Chem. Chem. Technol., 2018, Vol. 12, No. 1, pp. 101–108 Chemical Technology

ACID HYDROLYSIS AND ETHANOL PRECIPITATION FOR GLUCOMANNAN EXTRACTION FROM CRUDE PORANG (AMORPHOPHALLUS ONCOPHYLLUS) TUBER FLOUR

Andri Kumoro^{1, *}, Tunjung Yuganta¹, Diah Retnowati¹, Ratnawati Ratnawati¹

https://doi.org/10.23939/chcht12.01.101

Abstract. Extraction of glucomannan from crude porang flour by acid hydrolysis and ethanol precipitation was studied. Effects of acid concentration, temperatures and time were investigated, kinetics model of the process was developed and the parameters were evaluated based on experimental data. New data on yield and purity of glucomannan under various conditions were obtained.

Keywords: glucomannan, extraction, acid hydrolysis, modeling, mass transfer, kinetics.

1. Introduction

Glucomannan is one of the neutral polysaccharides that is composed of β -1,4 linked D-mannose and D-glucose with the molar ratio of mannose and glucose of about 1.6:1. The backbone structure is lightly branched (an approximate degree of branching of 8 %), with short side branches at the C-3 position of the mannoses [1]. The chain has 5–10 % acetyl group substitutes located at every 9 to 19 sugar units, which is believed to play important role in the solubility and gelling properties [2]. Being an amorphous polymer the average molecular weight of glucomannan ranges between 10^5 and 10^6 g/mol [3]. According to Yao-Ling et al. [4] glucomannan has been used in traditional Chinese medicine for millenniums for the healing of asthma, cough, hernia, breast pain, burns, and skin disorders. Further, recent clinical studies have revealed the potentials of glucomannan to reduce blood sugar, lower blood cholesterol, control body weight, and promote healthy microflora in intestinal [5]. Due to biodegradability and good gel-forming glucomannan is also widely used in the pharmaceutical field for controlled release drug delivery system [6]. In addition, due to its specific rheological and gelling properties, glucomannan is also abundantly used in food

and beverage industries as emulsifying and stabilizing agent for various food, drink, and cosmetic products [4].

Although glucomannan can be acquired from various botanical sources, the tuber of porang (Amorphophallus oncophyllus) plant, which belongs to the Aracea family, has been found to be the most potential source in view of its high glucomannan content and sustainable availability [7]. Generally, fresh porang tuber may contain 8–10 wt % of glucomannan [2]. Prior to the extraction of glucomannan, the porang tuber is washed, sliced, dried and milled; and the porang tuber flour (PTF) of refined powder is further separated by wind shifting. The glucomannan content in the crude porang tuber flour (CPTF) usually ranges from 50 to 70 wt % [8], whereas purified porang tuber flour (PPTF) should have glucomannan content of no less than 90 wt %. The impurities trapped in CPTF particles are usually coming from the tissue space [4], which mainly comprises starch, lipid, protein and ash [2]. As the main impurity, the starch may seriously affect the purity and quality of glucomannan, such as reducing viscosity and increasing turbidity [9].

High-quality porang flour can be obtained through separation of glucomannan granules from the smaller starch granules by conventional dry or wet processing. The dry process method includes grinding of dried porang tuber chips into CPTF, which is later purified via windsifting [10]. Unfortunately, porang flour obtained using this method is of low purity and is therefore sold as a lowprice food commodity [11]. To overcome this problem, a number of wet extraction methods have been developed to extract glucomannan from CPTF, such as enzymatic hydrolysis [12, 13], dialysis and ethanol precipitation [14], washing with water, aqueous alcohol [15] and benzeneethanol solution [16], high energy centrifugation [8], or a combination of aforementioned the Unfortunately, most of those processes are complicated; require higher operating cost and sometimes still result in low yield and product purity. Therefore, it is apparent that development of more efficient methods is needed to substitute the existing ones.

¹ Diponegoro University Prof. H. Soedarto,

SH Road Tembalang, Semarang, Indonesia 50275

^{*} andrewkomoro@che.undip.ac.id

[©] Kumoro A., Yuganta T., Retnowati D., Ratnawati R., 2018

Starch and glucomannan molecules may interact with each other and make their separation even more difficult due to the low solubility of starch under mild condition. Fortunately, gelatinization characteristics may efficiently boost starch solubility in water. Gelatinization temperature of crude porang flour is 341.5–350.6 K [17]. In fact, glucomannan molecules possess better swelling ability than starch molecules and become insoluble in aqueous ethanol, whereas the starch molecules do not. Glucomannan has the lowest solubility when ethanol concentration in the solution is about 45 vol %, by which its separation from the solution may take place via precipitation [11]. Alcohol also contributes to unfold glucomannan molecular chain and expose the impurities on the surface or trapped inside of porang flour particles to the solution for easier removal [18]. Obviously, these properties are favorable for extraction of glucomannan from porang flour by removal of the starch via hydrolysis [19] followed by ethanol precipitation of glucomannan [20].

In the case of glucomannan extraction via starch hydrolysis, the utilization of acid hydrolysis has never been widely studied. Operating variables such as temperature, reaction time, type of acid, acid concentration and solid-to-liquid ratio play critical roles in obtaining optimum acid hydrolysis of starch [21]. It is reported that the catalytic activity and selectivity of hydrochloric acid during hydrolysis of starch is higher than that of sulfuric acid [22] and phosphoric acid [23]. This high catalytic activity, non-disturbing residue after neutralization (sodium chloride) on glucomannan precipitation using alcohol and its simplicity are the advantage of using hydrochloric acid as catalyst over the other mineral acids. The drawback of acid hydrolysis is only slower reaction rate as compared to enzymatic hydrolysis [4]. The governing factor of the homogeneous acid catalysis turned out to be the acidity (pH) of the solution, which is directly proportional to concentrations of the hydroxonium ions (H₃O⁺) existing in the solution [24]. On the other hand, the temperature and the reaction time have been reported to have less influence on the hydrolysis reaction [25]. Jacobsen and Wyman [26] found that 5 wt % solid concentration could provide good uniformity of the reaction system with ignorable mass transfer effects on the degradation of lignocellulosic biomass. Thus, 1 wt % solid concentration or about 1:100 solid to liquid mass ratio was employed in this study.

There is very little information from previous studies on the influences of the extraction parameters on the extraction of glucomannan from CPTF using starch hydrolysis [13]. Only one literature source reported a simple modeling of the ethanolic extraction of glucomannan from CPTF [27]. There is also no rigorous report on the mathematical modeling of the extraction of glucomannan from CPTF available in the literature. In

view of the above, a simple acid hydrolysis process at various acid concentrations, temperatures and time was developed for the extraction of glucomannan from CPTF. In addition, a comprehensive mathematical model employing reaction kinetics and mass transfer approaches was also proposed to describe the real extraction phenomena.

2. Experimental

2.1. Materials

The crude porang tuber flour used in this study was obtained from PT. Prima Agung Sejahtera-Surabaya (Indonesia) with average particle size of 80 mesh. All of the chemicals used for extraction and analysis were of analytical grade (purity \geq 98 wt %) and procured from Sigma-Aldrich via authorized chemicals distributor in Semarang-Indonesia. All the chemicals were directly used without prior treatments.

2.2. Extraction Procedure

The extraction of glucomannan from crude porang flour was conducted via starch hydrolysis utilizing hydrochloric acid as catalyst. 10 g of crude porang flour were dispersed in 1000 ml of hydrochloric acid solution of predetermined concentrations (0.03125 to 1.0 M) in 2000 ml Pyrex® three-neck round bottom flask at room temperature. The mixture was heated in a water bath heater to achieve desired extraction temperatures (323, 333, 343 and 353 K) under continuous stirring. While the temperature was maintained at a desired value, continuous stirring was held to permit acid hydrolysis of starch and extraction of glucomannan. When the desired reaction time (0.25, 0.5, 1, 2, and 3 h) was reached, 50 ml sample was taken out of the extraction flask for reducing sugar analysis. Removal of insoluble materials was performed by diluting the remaining reaction mixture to 1000 ml with demineralized water and followed by centrifugation (9000×g, 30 min, 298 K). Afterward, rotary evaporation was carried out to reduce the volume of the filtrate to ~1/3 of the original volume. Glucomannan present in the solution was precipitated overnight by the addition of 95 vol % of ethanol at 277 K, and followed by centrifugation (9000×g, 40 min, 298 K). The resultant pellets were washed twice with anhydrous ethanol and further isolated by vacuum filtration, before being freezedried for 48 h. The dried material was milled and sieved to obtain purified glucomannan and was then subjected to purity analysis and yield determination.

2.3. Analyses

Starch content of crude porang flour was determined by acid hydrolysis method [28], while the

Kjeldahl method was applied to obtain the total nitrogen content for protein determination [29]. The protein content was then calculated by applying the nitrogen conversion factor of 5.7, as proposed by the U.S. Food Chemicals Codex (FCC) and European Commission [10]. In addition, the ash and fat contents were examined per AOAC Method 920.153 and 948.15 [30]. The reducing sugar of the sample was determined following the phenol-sulfuric acid colorimetry method [31]. Glucomannan purity was analyzed based on the reducing sugar content of the hydrolyzate and porang flour sample solution using the method previously used by Chua *et al.* [32]. The glucomannan yield was then calculated as the mass percentage of glucomannan obtained from initial mass of glucomannan in CPTF.

2.4. Mathematical Modeling

In the solid-liquid extraction, the mass transfer of an extractable solute from the inner part of the starting material particles to the bulk of the liquid may take place in two consecutive steps: first – the diffusion of solute in the inner particle and second - the convective mass transfer at the solid-liquid interphase. In the case of very fine porous particles, the diffusion of solute in the inner particle can be assumed to be very fast. The average sizes of porang flour and porang starch particles are 177 and 1.2-1.3 µm, respectively. While the amylose content of porang starch ranged from 17.4 to 18.2 % indicating that the CPTF particles are very tiny and porous. Then, the rate controlling step during extraction of glucomannan from CPTF may be assumed to be the rate of glucomannan transfer from the particle surface to the bulk of the liquid. Previous researchers also revealed that particle size less than 20–40 mesh (400–841 µm) presented little limitation on the hydrolysis rate of the biomass [33].

Extraction of glucomannan from CPTF particles was supposed to consist of several simultaneous mechanisms, *i.e.* dissolution of soluble sugar, hydrolysis of starch and dissolution and hydrolysis of glucomannan. In this study, the rate of the volumetric mass transfer of soluble sugar and glucomannan from CPTF particles surface to the hydrochloric acid solution was assumed to be the controlling step. The volumetric dissolution rate of soluble sugar from CPTF particles in the hydrochloric acid solution follows the following equation

$$\frac{dC_{SG}}{dt} = -k_{sa} \cdot (C_{SG}^* - C_{SG}) \tag{1}$$

where C_{SG} is the concentration of soluble sugar in the solution, g/ml; C_{SG}^* is the equilibrium concentration of soluble sugar in the solution in contact with solid surface, g/ml; k_{SG} is the volumetric mass transfer coefficient, 1/h.

A Henry like equation was used to represent the equilibrium correlation between concentration of soluble

sugar in the solution in contact with solid surface and the concentration of soluble sugar in the CPTF particles.

$$C_{SG}^* = H_1 \cdot C_{SGS} \tag{2}$$

where H_1 is Henry like constant for soluble sugar, g/ml. The soluble sugar content of the CPTF particles is determined by mass balance of soluble sugar in the extraction flask.

$$C_{SGS} = \frac{MC_{SG0} - VC_{SG}}{M} \tag{3}$$

where C_{SGS} is the concentration of glucomannan in particles, g/g; C_{SG0} is the initial concentration of soluble sugar in particles, g/g; M is the mass of CPTF particles, g; V is the volume of solution, ml.

The glucomannan volumetric mass transfer from CPTF particle surface may be assumed to be in the similar mechanism to that of soluble sugar. Unfortunately, under harsh condition hydrochloric acid solution may further hydrolyze glucomannan into sugar [34]. Therefore, the mass balance of glucomannan in the liquid phase can be written as:

$$\frac{dC_{GLU}}{dt} = k_{ca}(C_{GLU}^* - C_{GLU}) - k_1 \cdot C_{GLU} \tag{4}$$

where C_{GLU} is the concentration of glucomannan in the solution, g/ml; C_{GLU}^* is the concentration of glucomannan in the solution in contact with solid surface which is assumed to be the equilibrium concentration, g/ml; k_{ca} is the volumetric mass transfer coefficient, 1/h; k_1 is the reaction rate constant for glucomannan hydrolysis, 1/h. The correlation between the equilibrium concentrations of glucomannan in the solution with concentration of glucomannan in the CPTF particles is assumed to follow the Henry like equation.

$$C_{GLU}^* = H_2 \cdot C_{GLUS} \tag{5}$$

where H_2 is Henry like constant for soluble sugar, g/ml.

Then, the glucomannan content of the CPTF particles can be calculated by means of mass balance of glucomannan in the extraction flask.

$$C_{CLUS} = \frac{MC_{GLU0} - VC_{GLU}}{M} \tag{6}$$

where C_{GLUS} is the concentration of glucomannan in the particles, g/g; C_{GLU0} is the initial concentration of glucomannan in the particles, g/g; M is the mass of CPTF particles, g; V is the volume of hydrochloric acid solution, ml.

According to Saeman [35], the acid-catalyzed polysaccharide hydrolysis to glucose in a dilute acid batch system obeys the first-order pseudo-homogeneous kinetic model. Trajano and Wyman [36] reported that the crystallinity of polysaccharide played a significant role in resisting the dilute acid hydrolysis of starch. The

hydrolysis of starch is initiated by the cleavage of β -1,4-glycosidic bond of anhydroglucose. However, the crystal-linity of starch significantly retards the hydroxonium ions to penetrate into the starch and catalyzing the cleavage of the β -1,4-glycosidic bond [37]. As a consequence, only parts of the β -1,4-glycosidic bond in the starch linear structure has the tendency to be broken down. According to this point of view, the reactive portion of the starch that is not hindered by crystallinity was defined as $(1-\alpha)$ starch. Hydrolysis of amorphous fraction of starch of CPTF to produce reducing sugar can be written as:

$$\frac{dC_S}{dt} = -k_2 C_S (1-a) \tag{7}$$

where α is the degree of crystallinity, linear structure has more susceptibility to be broken down [38]; C_S is the starch concentration in the solution, g/l; k_2 is the reaction rate constant for starch hydrolysis, 1/h.

Therefore, if the purification of glucomannan from CPTF strictly involves all of solubilization of soluble sugar, starch hydrolysis, and glucomannan hydrolysis then the concentration of total sugar (C_{TGL}) in the solution will be:

$$\frac{dC_{TGL}}{dt} = \frac{dC_{SG}}{dt} - \frac{dC_S}{dt} + k_1 C_{GLU}$$
 (8)

$$\frac{dC_{TGL}}{dt} = k_{sa}(C_{SG}^* - C_{SG}) + k_2C_S(1-a) + k_1C_{GLU}$$
 (9)

The simultaneous differential equations (Eqs. (1), (4), (7), and (9)) were solved numerically using the Runge-Kutta method to obtain the volumetric mass transfer coefficient for soluble sugar and glucomannan as well as the reaction rate constant for glucomannan and starch hydrolysis by minimization of the sum of square error (SSE) between the calculated values and the experimental data of glucomannan, starch and total sugar concentrations.

3. Results and Discussion

During the extraction process, it was clearly observed that the dispersed porang flour particles absorbed water and swelled. As the heat was continuously supplied to the mixture, the starch in the flour experienced gelatinization. Therefore, the shearing effect of stirring was expected to intensively remove the gelatinized outer part of the starch molecules and dissolves them into the solution [39]. Thus, hydrolysis occurred immediately.

3.1. Proximate Composition of Crude Porang Tuber Flour

From the applications point of view, an ideal PPTF should possess high purity (containing ≥90 wt % of gluco-

mannan) [40]. However, CPTF produced by the traditional method generally contains significant amount of protein and starch, which essentially affect its quality. The chemical composition of CPTF used in this study is presented in Table 1.

It can be observed in Table 1 that glucomannan content of the porang flour used in this study was slightly lower than that of porang flour manufactured in China [15, 41], but still within the range of glucomannan content of porang flour produced in Thailand [8]. The protein content fell within the range of that mentioned in the literature [41]. However, the starch content was in the upper range of that given in the literature [41], suggesting that more extensive starch removal via acid hydrolysis is required to obtain high purity glucomannan. Ash, the total amount of inorganic composition, is a crucial parameter for evaluating quality. No fat content was detected in CPTF used in this study. Fat was also reported to be absent in porang flour manufactured in China [15, 41]. In the food production, including glucomannan, ash is highly essential to be kept in a controlled range; otherwise, the material may be considered as contaminated or disqualified. The differences in chemical composition of porang flour may be influenced by ecological environment, growing condition and harvest time [42]. Furthermore, the utilization of fertilizers, shades, planting densities and flour manufacturing process also may significantly affect the chemical composition of porang flour [18, 43, 44].

3.2. Effect of Catalyst Concentration

The effect of catalyst concentration ranging from 0.125 to 1 M was studied by extraction of CPTF at 333 K using CPTF: water ratio of 1:100 for 1 h. The profile of yield and purity of glucomannan are presented in Fig. 1.

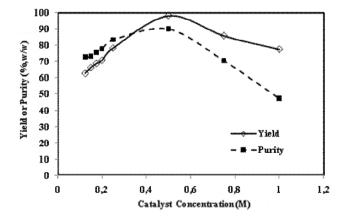


Fig. 1. Effect of catalyst concentration on yield and purity

Table 1

This work Literature [15] Literature [41] Component 57.6 59–60 Glucomannan 74.1 Starch 24.6 8.89 10-30 Protein 7.43 3.67 5-14 Soluble sugar 4.86 2.47 3–5 5.51 4.26 3.4-5.3 Ash

Chemical composition of porang flour (wt %)

As seen in Fig. 1, glucomannan yield increased drastically when catalyst concentrations increased from 0.125 to 0.5 M. However, a further increase in catalyst concentration had caused a gradual decrease of the glucomannan vield. Highest glucomannan vield (98.34 wt %) was obtained from extraction of CPTF using $0.5 \,\mathrm{M}$ hydrochloric acid solution. The highest glucomannan purity (90.18 wt %) was also achieved at that extraction condition. With this in mind, the starch removal from CPTF through acid hydrolysis is likely to be successful. Since pseudo-homogeneous acid hydrolysis of starch is influenced by the acidity (pH) of the solution, which is directly proportional to the concentrations of the hydroxonium ions (H₃O⁺) existing in the solution [24], then the concentration of hydroxonium ions at that condition is 0.5 M. Based on this principle, similar result was reported by Tanaka et al. [45] for recovery of glucomannan from porang flour using sulfuric acid. The highest recovery was achieved using 0.25 M sulfuric acid, which coincided with 0.5 M hydroxonium ions.

Generally, the rate of hydrolysis and the reducing sugar formation rise with increasing acid concentration, possibly due to the increase in the activity of hydrogen ions taking part in the reaction as a catalyst [22]. As expected, the purity of glucomannan increased steadily as acid concentration increased from 0.125 to 0.5 M. This is because more starch as the main impurity of CPTF being hydrolyzed into reducing sugar. However, purity of glucomannan decreased when the catalyst concentration was higher than 0.5 M. Commonly, the treatment with concentrated acid and/or high temperature causes the degradation of polysaccharides to form byproducts such as monosaccharides, furfural and hydroxymethylfurfural, thus reducing glucomannan purity [34]. decomposition of glucomannan into other products may have been the possible cause of this phenomenon [45].

3.3. Effect of Temperature

The effect of extraction temperatures ranging from 323 to 353 K was investigated by extraction using 0.5 M hydrochloric acid solution employing CPTF:water ratio of 1:100 for 1 h. The results are shown in Fig. 2. Generally, the rate of starch hydrolysis and mass transfer rise with

increasing temperature, possibly due to the increase in the activity of hydrogen ions taking part in the reaction as a catalyst [22], solubility [46, 47] and diffusivity coefficient of starch [48, 49]. Increasing extraction temperatures increased the mobility of starch granules, which further facilitated dispersion of starch molecules in water [50] and led to acid hydrolysis. The release of proteins from CPTF particles increased with increasing temperature [51] and so did the soluble sugar [15]. Similarly, acid hydrolysis increases the solubilization of ash from CPTF particles [52]. Proteins, soluble sugar and ash are not precipitated during glucomannan precipitation in 45 wt % aqueous ethanol solution. Therefore, the yield and purity of glucomannan increased steadily as temperature raised from 323 to 333 K. Glucomannan with the highest purity (91.03 wt %) was obtained from extraction of CPTF at 343 K as more starch molecules were hydrolyzed than at lower temperatures.

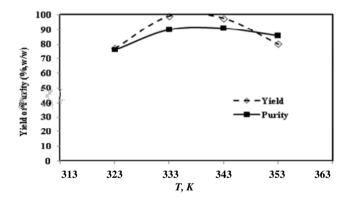


Fig. 2. Effect of temperature on yield and purity

However, the yield of glucomannan decreased when the temperature was further increased to higher than 333 K. Possible degradation of glucomannan *via* acid hydrolysis to form byproducts such as reducing sugar and other lower molecular weight fractions due to harsh extraction conditions at high temperature may be the cause of this phenomenon [53]. All those by-products are soluble in ethanol [54] and therefore are not recovered during ethanol precipitation step resulting in the reduction of glucomannan yield.

3.4. Mathematical Model Validation

In order to test the accuracy of the proposed mathematical model, a series of the experiments were conducted at temperatures ranging from 323 to 353 K using 0.5 M hydrochloric acid solution by employing CPTF:water ratio of 1:100 for 3 h. Concentrations of glucomannan and total sugar in the solution at certain extraction temperatures and times were taken. They were then used to verify the proposed model and find the optimum value of extraction parameters. The results are presented in Fig. 3 and Table 2.

Fig. 3a confirms that the crystalline region of CPTF starch exists at the studied temperatures, thereby resisting the hydrolysis of porang starch to some extent. As presented in Table 2, the value of α decreased with increasing reaction temperature, declining to 44.2, 17.42 and 8.61 % at 323, 333 and 343 K, respectively. As the temperature further increased to 353 K, the value of α was significantly reduced to zero, which showed that the majority of crystalline starch was transformed to an amorphous structure, thus acid could easily penetrate into the starch and catalyze the cleavage of the β -1,4-glycosidic bonds. It is also observed in Fig. 3a that sugar concentration increased proportionally to the reaction time at the beginning of the hydrolysis process, and followed

by a gradual increase after 1 h. Prolonged reaction time only slightly increased the sugar concentration, which was supposed to be the contribution of degradation of glucomannan into monosaccharides [55].

Fig. 3a and Table 2 indicate that at low temperatures (323–333 K), the total sugar concentration yield was more sensitive to variations in the parameter α than the rate constants k_1 and k_2 . Hence, α could be considered as the key factor in controlling the production of simple sugar under these experimental conditions. However, at elevated temperatures (343–353 K), because the value of α was almost negligible, its influence on simple sugar yield declined to an imperceptible level, thus the simple sugar production could be predominately controlled by the rate constants k_1 and k_2 .

Fig. 3b reveals that at the beginning of the process, the higher temperature promotes faster extraction rate as shown by rapid increase in glucomannan concentration. This phenomenon may be due to the effect of temperature on solubilization of glucomannan inside of the CPTF particles [56]. However, the glucomannan concentration decreased after 1 h, which is likely to be caused by degradation of glucomannan into monosaccharides [55]. Almost, no glucomannan degradation was observed at low temperature (323 K) as its concentration remains constant after 1 h.

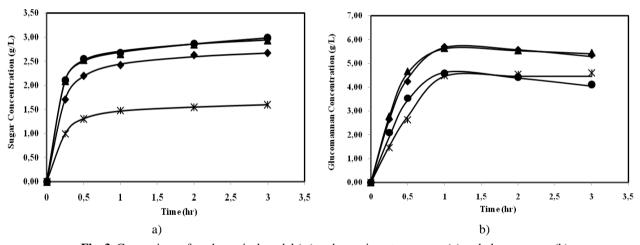


Fig. 3. Comparison of mathematical model (—) and experiments on sugar (a) and glucomannan (b) concentration profiles carried out at various temperatures, K: $323 \, (\mathring{\mathbf{U}}); 333 \, (\spadesuit); 343 \, (\blacktriangle); 353 \, (\bullet)$

Table 2

Optimum value of extraction model parameters at various temperatures

Parameters	Temperature, K			
	323	333	343	353
$k_1 \cdot 10^3$, 1/h	5.01	50.5	62.5	68.0
k ₂ , 1/h	4.83	5.78	7.03	7.22
<i>k</i> _{sa} , 1/h	1.15	1.25	0.84	0.82
k_{ca} , 1/h	8.14	14.7	14.4	10.3
H_1 , g/l	0.08	0.19	0.12	0.10
H_2 , g/l	10.2	21.1	15.4	14.4
α (–)	0.44	0.17	0.09	0

Since the solutes (glucomannan, starch and soluble sugar) are water soluble compounds, the beginning of the extraction process is basically dominated by dissolution rate of those compounds. It is observed that the temperature significantly influences the dissolution rate of those compounds. The increase of the mass transfer coefficient during the extraction at 323 and 333 K is more likely due to the decrease of CPTF size, which leads to the change of the limit layer thickness and water diffusion process inside the granule. Solid-liquid contact surface decreases with the increase of temperature and leads to increase of the volumetric mass transfer coefficient. Higher value of mass transfer coefficients (k_{ca} and k_{sa}) means higher rate of extraction and the extraction may reach equilibrium in a shorter time. Therefore, increasing temperature is favored for extraction because increased extraction rate reduced extraction time and led to higher glucomannan yield. The higher value of H at higher extraction temperature indicated that final concentration of solutes (glucomannan and soluble sugar) increased. When temperature increased, all the extraction kinetic model parameters increased. This phenomenon was also reported by other authors [57, 58]. Unfortunately, the mass transfer coefficients (k_{ca} and ksa) values appear to level off after 333 K. The gelatinization of CPTF starch at 343 K or higher have caused the solution became more viscous, which led to lower diffusivity, and therefore mass transfer coefficients values [59].

4. Conclusions

An efficient method for extraction of glucomannan from crude porang flour via starch removal using acid hydrolysis has been investigated. Catalyst concentration, temperature and reaction time essentially affected the yield and purity of glucomannan. Unfortunately, possible degradation of glucomannan under harsh conditions was observed. Confirmation of experimental data and mathematical model indicated that catalyst concentration and temperature significantly influenced the mass transfer and kinetic hydrolysis of glucomannan and starch in the porang flour. Glucomannan with the highest purity (91.03 wt %) was obtained from acid hydrolysis of porang flour using 0.5 M hydrochloric acid at 343 K for 1 h. The combined mass transfer and reaction approach has successfully described the extraction phenomena by which optimization of its application in industrial scale can be made.

Acknowledgements

The authors would like to acknowledge the support of the Ministry of Research, Technology and Higher

Education the Republic of Indonesia through Non Tax National Revenue-Diponegoro University Budget Execution List Year 2016 for International Scientific Publication Research Grant under contract No.:1052-43/UN7.5.1/PG/2016.

References

2013, **1**, 7.

[1] Xu Q., Huang W., Jiang L. *et al.*: Carbohydr. Polym., 2013, **97**, 565. https://doi.org/10.1016/j.carbpol.2013.05.007

[2] Takigami S.: Konjac Mannan [in:] Philips G. and Williams P. (Eds.), Handbook of hydrocolloids. Woodhead Publishing Limited, New York 2000, 413-424.

[3] Li B., Xie B. J.: Appl. Polym. Sci., 2004, **93**, 2775. https://doi.org/10.1002/app.20769

[4] Chua M., Baldwin T., Hocking T., Chan K.: J. Ethnopharmacol., 2010, **128**, 268. https://doi.org/10.1016/j.jep.2010.01.021 [5] Yao-Ling L., Rong-hua D., Ni C. *et al.*: J. Single Mol. Res.,

[6] Brostow W., Hagg Lobland H.: Materials: Introduction and Applications. John Wiley & Sons, New York 2016.

[7] Ohashi S., Shelso G., Moirano A., Drinkwater W.: Pat. US 6162906, Publ. Dec. 19, 2000.

[8] Tatirat O., Charoenrein S.: LWT-Food Sci. Technol., 2011, 44, 2059. https://doi.org/10.1016/j.lwt.2011.07.019

[9] Yoshimura M., Takaya T., Nishinari K.: Carbohydr. Polym., 1998, **35**, 71. https://doi.org/10.1016/S0144-8617(97)00232-4 [10] Parry J.: Konjac glucomannan [in:] Imeson A. (Ed.), Food Stabilisers, Thickeners and Gelling Agents. John Willey & Sons, Ltd., United Kingdom 2011, 198-216.

[11] Zhao J., Zhang D., Srzednicki G. et al.: Int. Food Res. J., 2010, 17, 1113.

[12] Wootton A., Luker-Brown M., Westcott R., Cheetham P.: J. Sci. Food Agric., 1993, **61**, 429.

https://doi.org/10.1002/jsfa.2740610408

[13] Fadillah, Rochmadi, Syamsiah S., Haryadi: J. Eng. Sci. Technol., 2015, Special Issue on SOMCHE 2014 & RSCE 2014 Conference, 1.

[14] Xing X., Cui S. W., Nie S. *et al.*: Bioact. Carbohydr. Diet. Fibre, 2014, **4**, 74. https://doi.org/10.1016/j.bcdf.2014.06.004 [15] Xu W., Wang S, Ye T. *et al.*: Food Chem., 2014, **158**, 171. https://doi.org/10.1016/j.foodchem.2014.02.093

[16] Chen L., Liu Z., Zhuo R.: Polym., 2005, **46**, 6274. https://doi.org/10.1016/j.polymer.2005.05.041

[17] Aprianita A., Vasiljevic T., Bannikova A., Kasapis A.: J. Food Sci. Technol., 2014, **51**, 1784. https://doi.org/10.1007/s13197-012-0696-x

[18] Jianrong Z., Donghua Z., Srzednicki G. *et al.*: Proceed. Asia-Pacific Symposium on Assuring Quality And Safety Of Agri-Foods, Thailand, Bangkok 2008, 345.

[19] Kumoro A., Ngoh G., Hasan M. et al.: Asian J. Sci. Res., 2008, 1, 412.

[20] Retnowati D., Kumoro A.: Reaktor, 2012, 14, 46.

[21] Taherzadeh M., Karimi K.: BioRes., 2007, 2, 472.

[22] Tasic M., Konstantinovic B., Lazic M., Veljkovic V.: Biochem. Eng. J., 2009, **43**, 208. https://doi.org/10.1016/j.bej.2008.09.019 [23] Fontana J., Mitchell D., Molina O. *et al.*: Food Technol. Biotechnol., 2008, **46**, 305.

[24] Salmi T., Murzin D., Maki-Arvela P. et al.: AIChE J., 2014, 60, 1066. https://doi.org/10.1002/aic.14311

- [25] Betancur A., Chel G.: J. Agric. Food Chem., 1997, **45**, 4237. https://doi.org/10.1021/jf970388q
- [26] Jacobsen S., Wyman C.: Ind. Eng. Chem. Res., 2002, **41**, 1454. https://doi.org/10.1021/ie001025+
- [27] Fadillah, Rochmadi, Syamsiah S., Haryadi: Proceed. 5th Int. Conf. on Chemical Engineering and Applications IPCBEE, Singapore 2014, 11.
- [28] Puswatien P., Siong T., Kantasubrata J. *et al.*: The ASEAN Manual of Food Analysis. Institute of Nutrition, Mahidol University, Phutthamonthon 2011.
- [29] AOAC: Official Methods of Analysis. AOAC International, Gaithersburg 1999.
- [30] AOAC: Official Methods of Analysis. AOAC International, Arlington 2005.
- [31] Čuesta G., Suarez N., Bessio M. *et al.*: J. Microbiol. Methods, 2003, **52**, 69. https://doi.org/10.1016/S0167-7012(02)00151-3
- [32] Chua M., Chan K., Hocking T. *et al.*: Carbohydr. Polym., 2012, **87**, 2202. https://doi.org/10.1016/j.carbpol.2011.10.053
- [33] Chang V., Holtzapple M.: Appl. Biochem. Biotechnol., 2000, **84**, 5. https://doi.org/10.1385/ABAB:84-86:1-9:5
- [34] Otieno D., Ahring B.: Biores. Technol., 2012, **112**, 285. https://doi.org/10.1016/j.biortech.2012.01.162
- https://doi.org/10.1016/j.biortech.2012.01.162 [35] Saeman J.: Ind. Eng. Chem. Res., 1945, **37**, 43.
- https://doi.org/10.1021/ie50421a009
- [36] Trajano H., Wyman C.: [in:] Wyman C. (Ed.), Aqueous Pretreatment of Plant Biomass for Biological and Chemical
- Conversion to Fuels and Chemicals. John Wiley & Sons, Ltd., West Sussex 2013. 103-123.
- [37] Brodeur G., Yau E., Badal K. *et al.*: Enzyme Res., 2011, **2011**, 787532. https://doi.org/10.4061/2011/787532
- [38] Xiang Q., Lee Y., Pettersson P., Torget R.: Appl. Biochem. Biotechnol., 2003, **107**, 505. https://doi.org/10.1385/ABAB:107:1-3:505
- [39] Kolusheva T., Marinova A.: J. Univ. Chem. Technol. Metall., 2007, 42, 93.
- [40] Fang W., Wu P.: Food Hydrocolloids, 2004, **18**, 167. https://doi.org/10.1016/S0268-005X(03)00044-4
- [41] Li B., Xia J., Wang Y., Xie B.: J. Agric. Food Chem., 2005, **53**, 7404. https://doi.org/10.1021/jf050751q
- [42] Brown D.: Aroids, Plants of the Arum Family. Timber Press, Oregon 2000.
- [43] Douglas J., Follett J., Waller J.: Acta Hortic., 2005, 670, 173.
- [44] Douglas J., Follett J., Waller J.: N. Z. J. Crop Hortic. Sci., 2006, **34**, 139. https://doi.org/10.1080/01140671.2006.9514398
- [45] Tanaka Y., Okamoto K., Matsushima A. *et al.*: Anal. Sci., 2013, **29**, 1049.

- [46] Sankhon A., Amadou I., Yao W. et al.: J. Agr. Sci. Tech., 2014, 16, 331.
- [47] Alan F., Hasanin A.: Agric. Conspec. Sci., 2009, 74, 45.
- [48] Gomi Y., Fukuoka M., Takeuchi S. *et al.*: Food Sci. Technol. Int., 1996, **2**, 171.
- [49] Jokić S., Velić D., Bilić B., Bucić-Kojic A.: Czech J. Food Sci., 2010. 28. 206.
- [50] Olu-Owolabi B., Olayinka O., Adegbemile A., Adebowale K.: Food Nutr. Sci., 2014, 5, 222.
- https://doi.org/10.4236/fns.2014.52027
- [51] Bui C., Siriwatwechakul W., Tiyabhorn W. *et al.*: J. Ind. Technol., 2016, **12**, 45.
- [52] Betancur A., Chel G.: J. Agric. Food Chem., 1997, **45**, 4237. https://doi.org/10.1021/jf970388q
- [53] Cheng L., Halawiah N., Lai H. et al.: Int. Food Res. J., 2010, 17, 1043.
- [54] Montanes F., Olano A., Ibanez E., Fornari T.: AIChE J., 2007, **53**, 2411, https://doi.org/10.1002/aic.11258
- [55] Chandel A., Chandrasekhar G., Radhika K. *et al.*: Biotechnol. Mol. Biol. Rev., 2011, **6**, 8.
- [56] Wongkitipong R., Prat L., Damronglerd S., Gourdon C.: Sep. Purif. Technol., 2004, 40, 147.
- https://doi.org/10.1016/j.seppur.2004.02.002
- [57] Chan C-H., Yusoff R., Ngoh G.: Chem. Eng. Res. Des., 2014, **92**, 1169. https://doi.org/10.1016/j.cherd.2013.10.001
- [58] Cisse M., Bohuon P., Sambe F. *et al.*: J. Food Eng., 2012, **109**, 16. https://doi.org/10.1016/j.jfoodeng.2011.10.012
- [59] Rakymkul Y.: MS Thesis, Swanson School of Engineering, University of Pittsburgh, Pennsylvania 2011.

Received: March 03, 2017 / Revised: March 15, 2017 / Accepted: August 22, 2017

КИСЛОТНИЙ ГІДРОЛІЗ ТА ОСАДЖЕННЯ ЕТАНОЛУ ДЛЯ ЕКСТРАКЦІЇ ГЛЮКОМАННАНУ З КЛУБНІВ *AMORPHOPHALLUS ONCOPHYLLUS*

Анотація. Досліджено екстракцію глюкоманнану з муки сирих клубнів кислотним гідролізом та осадженням етанолу. Досліджено вплив концентрації кислоти, температури та часу й розроблена кінетична модель процесу та її параметри оцінені на основі експериментальних даних. Отримані нові дані щодо виходу та чистоти глюкоманнану за різних умов.

Ключові слова: глюкоманнан, екстракція, кислотний гідроліз, моделювання, масообмін, кінетика.