Journal of Engineering and Applied Sciences 12 (Special Issue 7): 8147-8152, 2017
ISSN: 1816-949X

Alkalynated Treated Cottonii (ATC) Chips from *Eucheuma cottonii*, South Sulawesi, Indonesia

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Abstract: South Sulawesi has the largest contribution to seaweed export in Indonesia which also makes the province becomes the leading producer of seaweed in Indonesia that produces 1.517.690 tons/year consists of 1,087,678 tons/year *Eucheuma cottonii* and 430.012 tons/year *Gracillaria* sp. *Eucheuma cottonii* from South Sulawesi was the type of seaweed used in this research. The result of dry sea weed characterization is 20% water and 9.92 % impurity. The optimization process was conducted with two different variables which are KOH soaking time and KOH concentration. To attain optimal production process, it is necessary to perform result test which includes ATC chips yield, viscosity and gel strength at soaking time of 30, 60, 120 and 180 min and also at various concentration of KOH. ATC chips are the raw material of carragenan industry. The viscosity of ATC chips arises with longer soaking time and higher concentration of KOH. The concentration of KOH was gradually added from 0.1-0.5 N which results in not only higher viscosity but also improved gel strength. Yield of 0.2157 was obtained from ATC chips at 180 min soaking time and 0.5 N KOH. The acquired specification of ATC chips are suitable to those commercial Carrageenan of food grade and cosmetics type. At FTIR spectro test, all types of ATC chips show strong wavelength absorbance of 1210-1260 cm^{-1} (S = O from Sulfate esters) and 1010-1080 cm^{-1} (glycosidic linkage). The other chemical bond indicated as the Carrageenan compiler are 3,-6-anhydro-D-galactose at 928-933 cm^{-1}, D-galactose-4-sulfate at 840-850 cm^{-1} and 3,6-anhydro-D-galactose-2-sulfate at 800-805 cm^{-1}. Kappa Carrageenan demonstrates FTIR spectrum at 840-850 cm^{-1} which then confirms that the type of Carrageenan obtained from this research is Kappa.

Key words: ATC chips, *Eucheuma cottonii*, gel strength, viscosity, spectrum, carrageenan

INTRODUCTION

Indonesia as the big seaweed world producer with 3082113 tons of seaweed approximately holds 50% of seaweed production worldwide for types of Eucheuma, Gracilaria dan Kappaphycus in which Indonesia has great opportunity to become the world's seaweed supplier. The need of *Eucheuma cottonii* and *Gracilaria* sp. in the world reaches 274,100 and 116.000 tons, respectively whereas Indonesia contributes in exporting 80,000 tons of *Eucheuma cottonii* (about 29.19% of total needs) and 57.500 tons of *Gracilaria* sp. (about 49.57% of total needs) (Anggadireja *et al*., 2008; Anggadireja and Tim, 2011; Campo *et al*., 2009). South Sulawesi has the largest contribution to seaweed export in Indonesia which also makes the province becomes the leading producer of seaweed in Indonesia that produces 1.517.690 tons annually consists of 1,087,678 tons *Eucheuma cottonii* and 430.012 tons *Gracillaria* sp. (MMAF., 2005, 2009, 2011; Tangko, 2008; Tangko and Pantjara, 2007).

The seaweeds are extracted with alkali at elevated temperature (Distantina and Fahrurrozi, 2011; Velde *et al*., 2002). The alkaline treatment is an important and well-known reaction of carageenans and is used to commercially enhance gelation behavior (Hoffmann *et al*., 1995; Montolalu *et al*., 2008; Distantina and Fahrurrozi, 2011; Velde *et al*., 2002). Some resources confirm that the demand of Carrageenan will continue to rise up to 2.92% per annum (Anggadireja and Tim, 2011) which also indicates the increase of ATC demand as the raw material of Carrageenan end-product. ATC itself is a process of preserving seaweed as Carrageenan raw material using cold or hot alkali solution. The product is formed as chips/slices or powder with sufficient additional value. As for *Eucheuma cottonii,* the added value can be seen in Fig. 1.

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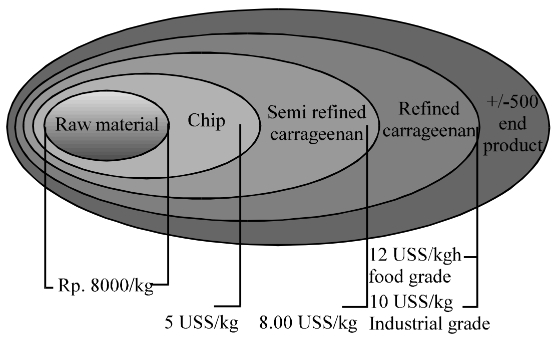

Fig. 1: Added value of *Eucheuma cottonii* seaweed (Anggadireja and Tim, 2011)

ATC chips is extracted from *Eucheuma cottonii* which is used as raw material for pure Carrageenan product as well as for binder and emulsifier in forage industry. To produced half-pure Carrageenan, the widely-used raw material is *Eucheuma cottonii* of which the methods known as Alkali Treated Cottonii (ATC). The objectives of the research are:

- To characterize dry seaweed as raw material
- To attain optimal production process for ATC chips such as soaking time and alkali concentration and characterize ATC chips

ATC is used as raw material to produce pure Carrageenan and further processed as binder and stabilizer in forage industry for European, American and Asia Pasific market (Anggadireja *et al*., 2008; Anggadireja and Tim, 2011). To manage an optimal production of ATC chip, it is essential to adjust the concentration of KOH and time variable to fulfill the qualification of ATC chips for national and global market. Carrageenan is sulfated linear polysaccharides extracted from various species of seaweed of rhodophyceae, especially, *Eucheuma cottonii.* Planted in Indonesia, *Eucheuma cottonii* yields Kappa Carrageenan which is the natural polymer capable of generating not also rigid gel but also thermo-reversible gel (Campo *et al*., 2009).

Seaweed with Carrageenan content is from *Euchema* genus. There are three categories of Carrageenan which are iota carrageenan known as spinosum, Kappa Carrageenan known as cottonii and lambda Carrageenan. Iota forms as soft and elastic jelly and kappa appears more rigid and stiff whereas lambda is more likely to be viscous rather than jelly. *E. cottonii* and *E. spinosum* is widely commercial as domestic raw material industry as well as export commodity (Anggadireja *et al*., 2008; Anggadireja and Tim, 2011). Based on market demand, the global need for seaweed artificial product will continue to rise in 2009-2015. The demand for raw material can be studied from the prediction of product capacity. The global demand of seaweed artificial product in 2009-2015 shows increment based on the market profile. The need of seaweed for Carrageenan in 2015 reaches 501,870 ton dry seaweed obtained from 466,740 ton dry *Eucheumea* sp. and others.

The process seaweed to become ATC basically involves simple procedures only which includes the boiling process in alkali solution at 80-85°C for 3 h, continued with neutralizing process with repeated rinsing with water. The seaweed is then sliced and dried to obtain the chip-form ATC. The aims of boiling process in alkali solution is to improve the melting point of Carrageenan above its boiling temperature to prevent seaweed from becoming pasta and also to enhance the strength of the Carrageenan gel (Anggadireja and Tim, 2011; Ciancia *et al*., 1993; NAP., 1986). ATC is used as raw material to produce pure Carrageenan and further, processed as binder and stabilizer in forage industry for European, American and Asia Pasific market (Anggadireja and Tim, 2011). To manage an optimal production of ATC chip, it is essential to adjust the concentration of KOH and time variable to fulfill the qualification of ATC chips for national and global market.

Carrageenan is sulfated linear polysaccharides extracted from various species of seaweed of *rhodophyceae* sp., especially, *Eucheuma cottonii.* Planted in Indonesia, *Eucheuma cottonii* yields Kappa Carrageenan which is the natural polymer capable of generating not also rigid gel but also thermo-reversible gel (Campo *et al*., 2009; Ciancia *et al*., 1993). ATC chips is an intermediate product acts as raw material for Carrageenan product, hence, the final test of ATC chip quality refers to the standard of Carrageenan. Carrageenan is commonly used as food stabilizer, thickener, gel generator, emulsifier and many applications in food industry, pharmacy and cosmetics. The characteristic of Carrageenan itself determines the value. The extraction process of Carrageenan from seaweed with the addition of alkali proves to enhance the mechanical characteristic of the gel (Ciancia *et al*., 1993; Hoffmann *et al*., 1995; Velde *et al*., 2002). The reaction of alkali addition is named as cyclization or desulfatation. This is a significant reaction and commercially used to improve the gel properties (Campo *et al*., 2009; Ciancia *et al*., 1993; Hoffmann *et al*., 1995; Distantina and Fahrurrozi, 2011; Freile-Pelegrin and Robledo, 2008) (Fig. 2).

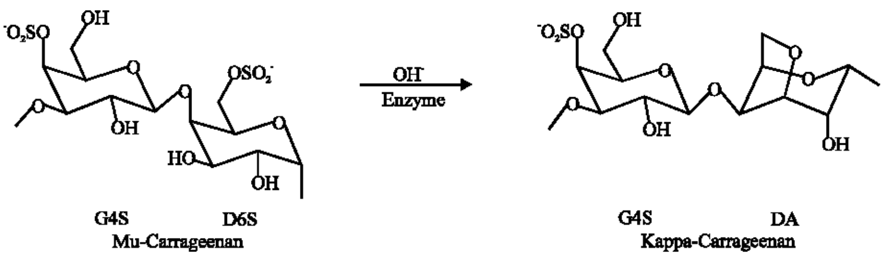

Fig. 2: Cyclization reaction with hydroxide to produce Kappa Carrageenan

MATERIALS AND METHODS

The main raw material in this research is dry *Eucheuma cottonii* from South Sulawesi and the reagents needed for the process is KOH. The analyzes for raw material and product include water content, gel strength, viscosity and Carrageenan yield. This research also needs some equipment such as sortation/grading, washer, boiling pan, drying tool, slicer, screening and quality control tool (Fig. 3).

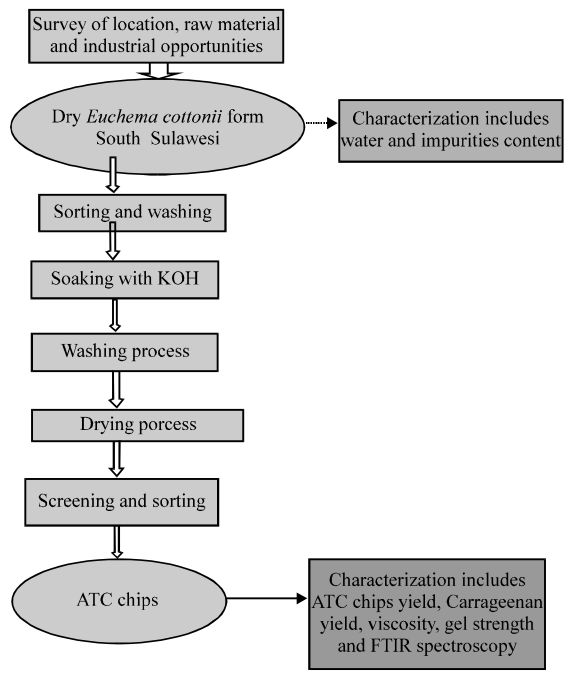

Fig. 3: Flowchart of the research

Process of ATC chips

Sorting and washing:
The seaweed is sorted and then washed manually. It is important to note the amount of seaweed (kg) can be processed by every personnel in 8 h. The data can further be used as industrial plan, especially, the layout and the manpower recruitment calculation.

Soaking with KOH (85°C): The boiling is conducted at 1 atm and optimal KOH concentration and optimal time to generate ATC chips that meets the requirement for food grade and trading. The experiment were carried out with different solvent (KOH of 0.1; 0.3 and 0.5 N) in triplicate.

Washing process: The washing process needs to be performed to obtain neutral ATC Chips with neutralized chemicals.

Cutting process: The cutting is performed by cutting machine to meets the standard of specification.

Drying process: The drying is performed to reach the standard of water content for marketing. In this stage, the optimum time variable is determined as standards.

Sorting process: The sorting is aimed to get uniform size as standard. Some parameters of ATC chips were determined, namely the yield, gel strength, viscosity and chemical structure. Yield is defined as ratio of ATC chips weight to dried seaweed weight. The gel strength was determined using the method described by Falshaw *et al*. (2001, 1998) and Distantina and Fahrurrozi (2011) with minor modifications. The powder of ATC chips was diluted by distilled water with heating to obtain a 1.5% (w/v) ATC powder solutions. For determining Gel Strength (GS), 10 mL solution was poured into a container (diam. 3.2 cm) and the height of solution was 1.3 cm. After cooling overnight at room temperature, the container was placed on balance. A stainless rod (surface area 1.2 cm^2) was pressed by hand into the gel surface until it collapsed, the maximum balance was noted. Gel strength is defined as ratio difference weight of before and after gel collapse to surface area of the rod. The calculated gel strength was an average of two determinations on the same sample. Intrinsic viscosity was determined experimentally by measurement of the viscosity of dilute concentration solution (Distantina and Fahrurrozi, 2011; Velde *et al*., 2002). Assessment of ATC chips chemical structure was performed by Fourier Transform Infrared spectroscopy (FTIR) Shimadzu. The spectra were recorded in the 4000-400 cm^{-1} region from thin film of powder of ATC chips.

RESULTS AND DISCUSSION

By characterization, the dry seaweed has 20% water and 9.92% impurities. There are 2 variables to be optimized which are KOH soaking time and KOH concentration. In order to find the best process production, it is necessary to perform product testing on ATC chips yield, Carrageenan yield, viscosity and gel strength in every time variable and KOH concentration variable. The following table shows result of ATC chips analyzes in various time and KOH concentration (Table 1).

The soaking time used for the process is 30, 60, 120 and 180 min. It is confirmed that the longer the soaking time, the higher the viscosity of produced Carrageenan. Moreover, the more concentration of KOH results in the higher the viscosity of Carrageenan (Fig. 4).

By varying the soaking time and the concentration of KOH, it can be confirmed that the longer the soaking time, the higher the strength of Carrageenan gel. Consequently, by higher concentration of KOH, the strength of Carrageenan gel is also increased (Fig. 5).

From the experiment, the KOH concentration was varied from 0.1, 0.3 and 0.5 N. The longer soaking time results in higher viscosity and higher strength of Carrageenan gel. The highest value is at 180 min soaking time and 0.5 KOH concentrations which is 717.79 g/cm^2.

Meanwhile, the FTIR spectroscopy displays the strongest wavelength is at 1210-1260 cm^{-1} (S = O from Sulfate esters) and 1010-1080 cm^{-1} (glycosidic linkage) in all type of Carrageenans. The other chemical bond indicated as Carrageenan compiler is 3,-6-anhydro-D-galactose at 928-933 cm^{-1}, D-galactose-4-sulfate at 840-850 $cm^{-1}$and and 3,6-anhydro-D-galactose-2-sulfate at 800- 805 cm^{-1}. Kappa Carrageenan is shown by FTIR at 840-850 cm^{-1}. At the end, the FTIR results proves that the Carrageenan produces is Kappa type as shown in Fig. 6.

Table 1: ATC chips analyzes in various time and KOH concentration (temperature of soaking KOH 85°C)

KOH concentration N	Soaking time (min)	Viscosity (MPa)	Gel strength (g/cm^2)	ATC chips yield
0.1	30	254.7	218.28	0.2572
0.1	60	270.3	246.57	0.2456
0.1	120	320.0	266.17	0.2254
0.1	180	327.0	296.47	0.1888
0.3	30	298.3	249.92	0.2565
0.3	60	307.7	274.93	0.3171
0.3	120	318.0	379.35	0.2238
0.3	180	342.7	441.92	0.2808
0.5	30	312.3	282.14	0.3051
0.5	60	478.0	374.64	0.3262
0.5	120	528.0	529.37	0.2361
0.5	180	541.3	717.79	0.2157

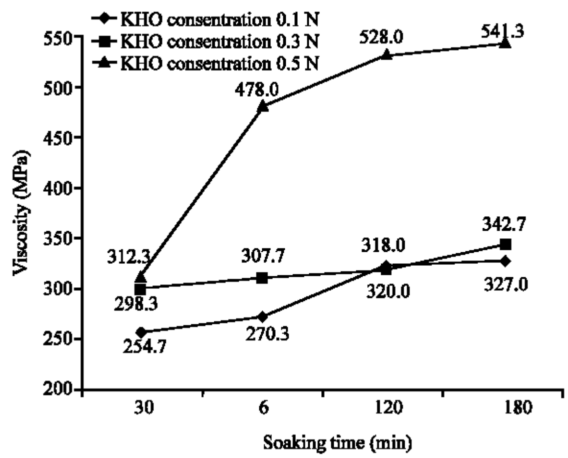

Fig. 4: The influence of KOH concentration to Carrageenan viscosity at various soaking time

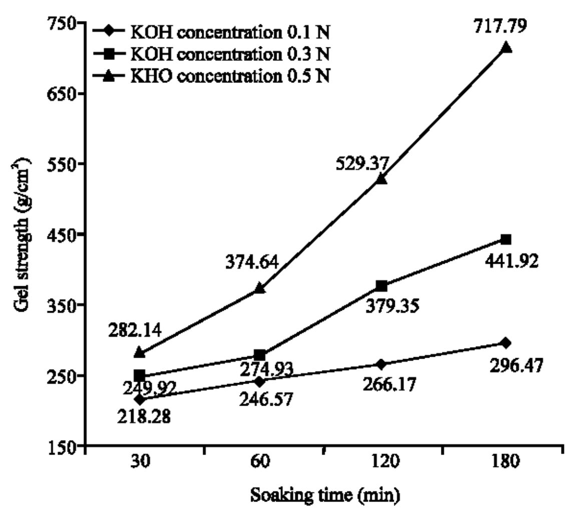

Fig. 5: The influence of KOH concentration to Carrageenan gel strength at various soaking time

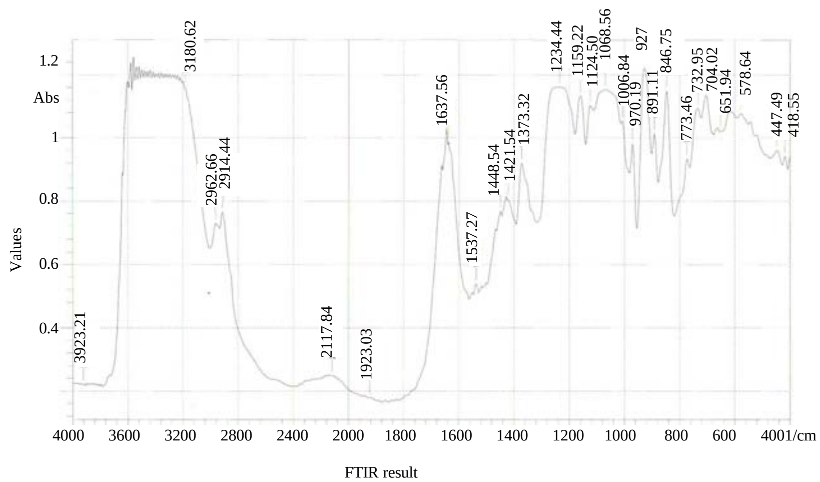

Fig. 6: FTIR result on ATC chips from dry *Eucheuma cotonii* at 3 h soaking time and 0.5 N KOH

CONCLUSION

To sum up, the following are the conclusion of this research:

- By adding time at the KOH soaking process and increasing the concentration on KOH, the viscosity and Carrageenan gel strength will be improved
- The optimum result (gel strength 717,79 g/cm^2 and viscosity 541.3 MPa, yield of ATC chips 0.2157) is obtained at 180 min soaking time, 85°C temperature and 0.5 KOH concentration.
- FTIR verifies the product is Kappa Carrageenan

ACKNOWLEDGEMENTS

The researchers thank to Kopertis III and Directorate General of Higher Education Indonesia for financial support of this research through research grant of ‘Hibah Bersaing’ 2013, Contract number 026/K3/KM/SPK/2013.

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