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Carboxymethyl Konjac Glucomannan from Konjac Flour: The Effect of Media and Temperature on Carboxymethylation Rate

Sperisa Distantina[a)], Mujtahid Kaavessina[b)], Fadilah[c)], Amellia Setyani Putrie[d)], and Inas Novianti[e)]

Chemical Engineering Department, Faculty of Engineering, Universitas Sebelas Maret, Jl. Ir. Sutami 36 A Surakarta 57126, Indonesia.

[a)]Corresponding author: sperisa_distantina@staff.uns.ac.id
[b)]mkaavessina@staff.uns.ac.id
[c)]fadilah@staff.uns.ac.id
[d)]amelia0705@gmail.com
[e)]novianti180@gmail.com

Abstract. To increase the solubility of porang flour or konjac flour in the water, the konjac flour was modified chemically into carboxymethyl konjac-glucomannan (CM-KGM), so that the utilization of the product may be wider. The aims of this research were to study the effect of ethanol concentration as the solvent media (50% ethanol and 90% ethanol) and temperature (45-50 ^{O}C dan 65-70 ^{O}C) on the rate of degrees of substitution (DS) formation in carboxymethylation step. CM-KGM was prepared by alkalization of konjac flour using sodium hydroxide for 30 minutes at 30^{O}C. Then, the product of alkalization was carboxymethylated using sodium monochloroacetic (Na-MCA) with ratio 1:1 gram flour/NA-MCA. Based on the experimental results, the higher DS was attained by carboxymethylation using media solvent of 90% ethanol and temperature carboxymethylation 65-70^{O}C. The relationship between temperature and reaction constant (k) follows: k = 0.3082 exp ((-15,277)/(8.314 T)).

INTRODUCTION

The glucomannan flour is polisaccharides containing cellulose and starch. Glucomannan is composed of D-glucose and D-mannose monomers with β-1,4 linkages[1]. Due to the presence of hydroxyl groups in the repeated unit of the polisaccharides chain, the glucomannan may be chemically modified in order to get new material with wider functional properties applications. Carboxymethylation method is a favorite method of polysaccharide modification, which aims to change hydroxyl groups into carboxymethylated form [2]. The carboxymethyl structure can increase the solubility of polysaccharide in water. Carboxymethylcellulose (CMC) is a green polymer with great important in pharmacy, medicine, cosmetics, and food industries. Commercially, the CMC is generally made from raw material wood pulp. By using alternative raw materials from glucomannan, it will indirectly affect the reduction of tree-cutting action by the producer of CMC. Carboxymethylated polysaccharide can be made from the polysaccharide into form of Na-CMC in a way alkalization with NaOH and then carboxymethylation with sodium monochloroacetic (Na-MCA). The quality of the CMC can be seen from the number of carboxyl groups attaching to the cellulose [3,4]. The number of carboxyl groups attached to the powder, is known as degree of substitution (DS).

Recently, various polysccharides have been carboxymethylated [2, 4, 5, 6, 7] for broader industrial applications, such as in food processing, paper and pulp, pharmaceutical, and well drilling. Our research group works related with chemically modification of polysaccharide in order to enhance the property of origin polysaccharides [8-10]. This

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present work prepared carboxymethyl konjac-glucomannan (CM-KGM) from glucomannan flour of corms of porang (*Amorpholhopallus muelleri* Blume). The aims of this research were to study the effect of concentration ethanol as the solvent media and temperature on the rate of degrees of substitution (DS) formation in carboxymethylation step. Kinetic for extractions of glucomannan from porang has been investigated [11]. As far as we know, there is no paper reported the study of carboxymethylation rate. The knowledge of rate of DS formation is essential to optimize both plant design and operation process. This work developed the mathematical model that can be used to predict the rate of DS formation.

The reaction of CM-KGM formation can be written in Eq.(1) to (3).

$$\text{Cel-OH} + \text{NaOH} \xrightarrow{\text{Alkalization}} \text{Cel-ONa} + H_2O \quad (1)$$

$$\text{Cel-ONa} + \text{Cl} - CH_2COONa \xrightarrow{\text{Carboxymethylation}} \text{Cel-O}CH_2COONa + \text{NaCl} \quad (2)$$

Overall, the reaction can be written as follows:

$$\text{Cel-OH} + \text{Cl–}CH_2COONa \xrightarrow{\text{NaOH}} \text{Cel-O}CH_2COONa + H_2O + \text{NaCl} \quad (3)$$

The rate of DS formation as depicted in Eq. (4).

$$\frac{d[DS]}{dt} = k.[Ds]^n \quad (4)$$

Where k is reaction constant, n is reaction order, [DS] is degree of substitution, and t is time of carboxymethylation step.

The DS formation mathematical models were derived from equation (4) with variation on reaction order of n. If n=0, 1, and 2, the DS formation model can be written in Eq. (5) to (7) respectively.

$$Ds = Ds_0 + k_1 t \quad (5)$$

where k_1 is reaction constant (mole/liter/min).

$$Ds = Ds_0 \exp(k_2.t) \quad (6)$$

where k_2 is constant reaction (1/min).

$$Ds = \frac{1}{\frac{1}{Ds_0} - k_3 t} \quad (7)$$

where k_3 is constant reaction (liter/mole/min).

MATERIALS AND METHODS

Materials

Polisaccharide material that used in this research was glucomannan flour from corms porang obtained from local market, Central Java, Indonesia. Another chemical materials used, namely $ClCH_2COONa$ (Na-MCA), NaOH, C_2H_5OH, HCl, and other chemicals were purchased and used without further purification.

CM-KGM Preparation

The CM-KGM preparation was based on the previous researcher method [12]. Preparation of CM-KGM was done with 2 processes separately and respectively. The first process was alkalization. In three neck rounded flask, 5 grams of glucomannan flour was mixed with 100 ml aqueous NaOH 10% in media of ethanol 200 ml (90% and 50% ethanol concentration wt) in temperature of 30 ^{O}C for 30 minutes. The mixture was stirred with magnetic stirrer for 30 minutes. The second process was carboxymethylation. In this step, 5 g Na-MCA in 20 ml water was added into the mixture produced by previous alkalization. The mixture was then heated up to 40-45 ^{O}C and 65-70 ^{O}C certain time. For studying the rate of DS formation, the same above processes were conducted for other reaction time.

CM-KGM Purification

CM-KGM product was purified by dispersing it in ethanol 96% until neutral pH, and then the CM-KGM was filtered and dried at temperature 100^{O}C until a constant weight was attained. After dried, the product was screened using 50 mesh screening.

Determination of DS

The DS value was determined by back titration method [13]. Firstly, CM-KGM must be changed into H-CM-KGM. Five grams of CM-KGM was dissolved in 100 ml HCl 1.8 M by continuously stirred for 30 minutes. The dispersion was then filtered. In order to remove the excess acid, the precipitate was washed using ethanol, until the conducivity of the filtrate was about 25 ɥs/cm. Then, the precipitate dried at 50^{O}C for 2 hours.

After H-CM-KGM was formed, the H-CM-KGM was converted into soluble sodium salt. The value of DS was determined using back titration method. The 0.5 grams H-CM-KGM was dissolved in 20 mL of 0.2 M NaOH and added aquadest so that the volume of the solution became 100 mL. The 25 mL of the solution was poured into an erlenmeyer flask and diluted by addition of distilled water. The excess of NaOH was back-titrated using standard 0.05 M HCl, and phenolphtalein was used as the indicator. The titration was repeated for three times and the average value of the HCl volume was used for the calculations data. A blank was also titrated. The number of COOH was determined using Eq. (8).

$$\text{ncooh} = (\text{vb} - \text{v}) \times \text{MHCl} \times 4 \tag{8}$$

Where vb and v (in mL) is the volume of HCl for titration of the blank and the sample, respectively. MHCl (in mol/L) is the HCl concentration and 4 is the ration of the total volume (100 mL) and the volume taken for titration (25 mL).

The DS was calculated using Eq. (9).

$$\text{DS} = \frac{162 \times \text{ncooh}}{\text{mds} - (58 \times \text{ncooh})} \tag{9}$$

Where 162 g/mol is the molar mass of an anhydroglucose unit (AGU) and 58 g/mol is the mass of an AGU for each carboxymethyl group substituted. The mass of dry sample (mds, gram) was calculated using Eq. (10) from known sample mass (ms, gram) and the water content (w water).

$$\text{mds} = \left(1 - \frac{\text{w water}}{100}\right) \times \text{ms} \tag{10}$$

RESULT AND DISCUSSION

Effect of Ethanol Concentration on DS

Carboxymethylation of glucomannan flour was carried out with sodium monochloroacetate in the presence of aqueous NaOH under solid-liquid heterogeneous conditions. The effect of ethanol concentration as solvent medium of carboxymethylation was studied in terms of the effect on DS of CM-KGM formed in the following experimental condition: interval reaction time 30 min to 150 min and reaction temperature 45-50^{O}C. Fig. 1 shows the result of DS using ethanol 50% and 90%.

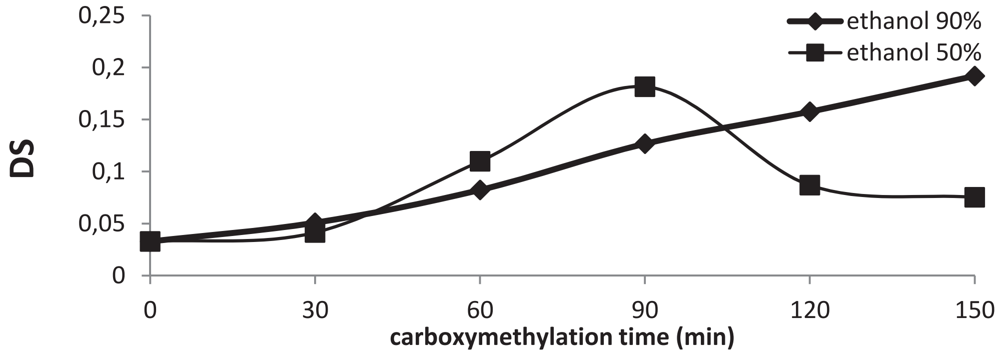

FIGURE 1. DS as function of carboxymethylation time with variation of ethanol concentration at 45-50^{O}C.

From Fig. 1, it is can be seen that using ethanol 90% the DS increased with the increasing of carboxymethylation time. Using ethanol 50%, the DS increased until 90 minutes, after this time the DS decreased. This may be caused the hydrolysis reaction leads the removal of sodium monochloroacetate during side reaction with formation of sodium glycolate [12]. Glycolate formation reduced the DS formation also reported by other article [4]. The higher water content in media of carboxymethylation improves this hydrolysis reaction.The solvent medium affected the miscibility of etherifying agents, Na-MCA. Compared with ethanol 50%, using ethanol 90% created condition that favours carboxymethylation rather than hydrolysis, therefore the higher DS resulted.

Rate of DS Formation

Fig. 2 and 3 show the comparison of DS obtained from experiment and DS obtained as function of carboxymethylation time from different model. Table 1 shows the values of reaction constant (k) from different model.

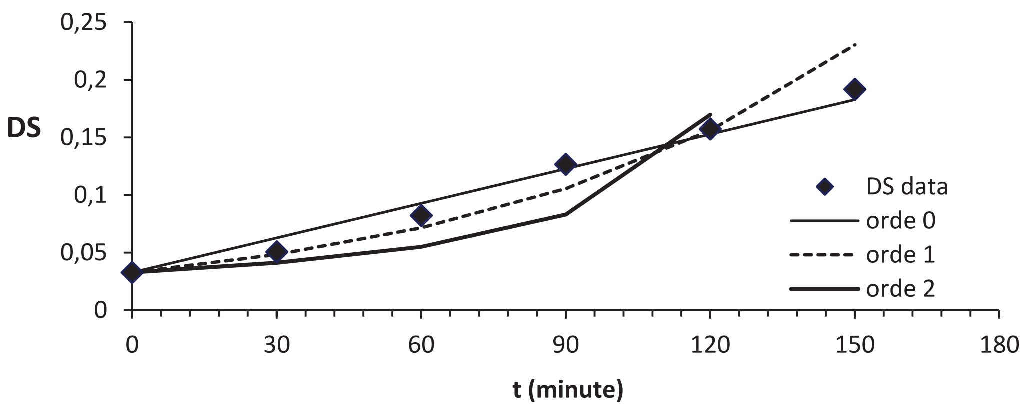

FIGURE 2. DS as function of carboxymethylation time (ethanol 90%, 45-50 ^{O}C) using different model.

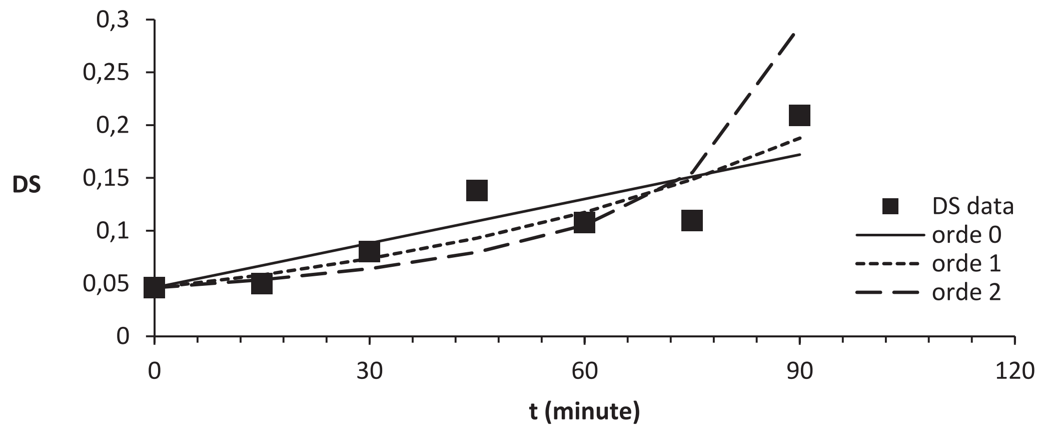

FIGURE 3. DS as function of carboxymethylation time (ethanol 90%, 65-70^{O}C) using different model.

TABLE 1. The k values for different model at various temperature (ethanol 90%)

Model	45 -50 ^{O}C		65 -70 ^{O}C	
	k	Error relative (%)	k	Error relative (%)
Eq. (5)	0.001	7.86	0.0014	23.51
Eq. (6)	0.013	9.23	0.0156	18.57
Eq. (7)	0.205	367	0.2032	25.55

Compared with temperature 45 – 50^{O}C, the reaction temperature 65 – 70^{O}C resulted higher DS. At 90 min reaction, carboxymethylation with temperature 65-70 ^{O}C produced DS was about 2.0, besides with temperature 45 – 50 ^{O}C the DS was about 1.3 (Fig. 2 and 3). The similar observations have reported by other researcher [4]. From the DS data collected from experimental and DS calculated from the model, it can be seen that the calculated values made agreement with experimental data for zero order and first order. This agreement was also described by the value of error relative. These error relative exhibited the difference of DS data and DS calculated. The lower of error relative means that the model was suitable with the phenomena of overall solid-liquid reaction in this work.

The Effect of Temperature on k

Table 1 shows the value of k with different carboxymethylation temperature. The effect of temperature on k was investigated by varying the temperature from 45^{O}C to 70^{O}C and reaction medium ethanol 90%. The mathematical model that used in studying the effect of temperature is model using zero order as expressed Eq. (5). Table 1 reveals when the carboxymethylation temperature increased, the k was higher. It was known that the enhancement of the reaction temperature will increase reaction rate as shown by Arhenius equation. Higher temperature increased the rate of reaction. The relationship k as function of temperature is presented in Fig. 4.

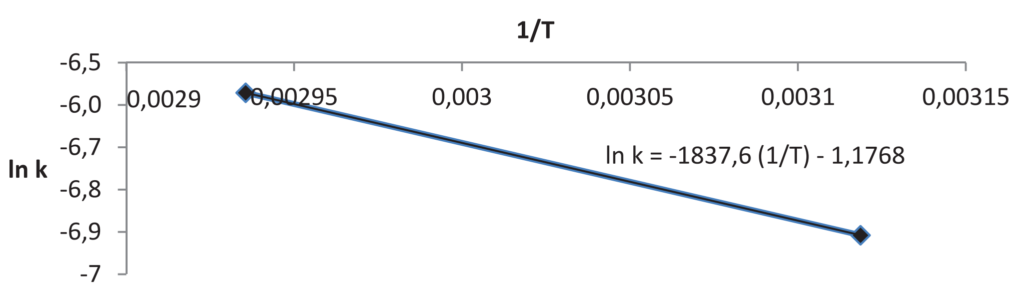

FIGURE 4. Relationship k and T.

CONCLUSION

Based on the results of the experiment can be took some conclusios, namely the higher DS was attained by carboxymethylation using media solvent of 90% ethanol compared with 50% ethanol, the rate of DS formation followed zero order or first order of reaction kinetic equation, and the relationship between temperature and reaction constant (k) follows: k = 0.3082 exp ((-15,277)/(8.314 T)).

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