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Preface

Proceedings of AESAP 2017 contains papers presented in technical session of the 2nd International Conference on Agricultural Engineering for Sustainable Agriculture Production, held at Bogor Agricultural University (IPB) in 23-25 October 2017.

This proceedings consists of 48 papers presented in the technical session of the conference. The papers cover a broad area in Agricultural Engineering. The papers discuss the topics in postharvest and food engineering, energy and environment, land and water resources engineering, system and management in agriculture, instrumentation and monitoring system, and agricultural machinery.

We would like to thank all authors for their efforts in preparing their papers. A great appreciation is also given to the reviewers for their assistance in reviewing the manuscripts. Special thanks to secretariat members for their assistance in formatting the layout of the proceedings.

Dr Desrial
Chairman of AESAP 2017

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Effect of Agitation in Alkalization Process on the Characteristics of Sodium Carboxymethyl Sago and Cassava Starches

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Effect of Agitation in Alkalization Process on the Characteristics of Sodium Carboxymethyl Sago and Cassava Starches

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Abstract. Sodium carboxymethyl starch (Sodium CMS) is a modified starch prepared by two successive processes, alkalization and etherification. Alkalization will change the activated hydroxyl group of starch to more reactive alkoxide (St-O$^-$), and then carboxymethyl group will substitute the hydroxyl group into sodium CMS. This research investigated the effect of agitation (1000 rpm of stirring and 4000 rpm of homogenization) in alkalization process to the modification of native starch into sodium CMS. Cassava and sago starches were mixed with sodium hydroxide (1.8 and 1.9 moles per mole anhydrous glucose units). The combination of NaOH and homogenizing gave the highest degrees of substitution for cassava (DS 0.73) and sago (DS 0.55) starches. The sodium CMS characteristics (paste clarity, water and oil absorption capacities, solubility, swelling power) were a function of mixing method but not on the amount of NaOH used.

1. Introduction

Starch is one of natural polymers that has been used in food and non-food applications. However, the utilization of native starch is limited in physical and chemical properties, since it is insoluble in cold water, easily degraded in high temperature, has low paste clarity and low stability. A common way to overcome these weaknesses is to modify the molecular structure of starch by physical, chemical, and or a combination of both treatments, which will improve the properties of native starch [1]. Modification of starch can be carried out by cleavage the molecular structure, rearranging the molecular structure, oxidation or substitution of the chemical group on the starch molecule [2], changing the chemical structure through D-glucopyranosyl starch linkage which consists of anhydrous glucose units (AGU). Carboxymethylation is one method of modification by substitution of the starch molecule, which produces starch with low gelatinization temperature, high solubility, and high shelf life. The carboxymethylation process takes place by substituting the native starch hydroxyl group (-OH) with the carboxymethyl group (CH_2COO-) to produce Na-carboxymethyl or carboxymethyl starch (CMS)[3]. The utilization of Na-carboxymethyl starch is used as a disintegrant in the pharmaceutical industry [4] as well as sizing and printing agent in the textile industry [5-6].

Carboxymethylation takes place through two stages, namely alkalization and etherification. The Na-carboxymethyl starch can be produced by the reaction between native starch and sodium monochloro-acetate (SMCA) by induction of NaOH [7]. Alkalization stage uses a strong base which converts an activated starch hydroxyl group and transforms it into a more reactive form of alkoxide (St-O-) [3]. The etherification process is conducted in the second stage by substituting the carboxymethyl group of SMCA with alkoxide and producing Na-carboxymethyl starch.

The formation of Na-carboxymethyl starch can be detected through the degrees of substitution (DS) produced. Factors that affect the production of Na-carboxymethyl starch include starch type, NaOH, and SMCA concentration. The alkalization stage also influences Na-carboxymethyl starch production. Agitation at this stage will determine the effectiveness of alkalization to activate the starch carboxyl group. Hasanudin [8] states that more collisions between molecules of a substance will cause the reaction to take place more quickly. Mixing can also expand the contact area so as to increase the chance of collisions between molecules. Each type of agitation will produce different reaction rates. Studies on the optimum concentrations of NaOH and SMCA have been conducted previously [3]. The type of starch used will influence the different characteristics of Na-carboxymethyl starch [3, 9].

This study aims to investigate the effect of agitation and mixing (stirring and homogenization) in the alkalization stage and the concentration of NaOH used on the characteristics of the Na-carboxymethyl starch produced from sago and cassava starches.

2. Materials and method

2.1. *Production of Na-Carboxymethyl Starch*

Production of Na-carboxymethyl starch is carried out based on Ref. [3] with slight modifications. The process was divided into two successive processes, alkalization and etherification (carboxymethylation).

2.1.1. Alkalization process. Cassava and sago starch were obtained from small industries in Bogor. Starch was dried and sieved to pass 100 mesh, and its moisture content determined for calculating the number of chemicals used in the reaction. About 50 g of starch is suspended in isopropanol with starch ratio: isopropanol 1:14 (w: v). Two types of agitation were used in this experiment, (1) hot magnetic stirrer with 4 cm magnetic bar and agitation speed of 1000 rpm and (2) Ultra Turrax homogenizer with 4 cm of rotor diameter and agitation speed of 4000 rpm. The suspension was then added NaOH at a ratio of 1.8 - 1.9 moles/mole of AGU (anhydroglucose unit) and mixed for 20 minutes at 40°C. Viscosity and density of each mixture was measured for determining the Reynold number of fluids

2.1.2. Carboxymethylation Process. The reactor used consists of a three-neck flask with reflux. Sodium monochloroacetate (SMCA) was added with a ratio of 1.5 moles/mole AGU. Continous stirring at 250 rpm was continued for 3 hours after the addition of SMCA with the reaction temperature kept constant at 40°C. After the mixing process, the pH value of the medium was set in the range pH 5.5 - 6.5 by adding 50% HCl solution to stop the substitution reaction process. The formed Na-carboxymethyl starch was washed with 85% ethanol and filtered until the filtrate gave a negative response to the silver nitrate solution indicative of the absence of SMCA. The Na-carboxymethyl starch is then dried with oven at 60°C.

2.2. *Characterization of Na-Carboxymethyl Starch*

Etherification parameters; the degree of substitution (DS) and reaction efficiency (RE) were determined according to ISO 11216-1998 method [10]. Characterization of Na-carboxymethyl starch solubility and swelling power, water and oil absorption capacities, and 1 % paste clarity at 650 nm were conducted with slight modification [11].

3. Results and discussion

The starch used in this study has amylose content of 25.12% for sago and 19.15% for cassava. Ref. [14] states that sago starch contains 27% amylose and 73% amylopectin, whereas according to Ref. [15], cassava amylose component was 17% and 83% amylopectin, which is in reasonable agreement with our findings. The amylose and amylopectin ratio will affect the characteristics of the Na-carboxymethyl starch formed. Amylose tends to be easier to swell when compared with amylopectin and this helps the distribution of chemical compounds into starch granules.

3.1. *Agitation and flow pattern in alkalization process*

The first step is alkalizing with NaOH as a promoter; therewith producing alkaline starch. Isopropanol serves as a reaction medium and will dissolve minor components such as fiber, ash, fat, and protein. The alkalization step is an opening step for activating the starch hydroxyl group (St-OH) into a negatively charged alkoxide group [3]. Repulsive force of the negative charge will make the starch granules swell [16] thus facilitating diffusion of chemicals into the starch granules [3].

Swelling is rarely a spontaneous process, and requires the input of energy, usually supplied by mechanical shear provided by various types of mixers; in this research, a magnetic stirrer and rotor-stator homogenizer are used. It is important to match the agitator and agitation condition to the characteristics of product; therefore, dimensionless analysis is used, as described in table 1. Cassava starch produced higher viscosity and swelling capability compared to sago starch, as well as low density of mixture. It is expected that these properties will be beneficial in the etherification process [17].

Table 1. Effects of agitation types and starch mixture to the Reynolds Number (N_{Re})

Type of agitation	Viscosity (Pa.s)	Density (kg/m^3)	Ø impeller (m)	Speed (rpm)	N_{Re}
Cassava Starch					
Stirring	0.12	857.35	0.04	1 000	11 431
Homogenizing	0.12	857.35	0.04	4 000	45 725
Sago Starch					
Stirring	0.02	876.05	0.04	1 000	70 084
Homogenizing	0.02	876.05	0.04	4 000	280 336

The results of N_{Re} calculation (table 1) for each type of stirring or agitation using both cassava and sago starch indicate a Reynolds number over 4000, which is indicative of turbulent flow [18] that is stronger in the homogenizer than in the magnetic stirrer.

3.2. *Characteristics of Na-Carboxymethyl Starch*

The alkalization stage weakens the alpha-helix in starch and breaks down the crystalline structure [16], which can facilitate solvent and SMCA entering the starch granules and substituting the alkoxide group with the carboxymethyl group from SMCA [17].

Table 2. Substitution parameters for carboxymethyl starch production

Parameter	Magnetic Stirring		Homogenizing	
	Moles of NaOH per mole AGU			
	1.8	1.9	1.8	1.9
Cassava Starch				
Degree of substitution	0.50 ± 0.02^a	0.53 ± 0.01^a	0.79 ± 0.02^b	0.82 ± 0.03^b
Reaction Efficiency (%)	33.27 ± 1.39^a	35.53 ± 0.68^a	52.56 ± 1.55^b	54.70 ± 1.94^b
Sago Starch				
Degree of substitution	0.54 ± 0.02^a	0.55 ± 0.02^a	0.70 ± 0.01^b	0.73 ± 0.02^b
Reaction Efficiency (%)	35.90 ± 1.63^a	36.93 ± 1.60^a	47.18 ± 0.97^b	48.60 ± 1.06^b

*Means within a row related to particular parameter with the same superscript letter are not significantly different as α=0.05 confidence level.

3.2.1. The degree of Substitution and Reaction Efficiency. The degree of substitution (DS) is the average number of substituents per anhydroglucose unit (AGU). Each AGU contains three hydroxyl groups, therefore the maximum DS value obtainable is 3. The degree of substitution in carboxymethylation of starch is defined as the average number of starchy hydroxyl groups substituted by the carboxymethyl group [19]. The factors that affect DS and are investigated here are starch type and amount of alkaline used; other factors can be substituent concentration, reaction temperature, and time, type of solvent and water content (see table 2).

The results of DS measurements (table 2) showed a medium degree of substitution (DS 0.50-0.82) on both sago and cassava starches, and the amount of NaOH concentration added does not affect the effectiveness of the alkalization reaction. This fact is related to the statement of Ref. [3], that the increasing of NaOH concentration in the reaction will increase the DS value. The higher NaOH concentration used will make the etherification reaction better because of the increased reactivity of the alkali starch to SMCA used in the reaction. The DS value for samples prepared with the homogenizer are higher than when mixed with a magnetic stirrer. During homogenization smaller droplets are made that are more reactive, leading to more reactive alkali starch groups so that etherification reaction can run more optimally.

3.2.2. Paste Clarity. The clarity level of starch paste is positively correlated with the swelling of starch granules (table 3); high swellability increasing the clarity of pastes [20]. Table 3 shows that clarity of Na-carboxymethyl starch pastes is higher than for native starch. The starch produced using a magnetic stirrer tends to have higher clarity than those produced using a homogenizer; the differences between cassava and sago are very small. Homogenization will cause the expansion of the amorphous regions resulting from the alkalization step which is positively correlated with water and oil absorption capacity.

Table 3. Physico-chemical characteristics of Na-carboxymethyl starch

Parameter	Native Starch	Magnetic Stirring		Homogenizing	
		Moles of NaOH per mole AGU			
		1.8	1.9	1.8	1.9
Cassava Starch					
1% Paste Clarity (%T)	81.03 ± 0.21^{a}	98.05 ± 0.48^{c}	97.58 ± 0.49^{c}	90.15 ± 0.27^{b}	89.80 ± 0.36^{b}
Water absorption capacity (%)	172.00 ± 0.01^{a}	986.44 ± 0.54^{b}	987.00 ± 0.56^{b}	989.56 ± 0.81^{c}	990.78 ± 1.36^{c}
Oil absorption capacity (%)	131.00 ± 0.33^{a}	200.89 ± 0.54^{b}	201.56 ± 1.56^{b}	204.67 ± 0.94^{c}	205.89 ± 0.98^{c}
Solubility at 70 °C	14.00 ± 0.01^{a}	44.00 ± 2.53^{b}	46.67 ± 2.07^{b}	68.00 ± 1.89^{c}	70.00 ± 0.94^{c}
Swelling power at 70 °C	9.07 ± 0.01^{a}	13.57 ± 0.64^{b}	14.01 ± 0.40^{b}	15.32 ± 0.18^{c}	15.97 ± 0.72^{c}
Sago Starch					
1% Paste Clarity (%T)	76.47 ± 0.31^{a}	96.50 ± 0.35^{c}	96.28 ± 0.68^{c}	89.85 ± 0.63^{b}	89.82 ± 0.57^{b}
Water absorption capacity (%)	110.67 ± 0.94^{a}	836.11 ± 1.86^{b}	838.67 ± 3.10^{b}	982.44 ± 0.81^{c}	982.89 ± 1.96^{c}
Oil absorption capacity (%)	120.67 ± 0.67^{a}	182.11 ± 0.89^{b}	184.11 ± 0.50^{c}	201.00 ± 0.81^{d}	202.00 ± 1.84^{d}
Solubility at 70 °C	20.00 ± 0.01^{a}	60.00 ± 2.53^{b}	62.67 ± 2.07^{b}	85.33 ± 2.07^{c}	87.33 ± 1.63^{c}
Swelling power at 70 °C	9.30 ± 0.01^{a}	12.73 ± 0.33^{b}	12.80 ± 0.30^{b}	14.11 ± 0.29^{c}	14.32 ± 0.73^{c}

*Means within a row related to particular parameter with the same superscript letter are not significantly different as α=0.05 confidence level.

3.2.3. Water and Oil Absorption Capacity. Table 3 shows that water absorption of starch increased after modification for both cassava and sago starch; which is in line with [23]. As mentioned, this increase occurs due to the loss of the crystalline structure [24], which weakens the structure of starch granules so water can easily enter. The ability of starch to absorb oils shows that starch also has a lipophilic portion. Oil absorption capacity is used to measure the product hydrophobicity; the increase in oil absorption is caused by the introduction of the Na-carboxymethyl group (CH_2COONa). The Na-carboxymethyl starch will absorb the oil in the form of a fatty acid (R-COOH). The tendency to bind between fatty acids and Na-carboxymethyl starch is related to the same molecular polarity. Natural starch (R-OH) will have more difficulty to bind to fatty acid (R-COOH) due to differences in polarity.
3.2.4. Swelling and solubility. Sodium carboxymethyl starch is cold water soluble starch, has high dispersed distribution, and excellent water absorption capacities compared to native starch. Carboxymethylation can improve the swelling and solubility of native cassava and sago starches (table 3). Sago starch revealed slightly higher solubility compared to cassava starch, since sago and cassava starches contained different amounts of amylose 25.12% and 19.15%, respectively and as a result different crystallinity. During the modification process, the molecular weight decreases and the degree of polymerization decreases [25], leading to an increase in the hydrophilic nature of starch [26]. The crystalline structure weakens and makes the starch more easily hydrated by water [16].

4. Conclusions
The production of Na-carboxymethyl starch can be carried out by carboxymethylation process using NaOH as an alkalizing agent and SMCA as etherification agent. The alkalization step becomes the initial stage that will affect to the etherification stage. The stirring type of the alkalization stage affects the efficiency of the reaction. The type of starch affects the characteristics of Na-carboxymethyl starch which is related to amylose and amylopectin compositions, but not too much. The highest DS values were found for sago starch treated with NaOH using a homogenizer that also has positive effect on paste clarity, solubility, swelling power, water absorption, oil absorption.

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