Microwave-assisted drying of semi-refined carrageenan origin from Lontar

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Abstract

Semi-refined carrageenan (SRC) was a processed seaweed product, with export value in 2018 reached 4.942 thousand tons. Semi-refined carrageenan (SRC) was produced commercially from Eucheuma cottonii type seaweed, through a heated process used alkali solution and the process of separation or recovery process, and the drying process of SRC. One alternative for the SRC drying process is by using microwaves, where the drying process can take place faster. The purpose of this study was to determine the optimum time and mathematical modelling of drying used microwaves in the SRC drying process. This study was carried out by extracting 200 gr of E. Cottonii seaweed with 9% KOH for 1 hour, then dried seaweed with a variation of dried time 5, 10, 15, 20, 25, 30, 40, and 45 minutes. In this study, the modified page drying model was obtained as a feasible model in representing the mathematical model of SRC drying, where the values of R is 0.9876 and RSME is 0.00483. The optimum drying time obtained in this study was 30 minutes.

A B S T R A K

Semi-refined carrageenan (SRC) merupakan produk olahan rumput laut, dengan nilai ekspor pada tahun 2018 mencapai 4.942 ribu ton. Semi-refined carrageenan (SRC) diproduksi secara komersial dari rumput laut jenis Eucheuma cottonii, melalui proses pemanasan menggunakan larutan alkali dan proses pengolahan proses pemisahan atau pemulihan, dan proses pengerengan SRC. Salah satu alternatif untuk proses pengeringan SRC adalah dengan menggunakan gelombang mikro, di mana proses pengeringan dapat berlangsung lebih cepat. Penelitian ini bertujuan untuk menentukan waktu optimal dan pemodelan matematis dari pengeringan menggunakan gelombang mikro dalam proses pengeringan SRC. Penelitian ini dilakukan dengan mengekstraksi 200 gr rumput laut E. cottonii dengan KOH 9% selama 1 jam, kemudian rumput laut dikeringkan dengan variasi waktu pengeringan 5, 10, 15, 20, 25, dan 30. Diperoleh model pengeringan halaman termodifikasi sebagai model yang layak dalam menerapkan asas model matematis pengeringan SRC, dimana nilai R adalah 0.9876 dan RSME adalah 0.00483. Waktu pengeringan optimum yang diperoleh dalam penelitian ini adalah 30 menit.

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1. Introduction

Based on data from the Central Statistics Agency, seaweed production in Indonesia in 2015 was 3.896 thousand tons, 2016 rose to 11.987 thousand tons, and in 2017 reached 12.047 thousand tons. In 2018, there are 12.056 thousand tons of seaweed production. Eucheuma cottonii, or with the scientific name Kappaphycus alvarezii is one type of seaweed that is generally widely cultivated in Indonesia. In Indonesia, Eucheuma cottonii types of seaweed are exported more by raw seaweed or raw materials without being processed into products with higher selling value. Carrageenan is a type of processed seaweed product with an increase in export value every year. According to data from the Central Statistics Agency (Badan Pusat Statistik (BPS)), the cost of carrageenan exports in 2017 was 4.11 thousand tons, and in 2018 it increased to reach 4.94 thousand tons [1].

Semi-refined carrageenan (SRC) is produced more by carrageenan producers compared to refined carrageenan (RC), because of the technology used is still simple and does not require high investment costs. Semi-refined carrageenan (SRC) had a low purity compared to refined carrageenan because it still
contains a small amount of cellulose. Alkaline solution mostly used to extract semi-refined carrageenan from Eucheuma cottonii. In the food industry, carrageenan is used as an emulsifier, stabilizer, thickener, gelling agent, and filler [2].

The SRC production process includes the process of extracting seaweed using alkaline solutions, the separation process, and the SRC drying process. The SRC drying process generally aims to reduce water content so that it can inhibit the growth of bacteria and other microbes, besides that to reduce the volume of storage, facilitate further handling, and to facilitate transportation and distribution to consumers [3]. The SRC drying process is still done conventionally by utilizing sunlight or by using an oven. Drying by using sunlight is used for reasons cheaper and more straightforward. However, the process has several disadvantages, which require extensive land for the drying process, are very dependent on weather conditions, and allow contamination from the environment [4]. Several studies on the SRC drying method have been carried out previously, including the SRC drying process with conventional heating and ohmic heating [5], spray dryer [6] solar tunnel dryer [7] and cabinet dryer [8].

One of the alternative dryings in SRC that need less time then a conventional method that requires a long time is with the microwave method. The drying of microwaves for agricultural materials that contain lots of water such as aloe vera can take place faster, so it can save time and energy. The microwave drying process shows a shorter time compared to conventional drying [9]. Based on the description above, this study needs to determine the effect of microwave-assisted drying methods to save time and energy so that the SRC drying process will be shorter.

2. Materials and Method

Eucheuma cottonii algae were purchased from Lontar, Banten. Before the extraction, Eucheuma cottonii was rinsed by using distilled water to reduce the impurities and salts, then dried at 60°C for two hours. The Folin-Ciocalteau’s Reagent and gallic acid (C6H7O5) were purchased from Sigma-Aldrich Japan (Tokyo, Japan). Sodium carbonate (Na2CO3), KOH, and ethanol (C2H5OH, 99.5%) were supplied by Merck (Germany).

The preparation stage in this study is to prepare Eucheuma cottonii type seaweed. First wash Eucheuma cottonii using water to remove dart that attaches to the plant and reduces the salt content. Then, Eucheuma cottonii drains for 10 minutes until the water content is reduced. Next, cut Eucheuma cottonii with a size of 1 cm. Then weigh the Eucheuma cottonii. Dry red algae (K. alvarezii) washed using distilled water algae 1 cm washed. The extraction was performed by heating at 70°C for 1 h using 9 percent KOH by continuous stirring. After extraction, the waste of algae (solid materials) was separated from the viscous filter. The filtrate was then neutralized by a 1% HCl solution up to pH 7 [10]. Carrageenan gel was isolated from alcohol and water by filtration. Carrageenan was dried using a drying cabinet with a drying time of 5, 10, 15, 20, 25, 30, 35, 40, and 45 minutes.

3. Result and Discussion

The results were carried out, an analysis of the one-way ANOVA statistical test was conducted where the statistical test of this ANOVA was aimed to determine whether the time variation in seaweed drying had a substantial effect on the carrageenan produced. ANOVA is considered an accurate research method for conducting experiments that attempt to prove or reject the hypothesis mathematically [11]. The following are the results of one-way ANOVA statistical analysis with time variations on the carrageenan water content produced.

| Table 1. Results of ANOVA analysis of data on water content. |
|------------------|-----|------|------|--------|------|
| Source of variation | SS  | df   | MS   | F     | P-value | F-crit |
| Between groups    | 2745.652 | 1 | 2745.652 | 29.27514 | 5.77E-05 | 4.493998 |
| Within groups     | 1500.605 | 16 | 93.78782 |         |         |       |
| Total             | 4246.257 | 17 |       |        |         |       |

Based on the calculation of the calculated F and F-critical values, it is found that the estimated F-value is higher than the significant F-value. According to ANOVA analysis, where the purpose of this analysis is to determine the essential independent variables and how they affect the response [12]. It can be concluded that the treatment of variation in seaweed drying time has a significant effect on the moisture content produced.

3.1. Analysis of The Drying Model

Analysis of the drying model is a mathematical equation that can show a drying model that is by the behavior of moisture ratio (MR). In this study, there are four observed drying kinetic models, namely the Newton model, Modified Page model, Page model, and the Henderson-Pabis model. The drying model was analyzed first by linearizing the drying kinetic models. The following is a linear form of each drying kinetic model.

After all kinetic models are linearized, trend line testing is carried out on each graph of the drying kinetics model. Constant values were obtained, and R2 values for each model were tested in all treatments. The following are the results of testing the trend line on each graph.

| Table 2. The values of constant, R2, and RSME of several drying models. |
|------------------|------|----------|----------|
| Drying modelling | Exponential Form | Linear Form |
| Newton           | MR = exp (-kt) | ln MR = -kt |
| Henderson-Pabis  | MR = a exp (-kt) | ln MR = ln (a) - kt |
| Page             | MR = exp (-kt^n) | ln (-ln MR) = ln (k) + n ln (t) |
| Modified Page    | MR = exp (-kt^n) | ln (-ln MR) = n ln (kt) |

(Source [13])
Based on the table above, it can be seen that from the four mathematical models, the results of semi-refined carrageenan (SRC) drying. Data of the modified Page model are the best mathematical models to represent SRC drying behavior. That is because the modified coefficient value $R^2$ is the highest among other mathematical models, so the modified page model can better serve the SRC drying kinetic in this study. That is supported by the RSME value of a minimal modified Page model close to zero, which is equal to 0.00483. This is similar to Fudholi et al. [14] analysis. On brown seaweed drying mathematical modeling, the Page model has the highest $R^2$ value, so the brown seaweed drying model is acceptable for the drying model Page. The Page model is shown to match the experimental data better than other models. Page model is better suited to drying herbs [15].

3.2. Relationship to White Degree with Drying Time

A white degree is one of the essential parameters for determining the physical quality of the SRC can be seen in Fig. 1 the final product [16]. Whitish-colored consumers generally prefer SRC with a high degree of brightness. From this study, the best white degrees were obtained, namely 63.3% in the treatment time of 30 minutes drying. This value shows the appearance of carrageenan with a color close to yellowish-white. The value of the white degree produced in this study is still lower than the value of the white degree of carrageenan from the results of the study by [17] where SRC is dried using an oven at 50°C for four hours has a white degree of 70.19% with the appearance of the resulting white color. The difference in color produced is due to the caramelization reaction that occurs when the drying process takes place materials with low water content can experience caramelization reactions [18]. The brightness of the material color during the drying process may decrease with the length of the drying time, [19].

![Figure 1. Carrageenan powder by microwave drying: (A) 20 minute, (B) 25 minute, (C) 30 minute, (D) 35 minute, (E) 40 minute, (F) 45 minute, and 5, 10, 15 minute still wet.]

3.3. FTIR Test Results

The other kappa-carrageenan chemical properties analyzed in this study were the identification of the kappa carrageenan functional group by analysis of Fourier transform infrared (FTIR). The explanation of the functional groups of kappa-carrageenan identified by infrared spectroscopy can be seen in Table 3 below.

| Wavelength range (cm$^{-1}$)* | Wavelength (cm$^{-1}$) | Type of bond | Functional group | Intensity  |
|-------------------------------|------------------------|--------------|------------------|-----------|
| 1220 -1260                    | 1232.51                | S = O        | Ester Sulfate    | Medium    |
| 1010 -1080                    | 1068.56                | C-O-C        | Glycosidic bond  | strong    |
| 928 - 933                     | 929.69                 | C-O          | 3,6-anhydrogalactose | Medium  |
| 840 - 850                     | 846.75                 | C-O-SO$_3^-$ | Galactose-4-Sulfate | Medium  |

The identification of the kappa carrageenan functional group with FTIR analysis in this study can be seen in Figure 2 below.

![Figure 2. FTIR test results.]

Carrageenan usually has strong, broad bands of all polysaccharides in the region of 1000 to cm$^{-1}$ with 1065 and 1020 cm$^{-1}$ for gelling and non-gelling types [20]. Based on the FTIR showed in fig. 2 that there was a sharp uptake in the numbers 1232.51 cm$^{-1}$ and 1068.56 cm$^{-1}$, narrow absorption at 929.69 cm-1, and 846.75 cm$^{-1}$. The results of the identification of functional groups against commercial carrageenan kappa with FTIR analysis showed the detection of sulfate ester groups at wave number 1232.51 cm$^{-1}$. The galactose-4-sulfate group at wave number 846.75 cm$^{-1}$, group 3,6-anhydrous galactose in numbers wave 929.69 cm$^{-2}$ and glycosidic group at wave number 1068.56 cm$^{-2}$. The presence of esters sulfate, galactose, and 3,6-anhydrous galactose are indicated the carrageenan type is kappa. Based on this, it can be stated that the commercial carrageenan used in this study is a type of carrageenan kappa.
4. Conclusion

Based on the results of the study it can conclude the Page model shown is best suited to experimental data than other models. This can be seen from the average values of the maximum R². The FTIR showed the identification of kappa carrageenan.

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