to have high average molecular weight**, low salts and fairly low ash because the material has not been placed in hot, dilute aqueous solution, clarified and recovered by the use of chemical precipitating agents such as alcohol or KCl.

3. **PES gels tend to have more color and odor** than clarified extracts but these factors can be reduced in process.

4. **Extracts made using KCL precipitation tend to have high KCl and total ash.**

5. **The alcohol-precipitation process is versatile but costly.** It can be used to manufacture carrageenan with a wide range of rheological characteristics.

6. **Fully modified PES can be pasted, clarified and recovere**d using a variety of methods including the freeze/thaw or gel/press KCl precipitation methods and alcohol precipitation. Other less commonly used methods include roll-drying, spray-drying and freeze-drying.

7. **Note that the composition of "food-grade PES" is essentially the same as petfood grade** or industrial grade except that the food-grade product must meet stringent standards of cleanliness (e.g. low mold and yeast; low bacterial counts; no "insect filth", raffia or other contaminants).

Table 5. Examples of chemical composition for kappa PES and kappa carrageenan compared to Food Codex specifications. Fiber content is the major factor differentiating E407 from E407a. (Data from Neish, 1994).

Item	Unit	PES	KCl gum from PES	alcohol extract	KCl extract	Food Codex specs
		E407a	E407			
Acid insoluble ash	%	15-25	15-20	20-40	to 35	>35
Acid insoluble matter (fiber)	**%**	**0.1-14**	**trace**	**trace**	**trace**	**>1.0**
Moisture	%	9-15	trace	trace	trace	n/a
Ester sulphate	%	4-10	4-10	5-15	4-10	4-10
Arsenic (As)	%	18-21	18-21	18-21	18-21	18-40
Heavy metals	ppm	0.8-2.5	n/a	0.2-1.5	n/a	>3
Lead (Pb)	ppm	>20	n/a	>10	n/a	>40
Viscosity	ppm	1.8-5.0	n/a	0.3-3.0	n/a	>10
(1.5%; 70ºC)	mps /	50-600	n/a	10-40	n/a	5+
Chlorides (Cl)	gm	0.2-2.0	0.2	0.2-2.0	8.3	n/a
Magnesium (Mg)	%	0.3-1.3	0.6	trace	0.3	n/a
Calcium (Ca)	%	0.5-1.5	0.4	1-4	0.5	n/a
Potassium (K)	%	4-8	5.3	3-12	10-15	n/a
Sodium (Na)	%	0.2-1.5	0.5	0.3-0.6	1-2	n/a
Residual alkali	%	0.2-1.4	trace	trace	trace	n/a
Synthetic polymer	meq	trace	nil	nil	nil	n/a
Total EDTA gum	**%**	**80-95**	**68-87**	**68-87**	**70-75**	**n/a**
Total alcohol gum	**%**	**66-82**	**68-87**	**68-87**	**70-75**	**n/a**