

Carrageenan in Seaweed (*Eucheuma* sp.) and Use of Carrageenan in Fishery Food Products: A Review

ABSTRACT

Carrageenan is a hydrocolloid compound found in red seaweed (Rhodophyta). Carrageenan-producing sources are *Eucheuma cottonii* seaweed with kappa carrageenan type and *Eucheuma spinoum* with iota carrageenan type. Kappa carrageenan is widely used in food products because its availability is very abundant in nature compared to iota and lambda carrageenan types. The boiling method with an alkaline solution is a method that is often used in extracting carrageenan. Carrageenan has properties as a stabilizer, thickener, gelling agent, and emulsifier. Carrageenan is widely applied in the food and non-food sector. In food products, carrageenan functions as a food additive, thickener, and emulsifier, and can increase the protein and fiber content of a food product.

Keywords: Carrageenan, Extraction, Food additives, Kappa carrageenan, Red Seaweed

1. INTRODUCTION

Seaweed is a fishery commodity that is classified as benthic macroalgae that live attached to the bottom of the waters [1]. Seaweed production in Indonesia in 2021 is 5,011,856 wet tons with 4,660,704 wet tons from seaweed cultivated in the sea and 351,152 wet tons from seaweed cultivated in ponds [2]. The amount of seaweed production is a problem because there are still minimal processing methods. Processing seaweed into semi-finished carrageenan products such as Semi Refine Carrageenan (SRC) and Refine Carrageenan (RC) will increase the added value of seaweed [3].

Seaweed can grow well in Indonesian waters, namely *Gelidium*, *Euचेuma spinosum*, *Euचेuma cottonii*, *Caulerpa* sp, and *Gracilaria* sp [2]. SKPP-RL21 results show that *Euचेuma cottonii* is the type of seaweed that is most widely cultivated in Indonesia at 78.63% and *Euचेuma spinosum* at 11.74% [2]. Seaweed that acts as a producer of carrageenan is red seaweed. Red seaweed (Rhodophyceae), especially *Euचेuma spinosum* or *Kappaphycus alvarezii* and *Euचेuma spinosum*, are the main sources of carrageenan which are abundant in nature [4].

Carrageenan is produced from seaweed through an extraction process using an alkaline solution or using water at high temperatures [5]. There are several methods of extracting carrageenan, namely precipitation, boiling, and evaporation. The alkaline solution used is a basic solution of NaOH and KOH [6]. The extraction process, type of seaweed, solvent concentration, and harvesting age greatly affect the quality and quality of the carrageenan produced [7].

Seaweed is a source of carrageenan, agar-agar, and alginate which is widely used in the food, cosmetic, pharmaceutical, textile, and paper industries [8]. Carrageenan in food products is widely used as a food additive because it functions as a gelling agent, stabilizer, thickener, and water binder and can increase the palatability of food products [9]. Utilization of carrageenan is carried out by verifying carrageenan products into powder form which aims to increase the usability and economic value of carrageenan [10]. Carrageenan is used

as a food additive in fishery products. Based on this information it appears that carrageenan from red seaweed (*Euचेuma* sp) has unique characteristics that can improve the quality of seaweed and can be used in fishery food products.

2. RED SEAWEED (RHODOPHYCEAE)

Seaweed is a widespread resource and is part of marine plants belonging to the benthic macroalgae that live attached to the bottom of the waters [1]. Seaweed belongs to the thallophyta division which only consists of thallus and has no differences between roots, stems, and leaves [11]. Seaweed is divided into four classes based on color differences, namely Chlorophyta (green), Chrysophyta (golden), Phaeophyta (brown), and Rhodophyta (red) [12]. Rhodophyta is a red alga caused by phycobilin pigments in the form of allophycocyanin, phycoerythrin, and phycocyanin which cover the color of chlorophyll [13]. There are several species of red seaweed (Rhodophyceae), but the ones that act as carrageenan producers are *Euचेuma cottonii* and *Euचेuma spinosum*.

2.1 *Euचेuma cottonii*

Euचेuma cottonii has the characteristics of a cylindrical or flat branched thallus, smooth surface, green, yellow-green, gray, or red [11]. *Euचेuma cottonii* seaweed lives in the photic layer which requires sunlight for photosynthesis [14]. *Euचेuma cottonii* has another name, namely *Kappaphycus alvarezii* because the carrageenan produced includes the kappa carrageenan fraction [15]. The carrageenan content in *Euचेuma cottonii* seaweed is 67.50% [16].

2.2 *Euचेuma spinosum*

Euचेuma spinosum has the following characteristics, namely the branching of a cylindrical thallus with a sharp tip, overgrown with nodules (protrusions), in the form of soft spines arranged to rotate regularly around the branch, the number of thorns is more than that found in *Euचेuma cottonii* [11]. *Euचेuma spinosum* when living in water is green to reddish and when it is dry it is brownish-yellow [17]. *Euचेuma spinosum* has high economic value because it has benefits as a raw material for making agar-agar flour, alginate, and

carrageenan which are used in the textile, cosmetic, and food industries [18]. *Eucheuma spinosum* produces carrageenan with the iota carrageenan type [19]. The carrageenan content in *Eucheuma spinosum* seaweed is 65.75% [20].

3. CARRAGEENAN

Carrageenan is a hydrocolloid compound consisting of ammonium esters, calcium, magnesium, potassium, and sodium sulfate with galactose and the polysaccharide 3,6 anhydro galactose [21]. Carrageenan is a large part of the dry weight of seaweed compared to other components. Carrageenan is found in seaweed cells or their intracellular matrix [22]. Carrageenan has properties as a stabilizer, thickener, gelling agent, and emulsifier [23]. Carrageenan dissolves in hot water to form a clear viscous solution or slightly clear, but carrageenan is insoluble in ethanol, methanol, and isopropanol.

3.1 Characteristics Of Carrageenan

The characteristic of carrageenan is that it absorbs water easily and forms a gel. Gel formation is a condition in which polymer chains combine or cross-link to form a continuous three-dimensional mesh that captures the water in it and forms a strong and rigid structure [24]. Carrageenan can form a gel in water and is reversible or melts when heated and forms a gel when it is cold [25]. The specific characteristics of hydrocolloids are influenced by the basic structure or functional groups contained in carrageenan. The characteristics of carrageenan are differentiated based on the source of raw materials and functional groups [24].

3.2 Types Of Carrageenan

Types of carrageenan are distinguished based on the species of seaweed, the nature of the gel, and the structure of carrageenan. Carrageenan has several types, namely:

3.2.1 Kappa Carrageenan

Kappa carrageenan is produced from an alkaline process resulting from the elimination of μ -carrageenan and isolated from the seaweed *Eucheuma cottonii* (*Kappaphycus alvarezii*) [19]. Kappa carrageenan is composed of α -(1,3)-D-galactose-4-sulfate and α -(1,4)-3,6-anhydro-D-galactose with a content of 25% ester sulfate and 34% 3,6- anhydrogalactose [26]. Kappa

carrageenan has better gel strength compared to other types of carrageenan because there is a complete elimination of the sulfate group so that the molecular uniformity becomes uniform and the gel strength is high.

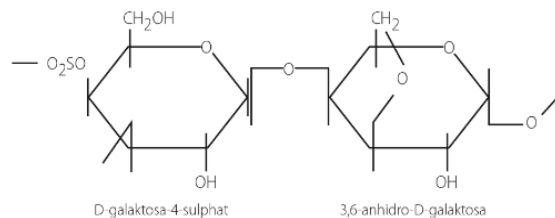


Figure 1. The chemical structure of kappa carrageenan

Source: Imeson et al. [26]

3.2.2 Iota Carrageenan

Iota carrageenan was produced from the alkaline elimination process of carrageenan and was isolated from *Eucheuma spinosum* seaweed. Its structure consists of a 4-sulfate ester group in all D-galactose groups and a 2-sulfate ester group in 3,6-anhydro-D-galactose. The disorder of the 6-sulfate ester group is replaced by a 4-sulfate ester group in D-galactose [19]. The 2-sulfate ester group in iota carrageenan cannot be removed by an alkaline solution so the lack of molecular uniformity causes gel strength to be reduced or not as strong as in kappa carrageenan. Iota carrageenan contains more than 30% sulfate.

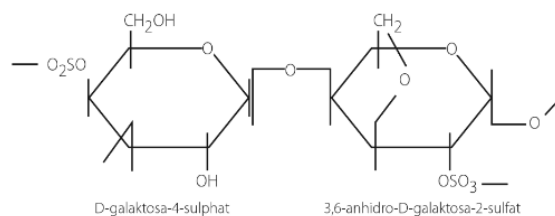


Figure 2. The chemical structure of iota carrageenan

Source: Imeson et al. [26]

3.2.3 Lamda Carrageenan

Lambda carrageenan is isolated from *Chondrus crispus* which is converted to θ -carrageenan (theta-carrageenan) by alkaline elimination. Lambda carrageenan contains disulfate-(1-4)-D-galactose residues and several 2-sulfate ester groups but does not contain 4-sulfate ester groups [26].

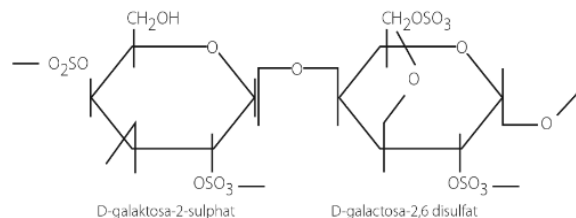


Figure 3. The chemical structure of lamda carrageenan

Source: Imeson et al. [26]

Table 1. characteristics of carrageenan types

Source: Prihastuti and Abdassah [4]

Carrageenan	Gel texture	Gel forming	Viscosity	Solubility in water
Kappa carrageenan	High and slightly syneresis	Gel with potassium ions	Low thixotropic	Soluble in water temperature <70°C
Iota carrageenan	Elastic and no syneresis	Gel with calcium ions	Moderate to high thixotropic	Soluble in water temperature <70°C
Lamda carrageenan	No syneresis	Does not form a gel	Moderate to high thixotropic and high viscosity	Soluble in hot water and partially soluble in cold water

4. Carrageenan Extraction Method

Carrageenan comes from the latex of seaweed which is extracted using extraction with water or an alkaline solution [5]. *Eucheuma cottonii* seaweed is processed through the extraction of alkaline solutions such as Potassium Hydroxide (KOH) or Sodium Hydroxide (NaOH) [7]. The function of using alkali in carrageenan extraction is to help the extraction of polysaccharides to be more perfect and accelerate the elimination of 6-sulfate from monomer units to 3,6-anhydro-D-galactose which can increase product reactivity to protein, yield value and gel strength [27].

There are several methods of extracting carrageenan, namely precipitation, boiling, and evaporation. The extraction method for boiling alkaline solution using the steam method is the same but in the hot alkaline extraction method there is no soaking step using an alkaline solution, but is boiled directly with the alkaline solution [6]. The thing that must be considered in the extraction process is the cooking process with an alkaline solution. Carrageenan is easily hydrolyzed in acidic solutions and is stable in alkaline conditions [28].

Seaweed extraction produces two types of carrageenan products, namely Semi Refined Carrageenan (SRC) and Refined Carrageenan (RC). Pure carrageenan is a carrageenan that has been released or free from cellulose through a precipitation process. Semi Refined Carrageenan (SRC) is a carrageenan product with a lower purity level compared to Refined Carrageenan (RC) because it still contains cellulose which precipitates with carrageenan [29].

Preparation of Semi Refined Carrageenan (SCR) by cleaning the seaweed and then extracting it with 10% KOH solution for 60 minutes at 70°C with a solution volume of 40 times the weight of dried seaweed [30]. Samples were filtered and washed with running water until the pH of the washing water was 8-9. Then the seaweed was cut into small pieces and dried in an oven at 50°C for 18 hours. The sample is made of flour and sieved using a 60-mesh sieve [31].

The next process is the manufacture of Refined Carrageenan (RC) by boiling the flour from the SCR results [32]. Boiling is carried out for 60

minutes at a temperature of 80-90°C and during boiling, stirring is carried out. The carrageenan solution was poured into a container containing isopropyl alcohol with a volume of 1 times the volume of the filtrate for the precipitation process. This process is carried out for ± 30 minutes. The carrageenan fiber was then filtered and dried in an oven at 50°C for 18 hours. The sample was mashed using a blender and sieved using a 60-mesh sieve [31].

5. Quality of Carrageenan

The quality of carrageenan has been established internationally by the Food and Agriculture Organization (FAO), the Food Chemicals Codex (FCC), and the commercial carrageenan quality standards [29]. According to

FAO, the quality of carrageenan has a yield value of >25%, ash content of 15-40%, moisture content of ≤12%, viscosity of ≥5%, and gel strength of >500 g/cm². The quality of commercial carrageenan has a moisture content of 14.34 ± 0.25%, ash content of 18.60 ± 0.22%, a protein content of 2.8%, fat content of 1.78%, crude fiber 7.02%, carbohydrates 68.48%, melting point 50.21±1.05°C, melting point 34.10±1.86°C, viscosity 5 cP and gel strength 685.5±13.43 g/cm². The quality of carrageenan [31] is close to the FAO criteria which have a yield value of 28%, water content of 11.26%, viscosity of 70 cP, and gel strength of 1370 g/cm² with 10% KOH concentration for 60 minutes at 70°C. The quality of other studies still does not meet the criteria set by FAO.

Table 2. Quality of kappa carrageenan

Alkaline Concentration	Yield (%)	Water Content (%)	Viscosity (cP)	Gel Power (g/cm ²)	Reference
KOH 12%	45,26	9,23	50,47	446,51	Ega et al. [29]
KOH 10%	39,05		59	1130,67	Arzani [31]
KOH 10%	28	11,26	70	1370	Arzani et al. [15]
KOH 8%	78,4		9,16	7	Jaya et al. [33]
KOH 5%	17,17	1,9		80,2	Gerung et al. [34]
KOH 1 %	45	10	6,02	174	Iswahyono et al. [35]
KOH 0,5%	28,05	5,6			Djurmudi et al. [6]

The quality of carrageenan can be seen from the yield value, water content, viscosity, and gel strength. Yield is the weight resulting from the seaweed extraction process. The higher the yield value, the higher the 3,6-anhydrogalactose produced which can affect the characteristics of the gel strength [31]. The high water content in seaweed can affect the carrageenan produced because it can prevent the entry of alkaline solution into the seaweed tissue so that it cannot extract carrageenan. Low water content can also cause the seaweed tissue to be hard so that it is difficult to be penetrated by alkaline solutions which makes it difficult to extract carrageenan. The maximum water content in SRC carrageenan products is 37% [36]. Viscosity is a value to determine the level of viscosity of carrageenan at a certain concentration and temperature. The higher the KOH concentration, the more salt will dissolve in the seaweed so that the viscosity increases [37]. The lower the concentration of KOH, the lower the viscosity [38]. The standard viscosity value is 5 cP,

therefore all tests have met the carrageenan standard criteria. Gel strength is the ability to change liquids into solids or gels that are reversible [31]. The higher the KOH concentration, the lower the gel strength. This is inconsistent with the existing data because KOH concentrations below 8% produce low gel strength. This low gel strength is due to the extraction method starting from the extraction process, the length of extraction time, the concentration of the alkaline solution used, the ratio of extracting water, temperature, and the type of alkali used [15].

6. Use of carrageenan in fishery food products

The use of carrageenan in the food industry depends on its solubility, gel strength, viscosity, reaction with proteins, and synergism with non-gelling polysaccharides. Kappa and iota carrageenan types act as gel formers while lambda carrageenan types act as thickeners. However, the most widely used food additive is Kappa carrageenan from *Eucheuma spinosum*

or *Kappaphycus alvarezii* seaweed. Carrageenan can increase product viscosity and serve as a food protective layer such as edible films and edible coatings [39].

Table 3. Carrageenan in fish food products

Product	Carrageenan type	Advantage	Reference
Tilapia Ekado	Kappa carrageenan	Food additives are used to improve the texture of Ekado.	Sipahutar et al. [10]
Patin Fish Brains	Carrageenan flour	A natural food additive to replace STPP to increase water holding capacity and dough stabilizer	Fauzi and Komarudin [40]
Kurisi Fish Brains	Carrageenan flour	Stabilize the product emulsion system	Putra et al. [21]
Kamaboko	Carrageenan flour	Binders that help improve the quality of the product gel	Sitompul et al. [41]
Rosella Mangrove Syrup	Carrageenan flour	Stabilizer to produce a gel structure with the right viscosity value	Putra et al. [42]
Blood Clam Meatballs	Kappa carrageenan	Gel-making material that is safe and of high nutritional value	Nurwin et al. [43]
Tuna Fish Meatballs	Kappa carrageenan	A natural thickening agent produced from seaweed	Sitepu et al. [44]
Gulamah Fish Meatballs	Kappa carrageenan	Increase protein levels	Mussayadah et al. [45]
Pempek Catfish	Carrageenan flour	Increase consumer preference for the product	Ririsanti et al. [46]
Kurisi Fish Sausage and Tilapia Fish Sausage	Kappa carrageenan	Emulsifying agent to maintain the emulsion system so that it is not easily damaged and increases product elasticity	Nico et al. [47]
Cucut Fish Skin Gelatin Jelly	Carrageenan flour	Increases the gel strength of the product	Suptijah et al. [48]

The use of carrageenan in fishery food products is a natural food additive that replaces the use of chemicals such as STPP (Sodium Tripolyphosphate) [40]. Carrageenan has similarities with STPP chemicals which function to increase water-holding capacity and dough stabilizer. Carrageenan can increase protein and fiber content in products because it comes from seaweed. Adding too much carrageenan to food products can cause the texture to become hard and reduce the protein content in it and conversely, the addition of less carrageenan causes the resulting product to become softer. The use of carrageenan as a food additive must be precise to produce a quality and preferred product.

7. CONCLUSION

Red seaweed is a producer of carrageenan compared to other classes of seaweed, especially in the species *Eucheuma cottonii* and *Eucheuma spinosum*. Carrageenan has three types, namely kappa, iota, and lambda. Kappa carrageenan has better gel strength compared to other types of carrageenan because there is a complete elimination of the sulfate group so that the molecular uniformity becomes uniform and the gel strength is high. Carrageenan has been widely applied in fishery food product research scale, starting from wet, semi-dry, and dry food products as well as in beverage products. However, carrageenan has not been widely used for home or company production scale due to limited knowledge about carrageenan starting from its properties, extraction process, and the content contained in carrageenan.

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