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# Production of Sago (*Metroxylon* Sp.) Starch Nanoparticles Using Hydrolysis-High Shear Homogenization (HSH) Method

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**Abstract.** Research on sago starch modification has been carried out to the form of starch nanoparticles. Starch nanoparticles is very potential to be used in the pharmaceutical, cosmetic, bioplastics and paper industries, as surface sizing, biodegradable coatings or adhesives. The technology of nanoparticle production has been quite developed, but there are some disadvantages, such as small yield, long processing time, expensive production equipment, and limited availability. The purpose of this study is to modify the efficient and applicable method to produce starch nanoparticles in the scale of mini plant. Method modification specified is a combination treatment of hydrolysis - high shear homogenization. This method has succeeded to obtain starch nanoparticles with 70% yield, and 36% crystallinity. The particle size obtained ranges from 118.6 nm. The optimal production process is obtained in 24 hours hydrolysis treatment and 3 hours of homogenization. The production cost of starch nanoparticles is 1.430,000 / kg.

## 1. Introduction

Starch is a renewable biopolymer produced from a variety of plants. The availability of starch, such as sago starch, is quite abundant in nature. Types of industries that utilize starch are food, chemical, pharmaceutical, paper, textile and cosmetic industries. Natural starch has a disadvantage as an industrial raw material. Its characteristics (viscosity, solubility, size) cannot merit the industrial requirements. This is what encourages industry players and researchers to continue to develop starch applications in the industrial world in order to increase added value.

One of efforts to increase the added value of starch is to modify it in the form of starch nanoparticles. Nanoparticle technology will improve starch characteristics so that it has low suspension viscosity at relatively high concentrations, and has high binding strength because of large active surface area. Unique new properties will emerge if the material is at the nanoscale due to changes in the functional properties of materials, which related to the changes of its dispersion properties. The technology of starch nanoparticles production has sufficiently developed. In general, nanoparticles production is done by two methods: breaking particles up to nanometer size (top down) and synthesizing very small-sized material (atoms or molecules) to assemble into the desired nanometer size (bottom up).

Hydrolysis is done by strong acids with low concentration. Regeneration methods are produced through precipitation of starch dispersed with organic solvents [1]; [2]; [3] which produce starch nanoparticles. The third method of nanoparticle production is mechanical and thermal treatment with high pressure homogenisation and microfluidizers [4]; a combination of high-pressure homogenization techniques with crosslinking [5], and production with extrusion processes [6]. Nanocrystal starch are produced in hydrolysis of starch using HCl and H<sub>2</sub>SO<sub>4</sub> at 35-45°C. Starch nanoparticles can also be produced from precipitation of complex formation among amylose fractions with hydrophobic components such as n-butanol [1]; [7] ; [2]; [8].



The application of nanoparticle or nanocrystal starch includes reinforcing or filler of synthetic/plastic polymers [9];[10], food additives, biodegradable composites, and drug carriers [11]; [12]; [13] and carriers of active food ingredients [14]; [15]. According to [16] nanoparticles have a very large surface area that makes nano-sized particles more active. In addition, the smaller size makes the binding effectiveness of active ingredients also greater because the active side is more dominant. Starch nanoparticles is also very potential to be used in the paper industry, as surface sizing, coating or biodegradable adhesive [17]. Research to develop starch into nanoparticles (new biomaterials) is still very open.

At present, the production of starch nanoparticles is still carried out in a laboratory scale. Some disadvantages of the previous methods are low yield, long processing time and quite expensive equipment. This causes the availability of starch nanoparticles is still rare in the market and the price is adequately high. Currently, starch nanoparticle products used for industry are BioTRED and Eco-sphere TM. This product is used for the tire industry and starch-based biolates. The method of supplying starch nanoparticles on a mini plant scale with low production costs and high yields is an interesting challenge. One way to overcome this is to modify an efficient and effective method for the production of starch nanoparticles which can be developed to the industrial scale [18].

The objectives of this research are (1) to obtain an efficient and applicable method modification in producing starch nanoparticles from sago in mini plant scale, (2) to obtain an optimal production process, (3) to know the nanoparticles starch characteristics of sago produced from the method. The results of this research are expected to increase the added value and expand the use of sago starch in the industrial world.

## **2. Research Methods**

### **2.1 Materials**

Materials used in this research are sago starch (*Metroxylon* sp.) aquadest, ethanol, NaOH, HCl, whatman 41 filter paper, packaging plastic of starch nanoparticles.

### **2.2 Equipment**

The tools used are magnetic hotplate stirrer, high shear homogenizer (self-designed), glass equipment, analytic scales, spray dryers Merk Buchi B290, vacuum pumps and thermometers. Meanwhile, the equipments used to characterize the starch nanoparticles are Particle Size Analyzer (PSA) Merk Malvern MAL1096681, Scanning Electron Microscopy (SEM) Merk Hitachi S-3400N and X Ray Diffraction (XRD) Merk Xpert Pro Analytical PW30/40.

### **2.3 Methodology**

This research will be conducted in 4 stages. Research phase 1 is the characterization of raw materials. Research phase 2 is a modification of the starch nanoparticles preparation method, which is a combination of hydrolysis (acid) - mechanical (high shear homogenization). Research phase 3 is to test the production of starch nanoparticles. Research phase 4 is the characterization and calculation of the yield of starch nanoparticles.

## **3. Results And Discussions**

### **3.1 Characteristics of Sago Starch**

The results of chemical, physical and functional characterization of sago starch (*Metroxylon* sp.) can be seen in Table 1. The quality standards of sago starch in Indonesia are listed in the Indonesian National Standard SNI 3729: 2008.

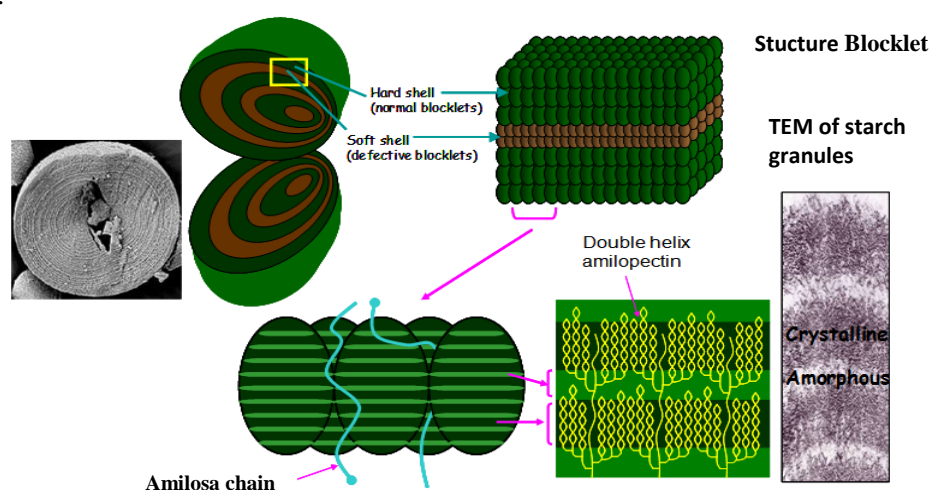
Starch is a glucose polymer with  $\alpha$ -glycosidic bonds arranged into amylose and amylopectin and also contains other ingredients such as lipids and proteins. Amylose and amylopectin components contained in starch granules have different ratios, in which the amylopectin component has higher ratio than amylose. These two components are one of the factors that can influence differences in physical, chemical and functional characteristics of starch. Straight amylose structures tend to be in the amorphous part of starch granules. Meanwhile, amylopectin which can form double helical structure is

responsible for the crystalline part of starch granules. According to Gallant et al., the structure of starch granule is blocklet as shown in Figure 1 [19].

**Table 1.** Chemical, physical and functional characteristics of sago starch

Parameter	Sago	SNI 3729:2008
<u>Chemical:</u>		
Water content (%)	13,75	Max 13
Ash content (%)	0,39	Max 0,5
Fiber content (%)	1,03	Max 0,5
Starch content (%)	85,16	Min 65
• Amylose (%)	28,93	-
• Amylopectin (%)	71,07	-
<u>Physical:</u>		
Form	Elips	-
Granule size (mm)	57,56	-
Fraciton passed 100 mesh (%)	68,65	-
Gelatinization temperature (° C)	85	-
White degree (%)	71,22	-
<u>Functional:</u>		
Solubility (%)	5,36	-
Water absorption (%)	60,38	-

Sajilata et al., suggested that low water content can increase starch crystallinity levels, while high water content causes starch to be more easily degraded by enzymes [20]. Based on the results of the characterization, the water content of the sago starch that will be used have not meet the specified quality standards so that further drying is needed to obtain water content below 13%. Crude fiber content is another minor component found in starch. This crude fiber consists of cellulose, hemicellulose, and lignin. The type of sago starch used has a high fiber content according to SNI 3729: 2008.



**Figure 1.** Structure of starch granules based on the "Blocklet" [19]

If compared to some other types of starch, sago starch granules have relatively large size which reaches an average of 57.56  $\mu\text{m}$  with size distribution 20 - 60  $\mu\text{m}$ . Large granule size indicates the high ability to absorb water in gelatinization. This allows natural starch to have high viscosity.

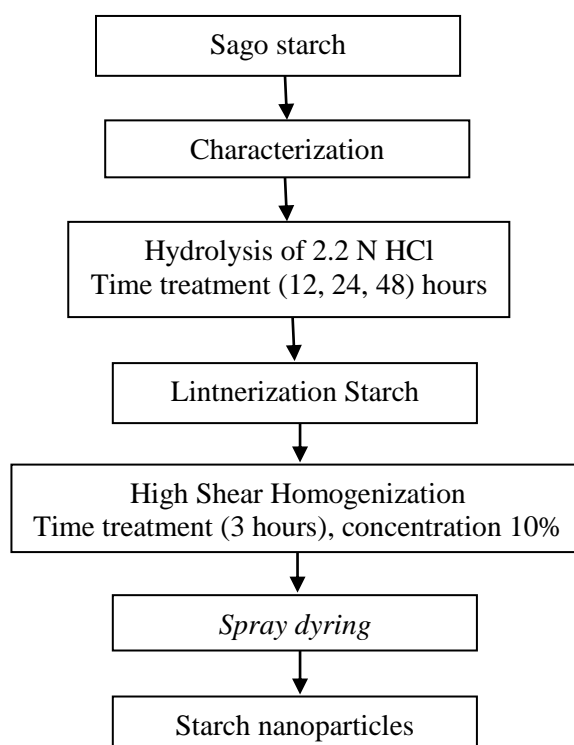
The color of sago starch is brownish white with lower white degree than tapioca starch. The research results of Pei-Lang et al., stated that browning of sago starch was caused by phenol compounds and polyphenol oxidase in the stem. Phenol compounds which play a role in the browning reaction are DL-epigallocatechin gallate and D-catechin. The white degree of starch is influenced by the water used in the grinding process, the duration of precipitation, and the temperature of the drying process [21].

### 3.2 Production of Starch Nanoparticles using Hydrolysis – Mechanical Treatment Method (High Shear Homogenization)

Modification of the method specified is a combination of hydrolysis (acid) - mechanical treatment (high shear homogenization). The method flowchart can be seen in Figure 2. Starch nanoparticles can be produced through two stages; hydrolysis which produces lintnerization starch (crystalline starch) and high shear homogenization.

Hydrolysis is done by low concentration of strong acid, that is 2.2N HCl. Angellier, et al., distinguish three stages of acid hydrolysis: fast, slow, and very slow [9]. The initial stage of acid hydrolysis is thought to hydrolyze amorphous parts in starch granules, while the slow stage is associated with erosion of the crystalline region. The result of this hydrolysis process is crystalline starch or lintnerization starch.

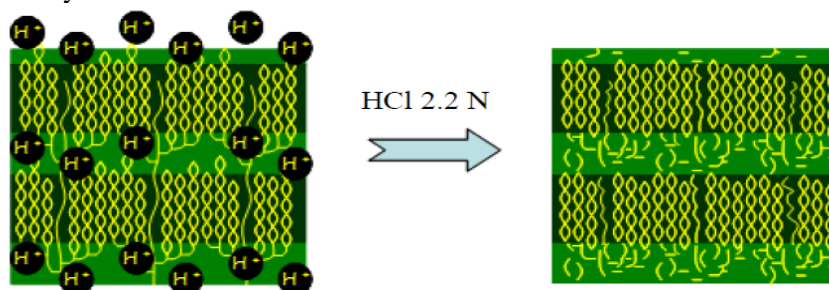
The lintnerization treatment was aimed to degrade the long chain amylose fraction and the branching point of amylopectin found in the amorphous region so that the short chain amylose fraction was produced with lower molecular weight. Lehmann et al., suggested that if the short-chain amylose fraction in starch increases, the more amylose fraction crystallized because the amylose fraction as a linear structure will facilitate cross-linking in the presence of hydrogen bonds so that the amylose structure forms a compact crystallite. With the lintnerization process, it is expected that there will be increasing of crystallinity in the starch produced [22].



**Figure 2.** Flowchart of hydrolysis-high shear homogenization method

An illustration of the amorphous and crystalline area destruction in the lintnerization process is presented in Figure 3. The lintnerization time can affect the level of degradation of the amorphous area

during the hydrolysis process. The longer lintnerization time can increase the rate of destruction of amorphous area by acids, and even will degrade the structure of amylopectin in the crystalline areas that can be reached by acids.



**Figure 3.** Illustration of degradation in amorphous areas during acid hydrolysis [23]

The process of degrading the amylose structure and the branching of amylopectin can affect the yield produced from the lintnerization process, the more structures that are broken into simple sugar that dissolve in the filtrate can produce lower yields. In 12, 24 and 48 hours of time treatment hydrolysis, sago starch has experienced an increasing degradation in amorphous areas along with the duration of hydrolysis process. It can be seen in Table 2 which shows the decrease in the yield value occurred along with the increase of hydrolysis time.

The lintnerization process causes destruction of the amorphous area in starch granules. Amorphous areas are the easier susceptible area to chemical reactions than crystalline areas because the bonds of hydrogen in amorphous areas are weaker than in crystalline areas. The long chain amylose found in the amorphous area is cut off by acid so that it becomes glucose.

The lintnerization process changes the chemical structure of the starch and has succeeded to reduce the size, but this process is not yet able to get starch in nanometer size. Therefore, to produce smaller particles, further processing steps need to be done. Starch particle size reduction can be produced through a mechanical treatment process, which is high shear homogenization.

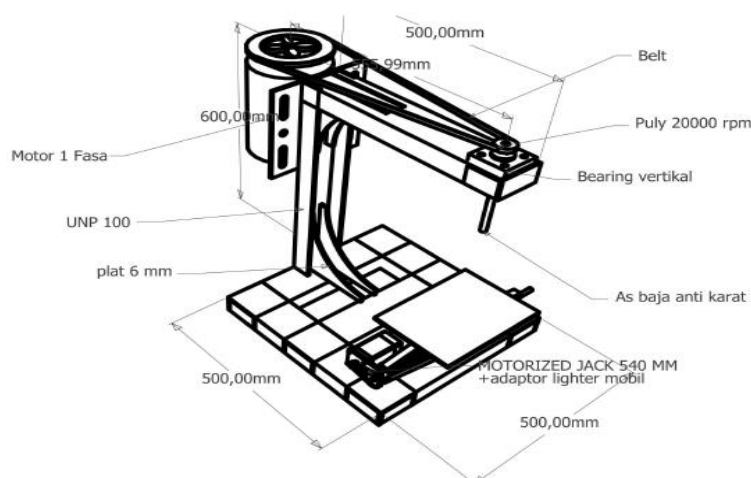
Homogenization is the process of uniformizing particle size in order to maintain the stability of a mixture formed from two phases that cannot be fused. Size uniformity is done by reducing particle size in the dispersed phase [24]. The size reduction process occurs because the force arising from the mechanical treatment given causes the fission to dispersed particles. According to Bylund (1995), in homogenization using a high rotation speed, the fission of particle is caused by the flow of turbulence emerged [25]. The high rotation speed produces many small turbulent streams which break the particles in contact with the flow so that it becomes smaller. The homogenization process is usually conducted with the help of a device called homogenizer.

*Homogenizer* designed in this research is intended to be a pilot plant which is expected to be applied as homogenizer for small-scale industries in the future. The design of the high shear homogenizer tool can be seen in Figure 4. This homogenizer uses a probe with a maximum speed of 21,000 rpm; made of stainless steel; and has function as a stirrer and solves starch particles with faster and more efficient time. Its production capacity is 100 grams / hour.

### 3.3 Characteristics of Starch nanoparticles

#### 3.3.1 Particle Size Analyzer (PSA)

The particle size of produced starch nanoparticles is tested by using Particle Size Analyzer (PSA). To determine changes in starch particle size at each stage of the process, the PSA test is carried out in the hydrolysis and homogenization stages. PSA test results can be seen in Table 2.



**Figure 4.** Design of High Shear Homogenizer Device

**Table 2.** Results of PSA testing with various treatments

Sample	Particle Size (nm)	Yield (%)
Acid hydrolysis:		
12 hours	789.3	80
24 hours	741	74
48 hours	738.1	72
HSH-acid hydrolysis:		
12 hours, 3 hours	86.31 – 480.3	75
24 hours, 3 hours	118.6	70
48 hours, 3 hours	58.93 – 357.5	66

Based on the characterization of raw materials, sago starch has an average size of 57.56  $\mu\text{m}$ . PSA test results show that there is a reduction in starch particle size at the hydrolysis stage, it is followed by a high-speed homogenization step which also succeed in reducing the size of the starch into starch nanoparticles. This shows that the method of hydrolysis - high shear homogenization can reduce the size of sago starch into nanoparticles.

### 3.3.2 X-Ray Diffraction (XRD)

Characterization of X-Ray Diffraction (XRD) is used to analyze the crystallinity of the starch nanoparticles produced by using HSH-hydrolysis method. The crystallinity of starch granules can be seen using the X-ray diffraction pattern method and can be determined by the integration of curves below the top of the amorphous and crystalline areas.

Natural starch changes crystallinity after being treated, such as lintnerization, which acid degrades amylose chains and branching of amylopectin found in amorphous areas so that the crystalline fraction of starch becomes more dominant. This process is expected to increase starch crystallinity. Sago starch has type A crystallinity with 32.9% degree of crystallinity [23]. XRD test results of starch nanoparticle products by using HSH-hydrolysis method can be seen in Figure 5. The calculation results of crystallinity value using the Segal formula based on XRD testing can be seen in Table 3.

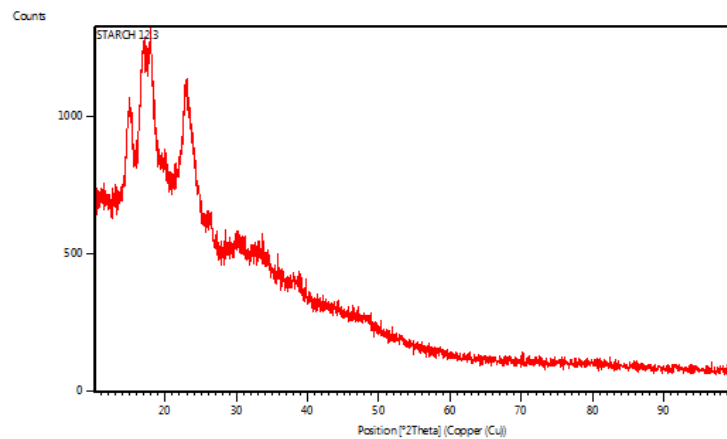
**Table 3.** The crystallinity value of sago starch nanoparticles

Sample	Crystallinity degree (%)
HSH-acid hydrolysis:	
12 hours, 3 hours	36
24 hours, 3 hours	35

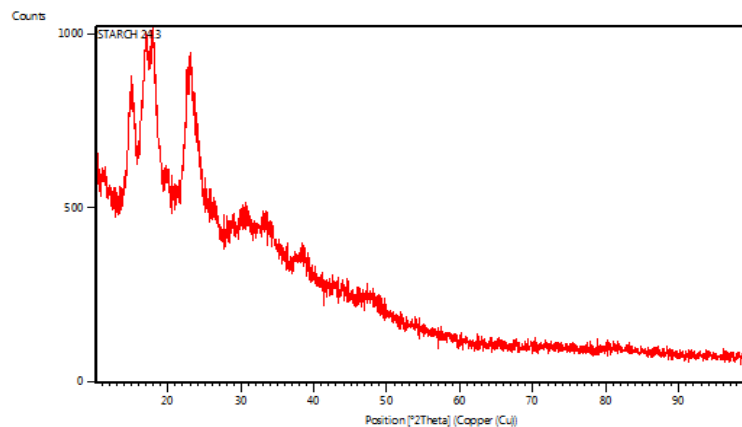
48 hours, 3 hours

36

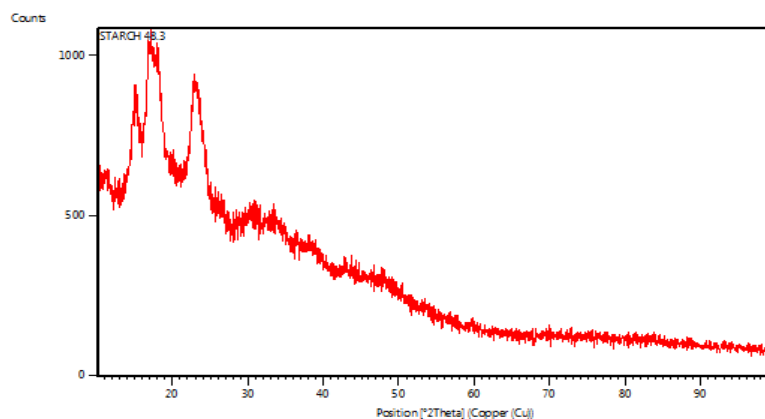
Lintnerization time can affect the degree of starch crystallinity, but does not affect the crystallinity pattern. The crystallinity of starch has increased from its natural starch after being hydrolyzed (lintnerization). After being lintnerized at different times, sago starch has the same crystallinity pattern as its natural starch. This shows that the lintnerization process only causes destruction of the amorphous area to obtain more crystalline starch and does not make structural changes.



(a)



(b)



(c)



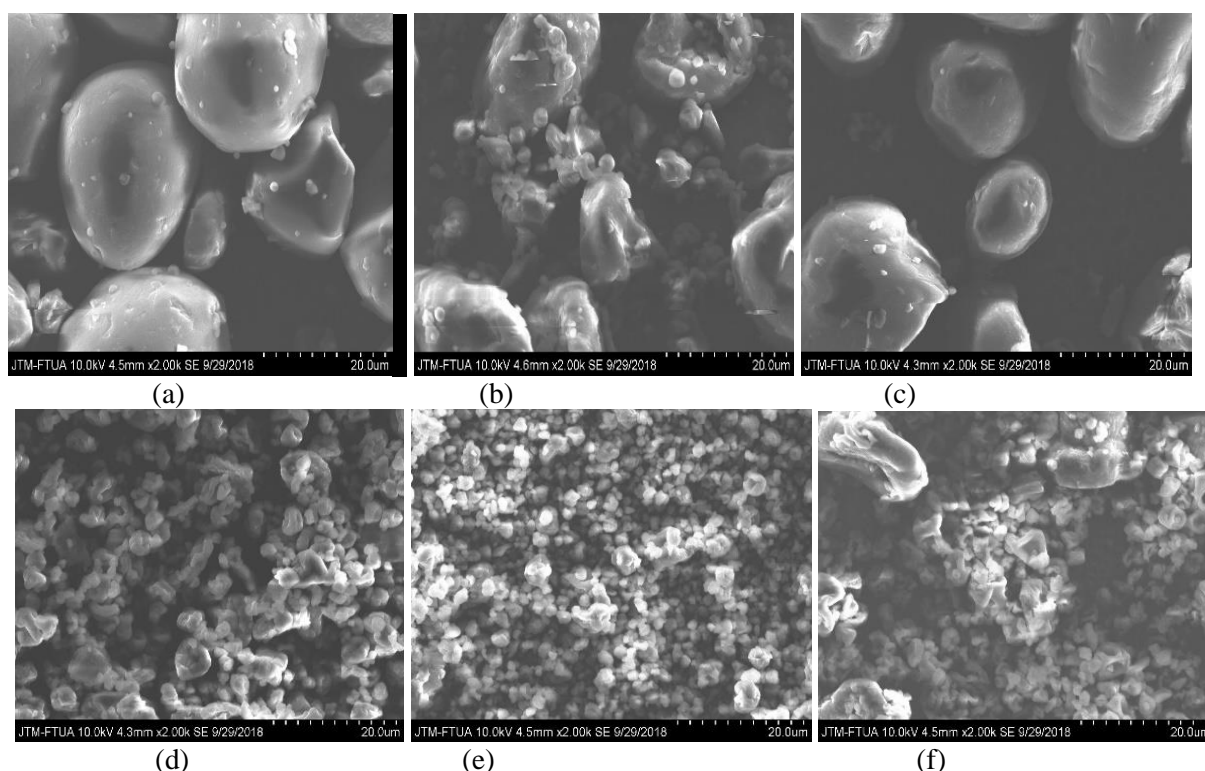
**Figure 5.** XRD test results (a) 12 hours of hydrolysis treatment-HSH 3 hours, (b) 24 hours of hydrolysis treatment – HSH 3 hours, (c) 48 hours of hydrolysis treatment-HSH 3 hours

The analysis results of crystallinity degree indicate that the high-speed homogenization process does not affect the crystallinity degree and crystallinity pattern. This can be seen from the same degree of crystallinity in the three treatments. The increase of crystallinity degree occurs in the hydrolysis stage which is able to increase the crystallinity degree from 32.9 % (original sago starch) to 36% (starch lintnerization).

### 3.3.3 Scanning Electron Microscopy (SEM)

Production of starch nanoparticles is done in two stages: hydrolysis and high-speed homogenization. To see the effect of each step on starch granules, it can be seen in the morphology of the starch granules. Morphology of starch granules can be seen using SEM. SEM test results of starch formed during the process of hydrolysis and homogenization can be seen in Figure 6. Based on the results of SEM analysis, sago starch which has done lintnerization process still has the same shape as its natural starch as shown in Figure 6 (a), (b), (c). At this stage, particle size reduction has occurred from the original starch with a size of 57  $\mu\text{m}$  to 0.7  $\mu\text{m}$ .

Figure 6 (d), (e) and (f) show that the high-speed homogenisation process affects the particle size and morphology. The starch size is smaller than the one produced by hydrolysis. Based on the analysis of starch morphology using SEM, it can be seen that the starch particles after homogenization are still not completely separated and still fused to form lumps. This happens because the starch nanoparticles have many hydrogen bonds on its surface so it tends to merge among the particles.



**Figure 6.** Test results of SEM (a) 12 hours of hydrolysis, (b) 24 hours of hydrolysis, (c) 48 hours of hydrolysis, (d) 12 hours of hydrolysis – HSH 3 hours, (e) 24 hours of hydrolysis - HSH 3 hours, (f) 48 hours of hydrolysis - HSH 3 hours

### 3.3.4 Yield

The yield of starch nanoparticles produced by the HSH-hydrolysis method can be seen in Table 2. The average yield at the final stage of the process reached 70%. This value is quite high compared to several other methods used by previous researchers. Kim et al., have obtained starch nanoparticles for 78% yield using a combination treatment method of hydrolysis-ultrasonication [26]. Liu et al., also succeeded in obtaining starch nanoparticles of 100% yield using high pressure microfluidiser method [4]. Although these have high yield, the methods developed by Kim et al., and Liu et al., are difficult to develop into a production scale (pilot plant). This is because the ultrasonication method is limited to laboratory capacity, while the high pressure microfluidiser method includes physical treatment that requires high energy process with the limited availability and expensive tools.

The yield value in the hydrolysis stage can reach average of 75%. The yield in the homogenization stage decreases about 5% from the previous hydrolysis stage. This decrease is not caused by loss during the homogenization process, but occurs in the drying process using a spray dryer. During the drying process, some of the starch nanoparticles attach to the tube wall of the spray dryer.

Based on the results of product characterization, the optimal production process is in 24 hours hydrolysis treatment and 3 hours homogenization. The starch nanoparticles are then stored in a sealed package in the freezer until the time of use (applied). The final product can be seen in Figure 7.



(a)



(b)

**Figure 7.** Lintnerized starch products (a), starch nanoparticles (b)

## 4. Conclusion and Suggestion

### 4.1 Conclusion

The combination method of hydrolysis - high shear homogenization has succeeded in producing starch nanoparticles efficiently. The optimal production process is obtained in 24 hours hydrolysis treatment and 3 hours homogenization. Characterization results show that starch nanoparticles have been obtained with the size of 118.6 nm, crystallinity degree of 36% and yield of 70%.

## 4.2 Suggestion

Further studies about the efficient drying process of starch nanoparticle production are needed to be conducted. Further studies regarding the optimization of the process by utilizing enzymes are also needed.

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## References

- [1] Kim JY, Lim ST. 2009. *Carbohydrate Polymers*; 76:110.
- [2] Ma X, Jiar R, Chang PR, Yu J. 2008. *Biomacromolecules*; 9(11):3314.
- [3] Kim JY, Yoon JW, Lim ST. 2009. *Carbohydrate Polymers*; 78:626-632.
- [4] Liu D, Wu Q, Chen H, Chang PR. 2009. *Journal of Colloid and Interface Science*; 339(1):117-124.
- [5] Shi A, Li D, Wang L, Li B, Adhikari B. 2011. *Carbohydrate Polymers*; 83:1604-1610.
- [6] Song D, Thioc Ys, Denga Y. 2011. *Carbohydrate Polymers*; 85:208-214.
- [7] Kim JY, Lim ST. 2010. *Carbohydrate Polymers*; 82:264-269.
- [8] Chin SF, Pang SC, Tay SH. 2011. *Carbohydrate Polymer*; 86:1817-1819.
- [9] Anggellier H, Molena-Boisseau S, Dufresne A. 2005. *Macromolecules*; 38(22) : 9161-9170.
- [10] Kristo E, Biliaderis CG. 2007. *Carbohydrate Polymers*. 68:146-158.
- [11] Simi CK, Abraham E. 2007. *Biobrocess Biosyst Eng*; 30:173-180.
- [12] Ortega MJS, Stauner T, Loretz B, Ortega-Vunuesa JL, Baston-Gonzalez D, Wenz G Schaefer UF, Lehr CM. 2010. *J. of Controlled Release*; 141:85-92.
- [13] Saboktakin MR, Maharramov A, Ramazanov MA, Mahkam M. 2007. *Nature and Science*; 5(3):30-36.
- [14] Namazi H, Fathi F, Dadkhah A,. 2011. *Hidrofobically Modifid Starch Using Long-Chain Fatty Acids for Preparation of Nanosized Starch Particles*. Scientical Iranica, Transaction : Chemistry and Chemical Enggineering.
- [15] Jafari Sm, Assadpoor E, Bhandari B, He Y. 2008. *Food Research International*; 41:172-183.
- [16] Chen G, Wei M, Chen J, Huang J, Dufresne A, Changg PR. 2008. *Polymers*; 49(7) :1860-1870.
- [17] Winarti C, T.C. Sunarti, Richana N, 2011. *Buletin Teknologi Pascapanen Pertanian*. Vol. 7 (2). 104-116.
- [18] Kim Hee-Young, Sung Soo Park, Seung-Taik Lim. 2015. *Colloids and Surfaces B: Biointerfaces*; 126. 607–620.
- [19] Gallant D, Bouchet B, Baldwin P. 1997. *Carbohydrate Polymers*. 32 : 177-191
- [20] Sajilata MG, SS Rekha, RK Puspha. 2006. *J Comprehensive Rev in Food Sci and Food Safety*. 5:1-17.
- [21] Pei-Lang, A.T., A.M.D Mohamed, and A.A Karim. 2006. *Carbohydrate Polymers* 63:283-286.
- [22] Lehmann U, Rossler C, Schmiedl D, Jacobash G. 2003. *Starch/Nahrung/Food*. 43:60-63.
- [23] Srichuwong S, Sunarti TC, Takashi M, Naoto I, Makoto H. 2005. *Carbohydrate Polymers*. 60(4):529-538.
- [24] Fellow, A.P. 2000. *Food Proccession Technology, Principles and Practise*. 2nd ed. Woodread.Pub.Lim. Cambridge. England. Terjemahan Ristanto.W dan Agus Purnomo
- [25] Bylund, G. 1995. *Dairy Processing Handbook*. Tetra Pak. Lund, Sweden.
- [26] Kim, H.Y., Han, J.A., Kweon, D.K., Park, J.D., Lim, S.T., 2013. *Carbohydrate Polymers* 93, 582-588.