Modification of Cassava Starch Using Lactic Acid Hydrolysis in The Rotary-UV Dryer to Improve Physicochemical Properties

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Abstract. Food security should be supported in an effort to utilize local products into import substitution products. Cassava starch has the potential to be developed into semi-finished products in the form of flour or starch which does not contain gluten but can inflate large baking process, potentially as a substitute for wheat flour-the main ingredient for making bread. The characteristic of the starch is influenced by the type of starch composition and structure. Natural starch has physicochemical properties i.e. a long time cooking and pasta formed hard. These constraints allow us to modify cassava starch by a combination of lactic acid hydrolysis and drying with rotary UV system. Modified cassava starch is expected to be used as a substitute for wheat flour. The aim of the research which is a combination of lactic acid hydrolysis and drying using a rotary UV system is to examine the optimum operating conditions in the drying process of starch hydrolysis with parameter the physicochemical and rheological properties of modified cassava starch. The initial process study is to hydrolyze cassava starch using lactic acid. Furthermore, hydrolyzed cassava starch is then dried using UV light in the rotary dryers system. There are a variety of changing variables, i.e. time of irradiation cassava starch-lactic acid hydrolysis products in the rotary UV light and air drying temperature. The research results show that modified starch has a better characteristic than the natural starch. From the analysis, the best point of swelling power, solubility and baking expansion is consequently 15.62 g/g; 24.19 %; 2.21 ml/gr. The FTIR result shows that there is no significant difference of the chemical structure because the starch modification only change the physical characteristics. From the SEM analysis, we can know that the size of the starch's granule changes between the natural starch and the modified starch..

1 Introduction

Starch is a mixture of the two polysaccharides with amylose as straight chain and amylopectin as branched chain [15]. Various kinds of starch have different properties depending on the length of the chain of carbon atoms as well as a comparison between the straight and branched molecules chains [7]. Generally starch contain of 15-30% amylose starch, 70-85% amylopectin and 5-10% others material [26].

Starch that commonly used is a natural starch without treatment modification (native starch) therefore, a natural starch has little additional materials [20]. Natural starch has a limited solubility in water and susceptible starch gel syneresis (separation of water from the gel structure) due to retrogradation starch. Modified starch is a starch that has done physical treatment, chemical or a combination that aims to change one or more of the properties of starch [4]. Starch modification changes the properties of starch which are less profitable so that it can be used more widely. Some properties of starch that

can be changed is the gelatinization temperature, gelatinization characteristics during the process, and starch resistance to high temperature.

This experiment focused on the combination of lactic acid hydrolysis process with the rotary drying in addition with UV light on cassava starch, so that the modified product is expected to have properties that almost the same with flour.

Experiment on modification of cassava starch using combination process lactic acid hydrolysis and microwave heating has been conducted with the results that the physicochemical and rheological properties of modified starch changed significantly compared to the native starch [17]. Combination process method of lactic acid hydrolysis and hydrogen peroxide oxidation for cassava starch modification also gives results on improvement in baking expansion of modified starch and showed that the modified starch can substitute wheat flour in optimum condition process [18].

The experiment about combination of chemical and physical modification of cassava starch using lactic acid

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and ethanol under oven and solar drying has also been conducted with results that indicate that the high concentration of lactic acid and ethanol will increase the swelling power of modified starch. It was also determined that starch modified by using esterification and drying using the solar drying method is more effective than using oven drying [19].

The focus of this experiment is to examine the change in physicochemical and rheological properties of modified cassava starch compared to the natural starch by using the combination process of lactic acid hydrolysis and uv-light drying.

2 Materials and Methods

2.1 Materials illustrations

Tapioca starch by the brand of Mount Agung was obtained from Semarang (Indonesia). Other chemicals which were used as additives for process analysis with analytical grade, were obtained from PT. Merck (Germany).

2.2 Preparation of Lactic Acid Solution

Lactic acid solution was prepared by dissolving lactic acid 1% w / w in 250 ml of water. The solution was left for overnight to make more active lactic bacteria.

2.3 Experimental Procedure

Tapioca starch in accordance with the variable (100 g and 200 g) was dissolved in the lactic acid solution that has been made before. Stir well for 15 minutes at room temperature. After that the solution was filtered using filter paper and cooling it by winding it up until the water content is reduced. The maximum allowable water content contained in the starch before drying is about 40%.

After the hydrolysis process, the drying process is carried out using UV rotary. Before we use, UV rotary tool prepared in advance. Turn the rotary tool, set the temperature (40 ° C, 50 ° C, 60 ° C, 70 ° C) and speed (10 rpm, 20 rpm, 30 rpm, 40 rpm) in accordance with the desired variable. Once ready, the dried tapioca will gradually dry up and in accordance with the expected results.

2.4 Swelling Power

Tapioca starch sample that has been dried taken 0,1gr and dissolved in 10 ml of distilled water. Then the solution is heated using a water bath with a temperature of 60 ° C for 30 minutes. Supernatant was separated using a centrifuge at a speed of 2,500 rpm for 15 minutes. Swelling power calculated by the formula:

$$\text{swelling power} = \frac{\text{weight pasta}}{\text{weight of dry sample}} \quad (1)$$

2.5 Solubility

Tapioca starch sample that has been dried taken 1 g and dissolved in 20 ml of distilled water, then the solution is heated in a water bath at a temperature of 60 ° C for 30 minutes. The supernatant was separated using a centrifuge at 3000 rpm for 20 minutes and then take 10 ml to be dried in the oven and the dry sediment weight recorded.

$$\% \text{solubility} = \frac{\text{weight of dry sediment}}{\text{volume of supernatant}} \quad (2)$$

2.6 Viscosity

The viscosity measurements carried out simultaneously by means of heating and stirring suspension of starch that is placed on a container on the instrument. The temperature of the sample to be analyzed very decisive change in the viscosity profile of a mixture.

2.7 Baking Expansion

Modified tapioca starch mixed with 12.5 grams of milk, butter, salt, sugar, eggs, water, yeast stirred with a mixer on medium speed for 5 minutes. Suspension (mixed dough) were weighed (50 g) was added to muffin tins and baked in the oven for 25 minutes at a temperature of 135°C. The cold muffin then weighed and measured to determine the specific volume (baking expansion) in ml / gram.

2.8 SEM Analysis

Scanning Electron Microscope (SEM) is a method in which an electron microscopic analysis produced the drawn sample by scanning the sample using a focused beam of electrons. These electrons interact with the electrons in the sample, produced various signals that can be detected as topography information about the sample surface and also its composition. SEM is able to get the highest resolution smaller than 1 nanometer.

2.9 FTIR Analysis

FTIR is a technique for analyzing organic materials, polymers, coatings, gas, biological samples, inorganic materials, and minerals. FTIR working principle is to emit infrared rays in the sample, after that, it will be shown in graphs consisting of absorbance and also the length of the wave. Cluster analysis contained in the sample was done by interpretation infrared ray absorption spectrum of the results by the sample.

Table 1. The Value of Swelling Power, Solubility and Baking Expansion of Starch as a Result of Lacto Acid Hydrolysis in the Rotary-UV Dryer

No	Variables			Swelling Power (g/g)	Solubility (%)	Baking Expansion (ml/g)
	Playback Speed (rpm)	Temperature (°C)	Capacity (g)			
1	10	40	100	15,62	10,22	1,69
2			200	11,50	15,64	1,59
3		50	100	15,44	11,16	1,67
4			200	12,90	20,22	1,72
5		60	100	12,67	11,16	1,28
6			200	12,61	11,70	1,32
7		70	100	13,70	10,65	1,43
8			200	12,89	10,74	1,06
9	20	40	100	12,19	8,04	1,29
10			200	13,78	13,84	1,62
11		50	100	10,58	10,13	1,61
12			200	12,81	11,72	1,91
13		60	100	11,00	11,67	1,54
14			200	12,02	24,19	1,83
15		70	100	12,73	6,57	2,01
16			200	12,09	19,00	1,97
17	30	40	100	7,50	3,52	2,01
18			200	12,71	19,27	1,81
19		50	100	8,46	6,63	1,82
20			200	13,49	11,36	1,78
21		60	100	7,25	5,39	2,14
22			200	13,09	16,04	1,83
23		70	100	12,01	21,13	1,77
24			200	13,01	18,19	1,56
25	40	40	100	11,50	14,65	2,21
26			200	14,92	9,63	1,71
27		50	100	15,06	12,21	2,00
28			200	11,95	15,01	1,84
29		60	100	10,58	11,32	1,90
30			200	12,79	8,68	1,54
31		70	100	15,73	8,94	1,98
32			200	14,95	13,62	1,68

3 Results and Discussion

3.1. Effect of Playback Speed, Capacity Dryer Feed and Air Temperature on Rotary UV on Swelling Power Value

From Table 1 it can be seen that the average power of modified starch swelling ranged from 7.25 to 15.73 g/g. In general, the swelling power of the modified starch is higher than natural starch which swelling value of 12.51 g/g. The increase in value is due to the swelling power when starch is heated with water media, the starch granules swell and open the resulting presence of heat energy. This heating also resulted in the weakening of the hydrogen bonds that connect between amylose-amylopectin, amylose-amylose and amylopectin-amylopectin [16]. Compactness starch granules will decrease and amorphous regions will be cut off, resulting in the hydration water by the starch granules. Most of amylose molecules will come out of the starch granules and water soluble. According Flenche [6], when the starch molecule is completely hydrated molecule will

spread to the media on the outside and the first out is to have a short chain amylose. And the higher of the heating temperature, the more amylose molecules that will come out of the starch granules. In addition, with the increase in temperature of the water molecules have higher kinetic energy so that makes it easier to penetrate the starch granule [9]. Hydrated starch will continue to expand as a result of the entry of water into the starch granules and trapped in the molecular composition of amylose and amylopectin [9].

Shown in Table 1 that there are 12 variables that have a swelling power value is smaller than the value of natural starch swelling power. Impairment swelling power is not due to the leaching of amylose due to heating temperature. Because it can be seen that the temperature of the heater is used instead of above the gelatinization temperature, but the cause that allows the use of a temperature of 40 ° C-70 ° C is the stretch between constituent molecular bonds of starch and starch granules opening. Thus, the drying process occurs retrogradation, where the water that goes into the granules will come out as a result of the drying

temperature, so that the bonding between amylose stretched back docked result in swelling power decreased [16].

In addition to the effects of temperature, from table 1 it can be observed on the effect of rotation speed on UV rotary tool used. Swelling power at variable values 4, 12, 20, 28 is equal to 12.9 g / g; 12.81 g / g; 13.49 g / g and 11.95 g / g. Rotational speed proved to be very influential on the value of the modified starch swelling power. This is consistent with research conducted by Bhattarai *et al* [3] which concluded that the rotational speed of rotary no significant effect on heat transfer. This heat transfer effect on the hydration of starch granules. Therefore, the value of swelling power that the difference was not significant in the treatment of different rotational speed.

Subsequent conditions the difference is the capacity of the feed is entered in the UV rotary dryer. Swelling power is strongly influenced by the bonds between the molecules making up the starch. The weight ratio of starch affect the value of swelling power. The highest value of swelling power for 31 variable that is equal to 15.73 g / g. It shows that the smaller the weight ratio of starch that is included as bait, then the reaction will run better [24].

Baking expansion or so-called starch swelling power is incident volume and maximum weight gain experienced by the natural starch in water. In addition, the swelling power is power that characterize the nature and development of a material that is related to the strength of flour [26]. Swelling power is due to the non-covalent bonding between molecules of starch. Swelling power occurs in the amorphous regions of starch granules are influenced by amylopectin. The number of high amylopectin starch resulted in an increase in the value of swelling. In addition, there is a negative correlation between swelling power and amylose content, where the swelling power decreases with increasing amylose content [14]. Amylose can form a complex with lipids and inhibit swelling value. According Moorthy [11] there are several factors that determine the value of the swelling power of starch, amylose-amylopectin ratio is the distribution of molecular weight and chain length and degree of ramifications. When starch is inserted into the cold water, the starch granules absorb water and have swelling. However, a limited amount of water absorbed only about 30% [25].

3.2 Effect of Playback Speed, Capacity Dryer Feed and Air Temperature on Rotary UV on Solubility Value

From Table 1 can be seen that the average solubility of modified starch ranged from 3.52 to 24.19%. In general, the solubility of the modified starch is higher than natural starch which has a solubility value of 10.01%. The increase in solubility of modified starch is caused by the structure of starch which undergo stretching due to the interaction of water and heat. The heat will weaken the hydrogen bonds so that the structure of starch mainly

amorphous regions become stretched [16]. Amorphous region is an area that has a lot of branching amylopectin and amylose molecules. Amorphous region is the part that can easily expand and undergo chemical reactions such as hydrolysis by acid or reacted by a functional group [8]. When stretched starch structure, starch will be easier to absorb water and have swelling (swelling power) resulting in increased solubility.

It can be seen from Table 1 that there are 8 variables that have values less than the solubility of natural starch. In variable 9, 15, 17, 19, 21, 26, 30, 31, solubility values of 8.04%; 6.57%; 3.52%; 6.63%; 5.39%; 9.63%; 8.68% and 8.94%. It happened because of retrogradation happened more. At higher temperatures stretching between bonding in amorphous regions are more prevalent. When there retrogradation when drying takes place, it would be a lot closer ties back so that the solubility is lowered [16]. According Olayinka *et al* [13] will increase the drying process chain association between amylose-amylose starch and amylose-amylopectin in amorf area, separate amylose and amylopectin fractions, increasing the cohesiveness of the material in the granules due to the interaction and pressure. In the process of heating the hydrogen bonds that stabilize the double helix structure in crystalline disconnected and replaced by water [12].

In addition to the heating temperature affect the solubility of the modified starch, starch weight ratio also affects the solubility value [24]. The smaller the weight ratio of starch, the reactions were run better and result in starch solubility tends to decrease. In contrast, when the weight of starch bigger then the reaction is unfavourable and solubility tends to increase. This is consistent with the results of research in which of the above table 9 it can be seen that the greatest solubility values contained in 15 variables with the value of the solubility of 24.19%.

According Zulaidah [26] solubility is the ability of a substance to be absorbed in water so as not to form an emulsion. The solubility of starch is one of the most important properties and are useful in a variety of industrial applications both food and non-food. Solubility values is also important to know to determine the suitability for conversion of dextrin in a variety of products. Each starch has a solubility that is different, then the solubility properties is one way to determine the type of starch which one to use. Factors influencing the solubility is the degree of polymerization (DP) and the size of the molecule. Temperature is also an important factor in determining the value of the solubility of starch.

3.3 Effect of Playback Speed, Capacity Dryer Feed and Air Temperature on Rotary UV on Baking Expansion Value

From Table 1 above it can be seen that the average Baking expansion of modified starch ranged from 1.06 to 2.21 ml / g. In general, the solubility of the modified starch is higher than natural starch which has a solubility value of 1.51 ml / g. The increase in the value of this expansion baking indicated by the increasing number of

water lost during the baking process. As the starch is gelatinized by heating, the water is absorbed on the starch molecules evaporate and cause high pressure which produces thrust for greater expansion [2]. According Moorthy [11], modified tapioca starch expands the capability greatly influenced by the amylose content. Where amylose can bind water well, so that the higher levels of amylose in the starch obtained dough will be easier to expand. Level developers are also influenced by the ratio of amylose and amylopectin (Martz, 1992). With acid modification, expansion baking results greater than usual tapioca caused a change in the rheological properties and its physicochemical.

Baking process is old technology that is still used and continue to be developed to produce bakery products. The term is not only used in the baking of bread making, but for all products that use flour (flour) as the main ingredients and sources of thermal energy through the process of radiation or convection. Expansion baking measurement process is done by making a dough and then performed the heating process. In the baking process is a physical phenomenon, chemistry, and biology that determines the quality of a product. Heat transfer and mass transfer occurs continuously and interconnected. In the process of baking, heat transfer occurs as a combination of conduction, convection or radiation to the dough (dough). With the heat transfer, mass transfer can then occur based on four stages, namely (1) Evaporation of water, (2) the movement of water into the gas phase, (3) Condensation water and (4) Diffusion of water [22]. In addition to the heat generated by the oven in the baking process, UV radiation on the hydrolysis process also affects the characteristics of modified starch in baking expansion. Reaction of energy UV radiation causes partial depolymerisation of amylose molecules and form a new bond with the hydrogen, which causes water to be more easily absorbed [21]. Water is absorbed at any starch granules will make the starch granules swell and coincident with each other thereby increasing the ability to expand flour.

3.4 Effect of Playback Speed, Capacity Dryer Feed and Air Temperature on UV Rotary for SEM analysis

SEM (Scanning Electron Microscope) is a method in which an electron microscopic analysis produced the first sample by scanning the sample using a focused beam of electrons. SEM consists of an electron absorption which produces an electron beam at an accelerated voltage of 2-30 kV. The electron beam is passed on some electromagnetic lens to produce an image size <10 nm in the samples shown in the form of a photographic film or tube into the screen. These electrons interact with the electrons in the sample, resulting in a variety of signals that can be detected as information on the sample surface morphology and composition. SEM is suitable for use in situations that require observation rough surface with magnification 20 times to 500,000 times.

Observations granules are very important for some applications [23]. According Moorthy [10] the size

distribution of starch granules depends on the source and type of starch produced. In general, starch granules are round and oval. Granule size show large variation is about 5-40 μm with round and oval shapes. Starch granule-shaped bowl (cup) and is very compact, but the modification process will break down the starch components into components that irregular shape [11].

Observations granule size is used SEM that shown in 1500 times. The sample used in this analysis is a modified starch and starch that has not been modified. Samples were analysed by using SEM has a variable rotation speed, temperature and UV rotary capacity. It can be seen that the size of the granules and granular form of each sample is greater than the starch that has not been modified. Size and shape of the sample other sample did not have a very significant difference that can be seen in Figure 1 - figure 5.

Fig. 1. SEM Analysed (1500x) for starch modified with speed of rotary UV is 40 rpm, temperature 40°C and feed capacity is 100 gr

Fig. 2. SEM Analysed (1500x) for starch modified with speed of rotary UV is 30 rpm, temperature 60°C and feed capacity is 100 gr

Fig. 3. SEM Analysed (1500x) for starch modified with speed of rotary UV is 20 rpm, temperature 70°C and feed capacity is 100 gr

Fig. 4. SEM Analysed (1500x) for starch modified with speed of rotary UV is 40 rpm, temperature 50°C and feed capacity is 100 gr

Fig. 5. SEM Analysed (1500x) for natural starch

3.5 Effect of Modified Tapioca Starch with Lactic Acid Combination and Drying UV Rotary Against sample analysis results using FTIR (Fourier transform infrared spectroscopy)

FTIR analysis is an analysis method using the instrumentation tool that aims to determine the functional groups contained in a sample by using a beam of infrared waves with a specific wavelength. The results

analysis is shown by read waveforms with peak absorbance wavelength as indicate a specific functional group. In Figure 6 (a), (b), and (c) the results of analysis of samples using FTIR. In Figure 6 (a) and (b), FTIR analysis using infrared rays with a wavelength between the ranges of 1000-3500 cm⁻¹. In the picture 1 look at specific wavelengths produce specific wavelength absorbance peaks indicating the presence of specific functional groups. From the data results shown that the modified starch and pure flour has the same functional group structure, other than that of Figure 6 (c) looks waveforms and absorbance between pure and modified tapioca nearly equal. The same functional group because the main constituent components of starch are amylose and amylopectin [5] and lactic acid hydrolysis modification process combined with UV radiation causes the breaking of the bond only amylopectin to form amylose [2]. It is this factor that led to the results and interpretation of data from the absorbance images were formed there was no significant change between pure and modified tapioca, in the absence of chemical reactions that form the new product compounds. In addition to UV radiation is generally more cause physical changes such as decreasing levels of water compared to chemical changes as well as a decrease in the degree of crystallization [1].

4 Conclusion

Based on observations and data from the research and experiments, obtained some conclusions below:

1. Increasing drying temperature will results in increase of the solubility and baking expansion meanwhile the swelling power value will decrease.
2. Lowering the dryer feed capacity will decrease the swelling power and solubility value while the baking expansion increase. The smaller the amount of starch inserted, the hydrolysis process will be more effective.
3. Rotational speed is not very influential in changing the physicochemical and rheological properties of the modified starch since it has no significant effect on the mass and heat transfer during drying process.
4. Modified cassava starch has better properties in comparison with the starch prior to modification. Modified starch has lower swelling power value but higher solubility and baking expansion than natural starch. FTIR analysis shows no change in chemical structure of starch while SEM analysis shows change in its physical characteristics..

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Fig. 6. Results of analysis of samples using FTIR. (a) and (b): FTIR analysis using infrared rays with a wavelength between the ranges of 1000-3500 cm⁻¹; (c): waveforms and absorbance between pure and modified tapioca.

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