ORIGINAL ARTICLE

Application of foam-mat drying with egg white for carrageenan: drying rate and product quality aspects

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Abstract Drying is a significant step in the production of carrageenan. However, current drying process still deals with too long drying time and carrageenan quality degradation. The foam mat drying is an option to speed up drying process as well as retaining carrageenan quality. In this case, the carrageenan was mixed with egg white (albumin) as foaming agent and methyl cellulose for foam stabilizer. The foam will break the carrageenan gels and creates the porous structure resulting higher surface area for water transfer. This research studied the effect of egg white and methyl cellulose on carrageenan drying at various air temperature, and thickness. As a response, the water content versus time was observed and the drying rate was estimated. Meanwhile, the carrageenan texture was verified by X-RD (X-Ray Diffraction) and TEM (Transmission Electron Microscopy). Results showed that the presence of egg white stablized by methyl cellulose can speed up drying rate as well as retaining the crystalline structure of carrageenan. The higher albumin content, the faster drying rate. However, the addition of albumin and methyl cellulose restricted not more than 30 % in the mixture for keeping carrageenan quality and purity. By adding egg white 20 % and methyl cellulose 10 %, the water diffusion and drying rate can be two fold compared with carrageenan drying without foam. The improvement can be higher at the higher temperature and thinner carrageenan sheets.

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Introduction

Carrageenan, a sulfated polysaccharide isolated from red seaweed, *Euchema cottoni*, is an important material used widely in the food industry. The material is normally used as a stabilizer and thickener for dairy, food and pharmaceutical products (MCPI Corporation 2009; Voragen 2002; Thommes et al. 2007). Several techniques can be used to produce carrageenan which involves extraction by alkali (NaOH or KOH), filtration, precipitation and drying (Hilliou 2006; Usov 2011; Falshaw et al. 2001). Drying plays an important role in this aspect as this would influence the quality of the dried product after processing (Thommes et al. 2007; Djaeni et al. 2012). Occasionally, carrageenan is dried in tray or spray dryer at air temperature of about 80 °C. Under this condition, the colour of carrageenan tends to turn brown and degradation of the protein content is observed. In addition to that, the gel strength of the product also decreases during application on food products (Thommes et al. 2007).

The main problem in drying carrageenan is the formation of gel between polysaccharide and water which inhibits the diffusion of water to the surface. Furthermore, wet carrageen is sticky and has high water affinity that makes it easy to agglomerate. Studies showed that carrageenan drying at elevated temperature shortened drying time but resulted in poor product quality (Thommes et al. 2007; Falshaw et al. 2001; Djaeni et al. 2012). Tari and Pekcan (2008) reported that the drying time of carrageenan was about 5 h at 50 °C with shrinkage value ranging from 70 % to 80 % of their initial volume. (Moreira et al. 2011) found that the drying time for bio films made of starch and carrageenan could be speeded up by using high air flow rates and drying time was

reduced to 2–3 h at medium temperature drying ranging 30–50 °C. However, this method is not yet applied for pure carrageenan.

Djaeni et al. (2012) reported improved carrageenan quality and shorter drying time by using adsorption drying with zeolite. In this method, the drying air was dehumidified by zeolite close to 0.0 % RH. Thus, drying was carried out under low humidity condition which enhanced the driving force of mass transfer and resulted in better carrageenan quality in terms of whiteness, coupled with shorter drying time.

Foam-mat drying under low or medium air temperature is a potential option for the carrageenan industry (Kudra and Ratti 2006). Studies reported higher drying rate and better product quality (colour, aroma and taste) in foam mat drying of mango (Rajkumar et al. 2007) and banana (Thuwapanichayanan et al. 2008; Falade and Okocha 2012). The presence of albumin as foaming agent helps in pore formation which increases the surface area for drying. Other reported studies of foam mat drying are such as in soymilk (Akintoye and Oguntunde 1991), mango pulp (Wilson et al. 2012), starfruit (Karim and Wai 1999), and tomato paste (Lewicki 1975).

The current research investigated foam mat drying for carrageenan using air dehumidified by zeolite inside an adsorption dryer. Such drying method has not been reported use in the carrageenan industry. The drying kinetics and product quality was investigated and compared.

Material and method

a. Carrageenan preparation

About 150 g of red seaweed, *Euchema cottonii*, was mixed and extracted by 9 l of warm water at 70–80 °C at stirred plate. After 2 h, the mixture was filtered by using whatman paper aided by vacuum pump. The extract containing carrageenan was then coagulated by potassium chloride (2.5 %). The slurry containing about water 96 % and carrageenan 4 % was then ready to be mixed with the foaming agent.

b. Foam-carrageenan mixture

The carrageenan product (from point a) in amount of 70 g with 4 % purity (96 % water), was fed in the mixer. The product was then mixed with the foaming agent (albumin) and methyl cellulose (E. Merck) as a foam stabilizer. To keep the semi refined carrageenan purity, the amount of albumin and methyl cellulose in the mixture is set not more than 30 %. For the first experiment, the mixture contained 10 % albumin, and 20 % methyl cellulose. The mixing process was performed until the homogenous mixture reached. To speed up the homogeneity, about 30 ml water was added every 70 g carrageenan slurry. Hence, the mixture contained 61 g water

per gram dry carrageenan or 98.3 % water content in wet basis. The process was repeated for 15 % and 20 % albumin in mixture. All these materials were ready to be dried and compared with the carrageenan without foam.

Drying experiment

Ambient air (RH 70–80 %) at temperature between 29 and 33 °C was supplied to the adsorption column (column A in Fig. 1) which contains 1.5 kg of zeolite 3A particles (ZEOCHEM, Switzerland). About 70–80 % of moisture in the air was removed and the air temperature increases by 5–10 °C due to the release of adsorption heat. The dehumidified air (velocity of 0.50 m.s^{-1}) was then heated to the desired drying temperature (40–80 °C) and supplied to the drying chamber where the product was loaded on to a drying tray. Carrageenan sheets with 4 mm thickness and circle diameter of 7 cm was used.

Moisture content in carrageenan, air temperature, were measured every 10 min. The water content in carrageenan was measured by gravimetry, air conditions (ambient air, air entering and leaving the tray dryer) were measured by temperature and relative humidity sensors as indicated with T-RH1,2,3; humidity and temperature sensor KW0600561, Krisbow®, Indonesia, (see Fig. 1), air flow was measured with an anemometer (in Fig. 2 represented by F1, thermo-anemometer KW0600562, Krisbow ®, Indonesia). Drying was carried out for 120 min in all experiments. The drying process was repeated for various foaming composition at operational temperature 40, 60, 80 and 100 °C and thickness 2,3 and 5 mm.
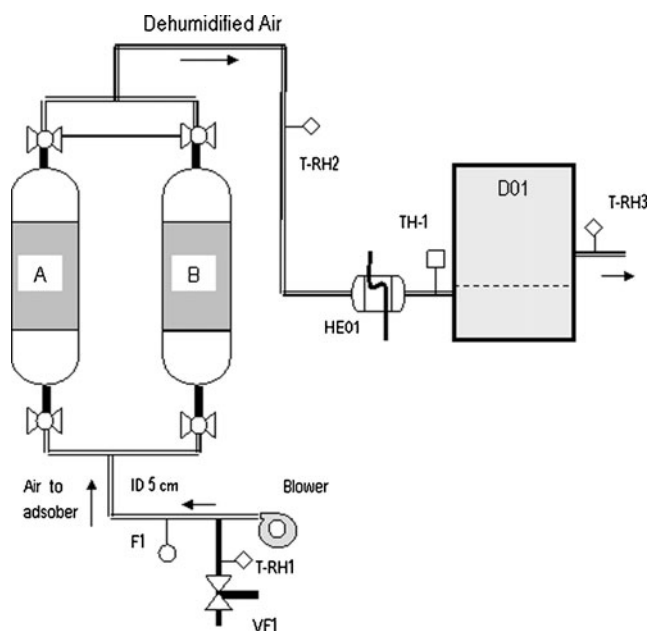

Fig. 1 Schematic overview and photograph of the experimental equipment. Internal diameter of columns A and B is 0.12 m, diameter of piping is 0.05 m, tray dryer size 0.40×0.25×0.60 m
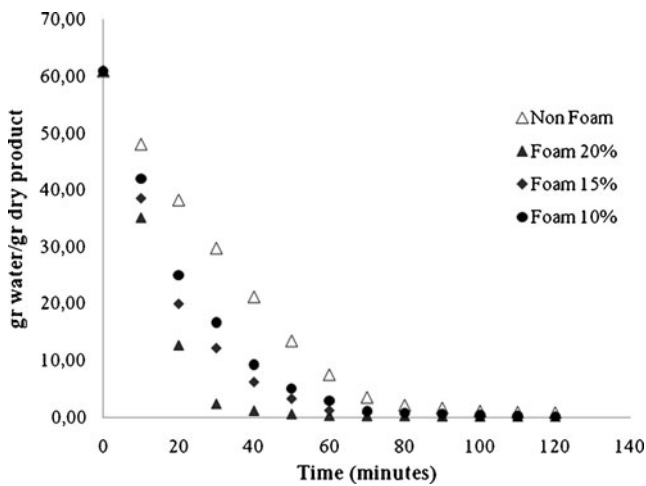
Fig. 2 Comparison of water content in carrageenan versus time for foam mat and non-foam drying at operational temperature 80 °C, air velocity 0.5 m.s^{-1} and carrageenan thickness 2 mm (time sampling is every 10 min, in the diffusivity estimation it was converted in second (s))

Effective diffusivity estimation

The foam mat was assumed as thin layer and moisture diffusivity (D_w) was estimated from the following equation (Doymaz 2006; Crank 1975):

$$MR = \left(\frac{8}{\pi^2}\right)\exp\left(\frac{\pi^2 D_w t}{4l^2}\right) \tag{1}$$

$$MR = \left(\frac{q_{e,p} - q_{w,p}}{q_{e,p} - q_{w,0}}\right) \tag{2}$$

Equation 1 can be linearized by applying natural log at both sides of the equation where the slope of the graph (ln MR versus t) can be used to estimate D_w. Here, MR is the
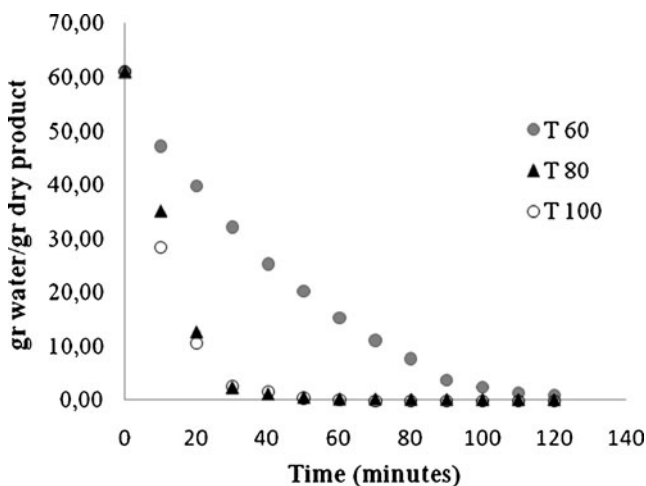
Table 1 The estimated water diffusivity for drying carrageenan with foaming agent

Temperature °C	$D_w \times 10^{-10}$, m^2.s^{-1}	From Eq. 5
60	2,74	$D_{30} = 1,95 \times 10^{-10}$ m^2.s^{-1}
80	6,47	$E_a = 30,86$ kJ.mole^{-1}
100	10,55	

mosture ratio, $q_{e,p}$ is the equilibrium moisture in carrageenan following the GAB (kg water/kg dry carrageenan), $q_{w,0}$ is the initial moisture in carrageenan (kg water/kg dry carrageenan), and $q_{w,p}$ is the moisture in carrageenan at time sampling. D_w is the moisture difussivitiy (m^2.s^{-1}), l is the thickness of carrageenan (m), and t is the time (s)

$$Slope = \left(\frac{\pi^2 D_w t}{4l^2}\right) \tag{3}$$

The equilibrium moisture content ($q_{e,p}$) for carrageenan is given by the GAB equation (Larotonda et al. 2005) as shown in Eq. 4.

$$q_{e,p} = \frac{BDKa_w}{(1 - Ka_w)(1 - Ka_w + BKa_w)} \tag{4}$$

where B, D and K are the GAB constants with the value of 23.3199; 0.1136; 0.8544, respectively. The a_w is the water activity which is assumed to be equal to the relative humidity (RH).

The relationship between the effective diffusivity and temperature can be described by using the Arrhenius relationship.

$$D_w = D_{30}\exp^{\frac{E_a}{R}\left(\frac{1}{(273.15+30)} - \frac{1}{(273.15+T_a)}\right)} \tag{5}$$

where D_{30} is the diffusion of water at 30 °C (m^2.s^{-1}), E_a is the activation energy (J.mole^{-1}) and R is the universal gas constant (8.314 J.mole^{-1}. K^{-1}).

Fig. 3 Response of water content versus time in carrageenan with foam at various operational temperature for air velocity 0.5 m.s^{-1}, and carrageenan thickness 2 mm with albumin 20 % (time sampling is every 10 min, in the diffusivity estimation it was converted in second (s))
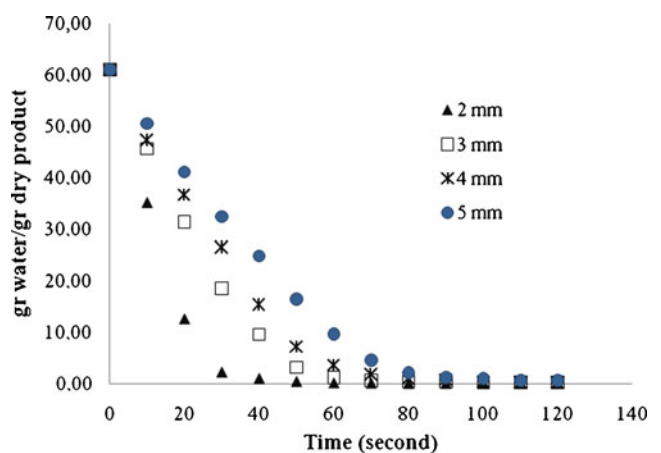

Fig. 4 Response of water content versus time at different carrageenan thickness for air velocity 0.5 m.s^{-1}, and operational temperature 80 °C with albumin 20 %
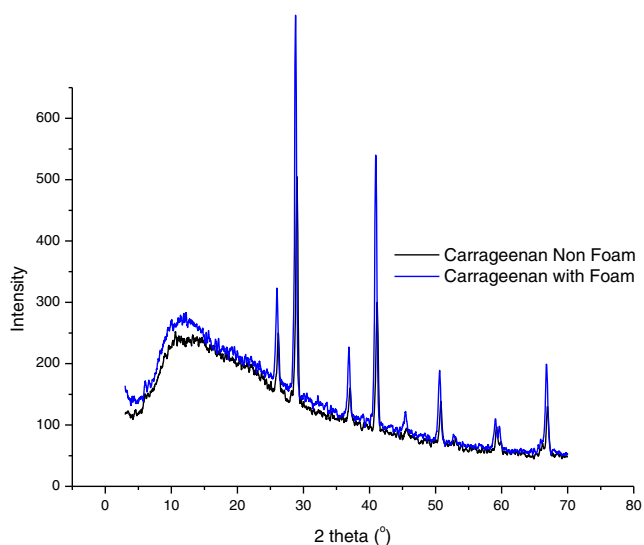
Fig. 5 The X-RD analysis for carrageenan with foam and without foam

Results and discussion

This section presents the influences of foaming agent on carrageenan drying at different temperature and carrageenan sheet thickness. Here, the moisture content during the drying was observed every 10 min, and the effective moisture diffusivity was estimated. In addition, the texture of carrageenan after drying was analyzed by X-RD (X-Ray Difraction) and TEM (Transmission Electron Microscopy). As comparison, the conventional carrageenan drying without foam is also presented.

a.   Effect of foaming on drying kinetics

According to the Fig. 2, it can be noted that foam mat drying can speed up drying time with the addition of the foaming agent. Drying rate is even comparable even at foam thickness of 4 mm which is comparable to 2 mm thick of carrageenan (without foam). The increase of foam content enhances the drying rate (water surface evaporation). This

because, the albumin forms the porous structure (foam) and breaks or opens the gel structure in carrageenan. While, the methyl cellulose stabilize the foam structure during the process. Hence, the moisture diffusion to the surface during drying can be kept high.

In contrast, drying of carrageenan without foaming at thickness of 4 mm was not successful at all. The observed result is in line with foam mat drying applied for other food products as reported in literatures (Ratti and Kudra 2006; Thuwapanichayanan et al. 2008). Even, the carrageenan drying with foam gives more significant effect compared to carrageenan drying without foam.

However, in the carrageenan drying the addition of foaming agent are limited not more than 20 % in the mixture. This is due to the presence of these materials influence the purity and quality of dried carrageenan product. By the limitation, the carrageenan quality for food or additive application still can be retained. The others literatures also showed that the addition of foaming agent and stabilizer is still below than 30 % as in the case of mango pulp (Rajkumar et al. 2007) and cowpea drying (Falade et al. 2003).

b.   Effect of temperature on drying kinetics at drying with foam

It can be seen from Fig. 3 that the moisture content decreases exponentially throughout the drying period and higher drying temperature resulted in higher rate of moisture diffusion and surface evaporation (Rajkumar et al. 2007; Thuwapanichayanan et al. 2008). For instance, at air temperature of 80 °C with drying time of 120 min, more than 95 % of moisture content can be removed. This is a very positive and significant improvement compared to the previous result with non-foaming drying (Thommes et al. 2007; Djaeni et al. 2012).

Using Eqs. 1–5, the water diffusion in carrageenan sheet, drying rate, and energy activation for drying were estimated, as shown in Table 1. Compared with previous result (Djaeni et al. 2012), the water diffusion in carrageenan for drying

Fig. 6 Transmission Electron Microscopy (TEM) analysis for carrageenan dried without foam (part a) and with foam (part b)
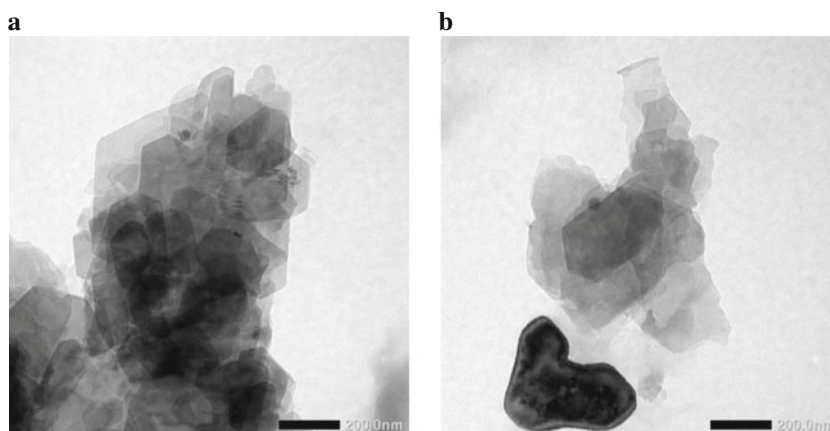
with foam is two fold. Using Eq. 5, the activation energy was estimated. With this parameter, the water diffusivity for extended operational temperature can be estimated.

c. Effect of carrageenan thickness on drying with foam

Figure 4 shows that thickness affects the drying rates with drying time significantly reduced as the foam thickness increased. At increased thickness the rate of moisture diffusion reduces due to the longer diffusional path along the thickness which results in lower moisture diffusivity value. In addition to that, heat transfer is more efficient and the faster heat penetration can initiate moisture diffusion in a shorter time.

d. Product quality

X-Ray Difraction (X-RD) was used to identify the effect of foaming on the size and crystal structure of carrageenan powder and Transmission Electron Microscopy (TEM) was used to have a closer look at the appearance of the particle under high resolution, respectively. As presented in Fig. 5, the crystal structures of both types of carrageenan are still similar which means that the foaming agent (30 %) does not change the crystal structure of carrageenan after foaming. However, the foam sample showed a slightly higher peak intensity at certain theta degree which could be due to the albumin that provide additional elements such as nitrogen. Besides, the foaming action destructed the tissue of carrageenan and this made the particle size appeared to be slightly smaller. However, the quality of crystal did not change as shown in X-RD analysis.

Figure 6 presents the result of X-RD analysis for carrageenan with non-foaming drying (part a) and foaming drying (part b). The foaming agent forms the pores inside the carrageenan tissue. The higher porosity increases the surface area for drying and the size of carrageenan particle tends to be slightly smaller (see Fig. 6 part b). This gives better contact between the drying air and the carrageenan particles which enhances the drying rates. The change in particle size and porosity does not change the quality of carrageenan as diagnosed with X-RD analysis.

Conclusion

This research looks into the effect of foaming agent namely egg white on carrageenan drying. The drying has been conducted at various thickness of carrageenan sheet, and temperature. The research showed that the presence of albumin (egg white) forms the pores inside the carrageenan tissue that can enlarge the surface area of drying process. This condition can speed up drying time and increase the water diffusivity. Thinner carrageenan sheet or higher air temperature result the faster drying rate and shorter drying time.

The carrageenan structure has been also verified for representing the quality. Using X-RD and TEM, the particle of carrageenan with foam is slightly smaller and tends to nano size. However, the characteristic of material does not change. It means that the foaming agent in amount of 30 % in the mixture, is still recommended for retaining the quality of carrageenan.

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