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A REVIEW : APPLICATION OF CARRAGEENAN AS A FOOD ADDITION

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KeyWords

Extraction, Grade, Eucheuma, Alkali, Viscosity.

ABSTRACT

The purpose of this article review is to examine the types of seaweed that produce carrageenan, carrageenan extraction procedures, carrageenan quality and application of carrageenan as food additives. Based on a review of various articles in several journals and other literature, it can be concluded that the types of carrageenan producing seaweed are Eucheuma, Gelidium, Gracilaria and Sargassum. There are two extraction methods for carrageenan, namely extraction in water and alkaline conditions. The extraction method in an alkaline environment is more widely used. Carrageenan quality can be observed from the ash content, moisture content, protein content, gel strength and viscosity. Carrageenan can be applied as an emulsifier in sausage.

INTRODUCTION

The vast area of Indonesian waters with abundant fish resources is a distinct advantage for Indonesia in obtaining foreign exchange. One of the potential fish resources in increasing the country's foreign exchange is seaweed. Various types of seaweed can be found in Indonesian waters, one of which is the type of seaweed that produces carrageenan (Hidayatun *et al*, 2012).

Carrageenan is a gelling and developer food additive (Jiao *et al*, 2011). Carrageenan solution can coagulate and stabilize particles. Carrageenan can be divided into three types, namely kappa carrageenan, lambda carrageenan and iota carrageenan (Winarno, 1996). Carrageenan is often called "dietary fiber" because of its high crude fiber content so it is very good in helping digestion.

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Picture 1: Seaweed Source of Carrageenan (Source: Allrichin, 2019)

Based on the chemical compounds it contains, there are seaweed that produces carrageenan (caragenophyte), gell (agarophyte) and alginate (alginophyte) (Dini *et al*, 2014). Carrageenan is very important in its role as a stabilizer, thickener, gelling agent, emulsifier, stabilizer, suspension, binder, protector, film former, syneresis inhibitor and flocculating agent (Anggadireja *et al*, 1986). The role of keragenan is mostly included in food additives. Therefore, this article aims to examine the types of seaweed producing keragenan, the extraction procedure of keragenan, the quality of keragenan and the application of karegenan as a food additive.

SEAWEED CARRAGEENAN RAW MATERIAL

The industry that uses seaweed as raw material and product additives is quite developed in Indonesia. The types of seaweed that are used as raw material for carrageenan include Eucheuma, Gelidium, Gracilaria and Sargassum. Its spread in Indonesia has been researched about two and a half centuries ago, as in the research project Buginesia III in the waters of South Sulawesi (1988-1990) has inventoried about 118 types of seaweed from 40 genus of red algae, 80 species from 21 genus of green algae and 36 species of 11 genus of brown algae (KKP, 2019).

Based on The International Code of Botanical Nomenclatur, Uterch 1952 in the 2019 KKP, seaweed (macro algae) is included in the Thallophyta division, which is a plant that has a leafless, trunked and rooted skeletal structure with the following details:

Divisi : Phyta
Subdivisi : Phytina
Class : Phyceae
Subclass : Phycidae
Order : Ales
Suborder : Inales
Family : Aceae
Subfamily : Oideae
Tribe : Eae

Red seaweed is a type of seaweed that produces carrageenan which is quite high, around 62-68% of its dry weight (Aslan, 1998). Another name for Eucheuma cotonii is Kappaphycus Alvarezii because the carrageenan produced by seaweed is included in the kappa-carrageenan fraction. The Eucheuma group cultivated in Indonesia is still limited to Eucheuma cottoni and Eucheuma spinosum seaweed. Several research in Indonesia show that *E. cottoni* produces kappa carrageenan while *E. spinosum* produces iota carrageenan (Dini et al, 2014).

Carrageenan is a hydrocolloid compound consisting of ester potassium, sodium, magnesium and potassium sulfate with galactose 3,6 anhydrogalactose copolymer. Kappa carrageenan is composed of α (1,3) -D-galactose-4-sulfate and β (1,4) -3,6-anhydro-D-galactose. Carrageenan also contains D-galactose-6-sulfate ester and 3,6 -anhydroD-galactose-2-sulfate ester. Carrageenan iota is characterized by the presence of 4-sulfate ester in each D-glucose residue and 2-sulfate ester groups in each 3,6-anhydro-D-galactose group. The 2- sulfate ester groups cannot be removed by the process of alkalizing as in kappa carrageenan (Dini et al, 2014).

CARRAGEENAN EXTRACTION METHOD

There are two main methods of extracting carrageenan, namely extraction in water (solution) and alkaline conditions. Extraction of carrageenan with hot water can maintain the original structure of carrageenan, but the filtering is quite difficult because of the high viscosity and the presence of residual solids in the extract. Therefore the extraction method with an alkaline solution for several hours is more widely used. Another benefit of using alkaline method is that it can increase the strength of the gel (Tran Nu Thanh Viet Bui, 2019).

In the research of Dini *et al*, 2014 extraction of *Eucheuma cottoni* and *Eucheuma spinosum* seaweed using dried seaweed from Madura with NaOH, HCl and aquades. The method used is the method with an alkaline conditions. The procedures are material preparation and extraction. Preparation of the ingredients were by soaking seaweed in salt water for 5 minutes, then rinsing it with fresh water and then drying and mashing 10 grams of dry seaweed. Add 350 ml aquades stirring so that it will form a seaweed gel solution. Put the seaweed gel solution into leher flask then heated and add the NaOH solution. After 40 minutes it will produce carrageenan extraction.

CARRAGEENAN QUALITY

The quality standard of carrageenan in the form of flour is 99% passes through 60 mesh filter and has 0.7 density (precipitated by alcohol) with a moisture contain 15% at Rh 50 and 25% at Rh 70 (Winarno, 1996). Actually, the quality standard for carrageenan in Indonesia has not been formally created. International quality standards of carrageenan has been determine by FCC (Food Chemical Codex), FDA (Food and Drug Administration) and

FAO (Food and Agricultural Organization). The carrageenan quality standards for the three versions above are listed in the following table:

Table 1: Carrageenan Quality Standards

Spesification	FAO	FCC	FDA
Water (%)	Max. 12	Max. 12	-
Sulfate (%)	15-40	18-40	20-40
Ash (%)	15-40	Max. 35	-
Acid insoluble ash (%)	Max. 1	Max. 1	-
Acid insoluble material (%)	Max. 2	-	-
Lead (%)	Max. 10	Max. 4	-
Viscosity 1.5% sol (cP)	Min. 5	Min. 5	Min. 5

Source: Skurtys 2010

Table 2. Carrageenan Quality Standards Specifications

Spesification	Commercial Carrageenan	FAO	FCC
Water (%)	14,39±0,25	Max 12	Max 12
Ash (%)	18,60±0,22	15-40	18-40
Protein (%)	2,80	-	-
Lipid (%)	1,78	-	-
Crued fiber (%)	Max 7,02	-	-
Carbohydrate (%)	Max 68,48	-	-
Melting Point (^{o}C)	50,21±1,05	-	-
Jendal Point (^{o}C)	34,10±1,86	-	-
Viscosity (cP)	5	-	-
Gel Strength gel (dyne/cm^2)	685,50±13,43	-	-

Source: Ega *et al* 2016

Various researches related to the quality of carrageenan have been carried out, including Ega et al (2016) with the addition of different levels of potassium hydroxide (KOH) concentration. Another research is Erjanan *et al* (2017) about carrageenan quality and gel strength from Kappaphycus alvarezii seaweed. Research results in Ega *et al* (2016) using KOH solution with the concentration of each sample (2%, 4%, 6%, 8%, 10%, 12%) for 30 minutes with a ratio of solvent and raw material 40 ml:1 gr is in the following table.

Table 3. Research Results of Ega et al (2016) Physical Properties of Carrageenan

Parameter	Potassium Hydroxide Concentrate					
	2%	4%	6%	8%	10%	12%
Viscosity (cP)	30,68±0,66	34,85±1,75	39,23±1,13	42,09±0,25	46,77±1,47	50,47±1,21
Gel Strength gel (dyne/cm^2)	551±4,59	540,66±2,80	500±1,89	459,93±7,18	451,27±2,47	449,51±7,42
Melting	35,48±0,87	34,37±0,90	31,44±1,21	30,60±1,46	28,41±0,54	25,56±1,18

Point (°C)						
Jendal Point (°C)	38,63±1,45	38,11±0,22	37,38±0,92	36,59±1,28	36,21±0,48	35,88±0,66
Rendemen (%)	34,43±1,57	36,01±1,19	36,92±1,19	40,61±2,23	43,04±2,82	45,26±1,26

Source: Ega *et al* 2016

Table 4. Research Results of Ega *et al* (2016) Chemical Properties of Carrageenan

Parameter	**Potassium Hydroxide Concentrate**					
	2%	4%	6%	8%	10%	12%
Water (%)	11,31±0,49	11±0,78	10,72±0,67	10,35±0,92	9,62±0,59	9,23±0,49
Ash (%)	20,08±0,66	21,91±0,75	26,59±1,45	29,88±0,19	32,74±0,52	33,68±1,7
Lipid (%)	1,50±0,26	1,43±0,07	1,25±0,05	1,04±0,15	0,89±0,29	0,37±0,24
Protein (%)	2,54±0,46	2,13±0,73	1,57±0,66	1,73±0,27	1,19±0,80	0,80±0,52
Crued fiber (%)	5,35±0,88	5,33±0,69	5,25±0,68	4,89±0,50	4,64±0,67	4,12±0,43
Carbohydrate (%)	59,24±1,31	55,5±0,05	54,63±1,35	53,11±0,44	52,25±1,19	51,81±2,73

Source: Ega *et al* 2016

The results showed that *Eucheuma cottonii* had an average viscosity of carrageenan in the range of 30.68-50.47 cP. These results indicate that the KOH concentration has a significant effect on viscosity, where the viscosity value increases with increasing KOH concentration. These results also comply with standardization according both to the FAO, FCC, and FDA where the minimum viscosity value of 5 cP. As for the gel strength value, the average gel strength value ranged from 449.51-559.51 dyne/cm^2 and these results indicated that the KOH concentration had a significant effect on the strength of the carrageenan gel. The higher KOH concentration, the lower strength of the resulting carrageenan gel. However, from the standardization of commercial carrageenan, the quality requirements have a minimum gel strength value of 685.50 dyne/cm^2, so the carrageenan that is produced in this research is not eligible yet.

The results of the analysis of diversity showed that the KOH concentration treatment had a significant effect on crude fiber content, where the higher KOH concentration the lower crude fiber content. In commercial carrageenan standardization, the quality requirement for crude fiber contain maximum is 7.02%, so the carrageenan produced in this research is eligible. KOH concentration treatment resulted in carrageenan carbohydrate contain of 51.81-59.24%.

In the second research by Erjanan *et al.* (2017) about carrageenan quality and gel strength from *Kappaphycus alvarezii* seaweed, The treatments used were concentration KOH solutions 0.05,0,1 and 0.15%, concentration KCl solutions 1, 1.15, 1.25, 1.5, 3 and 4.5%, with a water ratio 1:20 L & 1:30 L. Result from the research is in the following table.

Sample Code	Gel Strength g/cm^2	pH	Ash (%)	Water (%)
A	114.57	7.75	29.03	19.885
B	149.80	8.10	34.50	18.47
C	147.43	8.18	27.90	18.96
D	133.73	8.00	24.59	22.37
E	152.03	7.40	18.63	19.28
F	188.53	8.04	19.99	17.75

Table 5. Research Results of Erjana *et al.* (2017) Extraction of Carrageenan

Source: Erjana *et al.* (2017)

From these research, the quality results of the gel strength average values obtained ranging from 114.57 ± 188.53 g/cm. However, if it seen from the standardization of commercial carrageenan, the quality requirements have a minimum gel strength value of 685.50 dyne / cm2. Then the carrageenan produced in this research is not eligible yet. Furthermore, the value of the pH measurement of carrageenan extracted from *Kappaphycus alvarezii* seaweed was obtained with an average value of 7.40 ± 8.18. This value is included in the standard quality where this data is in the pH range required by SNI 16-4399-1996, namely neutral pH.

In the results of the analysis of the ash content, the values ranged from 18.63 ± 34.50. According to Winarno (1997), the presence of salt and other minerals stick to seaweed will affect the high ash content in the carrageenan. The ash content of this study shows that the ash content meets the carrageenan quality standard set by the FAO at 15 ± 40% and the FCC sets maximum of 35%. The results of the analysis water content in this research ranged from 17.75% - 22.37%. The water content value showed no difference between the treatments. However, this water content is still quite high if compared to the FAO standard for carrageenan flour, which is a maximum of 12%.

CARRAGEENAN APPLICATION

Seaweed is widely used in food and non-food applications that have undergone an extraction process. Due to its biodegradable nature, carrageenan is widely used as a food additive (Thakur and Thakur 2016). One of the applications of carrageenan that is used for food additives is as a food emulsifier. In the research of Ramasari et al (2012) carrageenan is used as an emulsifier in sausage to increase the value of gel strength and reduce water contain because the contain of sulfate groups in carrageenan is negatively charged along the polymer chain and is hydrophilic, which can bind water or other hydroxyl groups (Santoso , 2007).

With its ability to bind water, carrageenan is also used as a stabilizer, thickener, gel film former (binding to a material), syneresis inhibitor (to prevent water release) and flocculating agent (binding to materials). Before knowing the benefits of carrageenan in gelling, the food additives used were borax or STPP (Sodium tripolyphosphate). STPP is commonly used as a thickening agent for food. The use of chemicals in food has been limited, so it is necessary to make efforts to reduce the use of chemicals and replace them with natural ingredients. Carrageenan can be a safe alternative to borax and STPP (Mujamil, 2007).

CONCLUSION

Based on a review of various articles in several journals and other literature, it can be concluded that the types of carrageenan producing seaweed are Eucheuma, Gelidium, Gracilaria and Sargassum. There are two extraction methods for carrageenan, namely the extraction method in water and alkaline. The extraction in alkaline condition is more widely used. Carrageenan quality can be assessed from the ash content, moisture content, protein content, gel strength and viscosity. carrageenan can be applied as an emulsifier in sausage.

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