MODIFICATION OF LINDUR STARCH (*Bruguiera Gymnorrhiza L.*) BY OXIDATION USING SODIUM HYPOCLORITE AND FERRO SULPHATE CATALYST

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Abstract

Lindur fruit (Bruguiera gymnorrhiza L.) is widely available in Indonesia and has high carbohydrate content, so it has the potential to be developed as a new source of energy and starch. So far, the use of lindur fruit is still limited to substitute rice and snacks. The processing of lindur fruit into starch lindur and improvement of its properties through starch modification can expand its use in the food and non-food industries. The purpose of this study was to modify lindur starch by oxidation using NaOCl with ferrous sulfate as a catalyst. This research studied the effect of sodium hypochlorite concentration (2%, 4%, 6%, and 8%) and ferrous sulfate concentration (0%, 0.1%, 0.2%, and 0.3%) on the physicochemical properties of oxidized starch. The results are used to determine the optimal conditions. The results showed that all the variables studied affected the oxidation reaction of lindur starch. Oxidation at 4% NaOCl concentration and 0.2% ferrous sulfate concentration was able to produce the best values for carboxyl content, solubility, and swelling.
Keywords: starch, oxidation, sodium hypochlorite, lindur

INTRODUCTION

Starch is a carbohydrate polymer that has received the most attention because of its wide use. Apart from being the main source of calories for consumption, starch is used in various types of industries, both food and non-food because of its relatively cheap price, abundant availability, and flexible functionality. The largest use of starch is the food industry (57%), followed by the paper industry (28%), and the rest (15%) in the textile, fermentation, feed and other industries (Agung, 2019).

So far, starch used for various food and non-food purposes in the world, generally comes from corn, potatoes, cassava and wheat, with a total demand of 25.6 million tons per year. On the other hand, Indonesia still imports more than 378 thousand tons of modified starch per year with a value of approximately 73 million US dollars (Sarungallo et al, 2010). Therefore, domestic sources of starch need to be made real efforts to develop starch production and its derivatives (modified starch).

Lindur fruit (Bruguiera gymnorrhiza L.) is one of the most potential sources of starch and energy in Indonesia because it contains carbohydrates that are quite high, even exceeding the carbohydrate sources commonly consumed by the public such as rice, corn, cassava or sago (Sadana, 2007). Lindur tree is one of the species that make up mangrove forests, where the area of mangrove forests in Indonesia is the largest in the world, around 3,153,000 ha (Rahardian et al., 2019), with a fruit potential of 6,228.8 kg/ha (Yulianti, 2004). Lindur fruit bears fruit 3 times a year with a flowering period until harvest time of 6 months, so this fruit is always available throughout the year. According to Sarongallo and Santoso (2007), lindur fruit contains carbohydrates of 94.03% with starch content of 67.75%. With a fairly high carbohydrate and starch content, lindur fruit has the opportunity to be developed as a new starch source in Indonesia. The use of lindur fruit so far is still limited to substitute rice and snacks, such as cakes, lunkhead, sticks, and others (Rosulva et al., 2021). So in this study, modification of lindur starch using the oxidation method will be carried out so that it has wider uses in the food, paper, and textile industries.

Natural starch is known to have weaknesses in its characteristics, which are susceptible to processing conditions (not resistant to stirring, acidic conditions, and high temperatures), unstable viscosity, limited water solubility, starch gel easily undergoes syneresis, and high tendency to retrograde (BeMiller). and Whistler, 2009; Haryani et al, 2020). Therefore, starch needs to be modified to produce better properties to improve the previous properties or to change some of the previous properties.

Modified starch is starch in which the hydroxyl group has been changed by a chemical reaction (esterification, sterification or oxidation) or by disrupting the original structure (Tharanathan et al., 2005; Haryani et al, 2020). Oxidation is one of the most important and widely used forms of chemical modification. This is because the starch produced has a low viscosity, neutral taste, high paste stability, good bonding and film formation properties, and higher clarity (Tethool et al., 2012; Haryani et al., 2020).

Modification of lindur starch by oxidation is needed to develop its potential as a wider food ingredient. The modified method used in this research is the oxidation method using NaOCl as an oxidizing agent. NaOCl is the most widely used oxidizing agent in starch modification processes on an industrial scale (Chan et al. 2011; Xiao et al. 2012; Fitria et al. 2018). Oxidative modification of starch can be carried out using an iron/copper sulfate catalyst (Wing and Willet, 1997; Ariyanti et al. 2014) and in this study ferrous sulfate was used as a catalyst. The purpose of this study was to examine the effect of variable concentration of oxidizing agent and catalyst concentration on the physico-chemical characteristics of oxidized lindur starch.

METHOD

Materials

The materials used in this study were lindur fruit (Bruguiera gymnorrhiza L.) obtained from Demak, Central Java, sodium hypochlorite, ferrous sulfate, sodium metabisulfite, aquadest, NaOH, and PP indicator, which were obtained from the chemical store Multi Kimia Raya in Semarang

Procedure

The research was conducted in 3 stages, namely: the stage of making lindur fruit starch flour, the stage of starch oxidation and analysis of the results.

a. Stages of Making Lindur Fruit Starch Flour

This process begins with peeling, cleaning, cutting and grinding the lindur fruit which was previously added with 0.05% (w/v) sodium metabisulfite and 1:2 (w/v) water. Lindur fruit pulp is allowed to stand for 15 minutes and then filtered with a filter cloth. The starch solution was precipitated at 4°C for 12 hours. The precipitated water is removed and the starch is dried. The starch flakes were then ground and sieved through a 100 mesh sieve.

b. Starch Oxidation Stage

The steps for the oxidation process of lindur fruit starch were initiated by making a suspension with a composition of 40% by weight, namely 40 grams of starch and 100 ml of aquadest, with continuous stirring. The pH of the solution was adjusted to 9 with the addition of 0.5 N NaOH solution. The ferrous sulfate catalyst was then added according to variations (0%, 0.1%, 0.2%, and 0.3%), followed by the addition of sodium hypochlorite according to the variables (2%, 4%, 6%, and 8%) with dripping little by little for 20 minutes. The next step, the pH of the solution was returned to the initial pH (pH 9) with the addition of NaOH and the reaction was stopped after reaching 60 minutes. The sample was filtered and washed with distilled water, until the pH became 6.5-7, then dried in an oven at a temperature of 50°C until completely dry, mashed and sieved to obtain a homogeneous size.

c. Analysis of the results

To determine the physicochemical characteristics of the modified starch, an analysis of the carboxyl content, solubility, and swelling power of oxidized starch was carried out. The methods used were carboxyl content (JECFA, 1997), solubility (Kainuma et al., 1967), and swelling power (Leach at al., 1959).

RESULTS AND DISCUSSION

Effect of Oxidizing and Catalyst Concentration on Carboxyl Levels

The results of the oxidation modification of lindur starch at various concentrations of oxidizing agent NaOCl and catalyst concentration of FeSO4 to carboxyl content are shown in Figure 1.

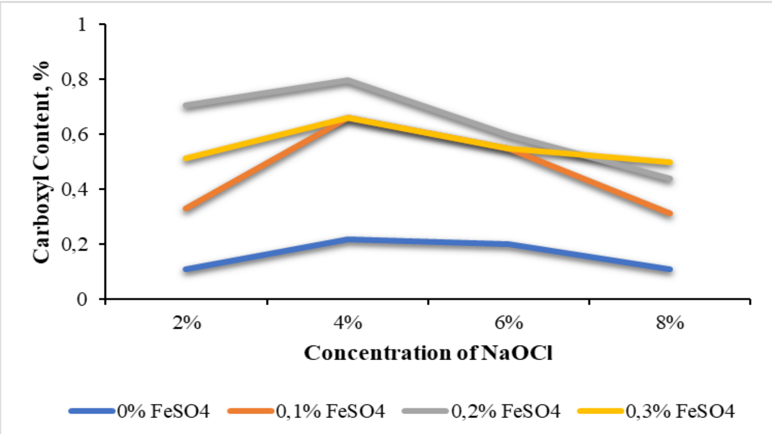

Figure 1. Graph of the relationship between NaOCl concentration and carboxyl content of modified lindur starch at various concentrations of FeSO4

Figure 1 shows that in general the carboxyl content of lindur starch increased with increasing NaOCl concentration from 2 to 4% at all catalyst concentrations. However, increasing the concentration of higher oxidizing agents (6 and 8%) did not increase the carboxyl content of modified lindur starch. The increase in the carboxyl content was due to further oxidation of the formyl group (-CHO) to a carboxyl group (-COOH), while the decrease in the carboxyl content after a concentration of 4% occurred because the more oxidizing agents were added, the more oxidized amylose and amylopectin molecules became carboxyl groups. many. However, the carboxyl group will react with the hydroxyl group to form cross-links so that the carboxyl content of the modified starch decreases (Ariyanti et al, 2014).

Figure 1 also shows the effect of the concentration of FeSO4 catalyst on the carboxyl content of lindur starch at various concentrations of oxidizing agents. The highest oxidized carboxyl content was obtained with the addition of 0.2% catalyst with 4% NaOCl concentration, which was 0.798%. This is in accordance with JECFA requirements that the maximum carboxyl content obtained from the oxidation process is not more than 1.1% (JECTA, 1997; Fatchuri and Wijayatiningrum, 2009).

Effect of Concentration of Oxidizer and Catalyst on Solubility

The effect of NaOCl oxidizing concentration and FeSO4 catalyst concentration on the solubility of starch modified by oxidation can be seen in Figure 2.

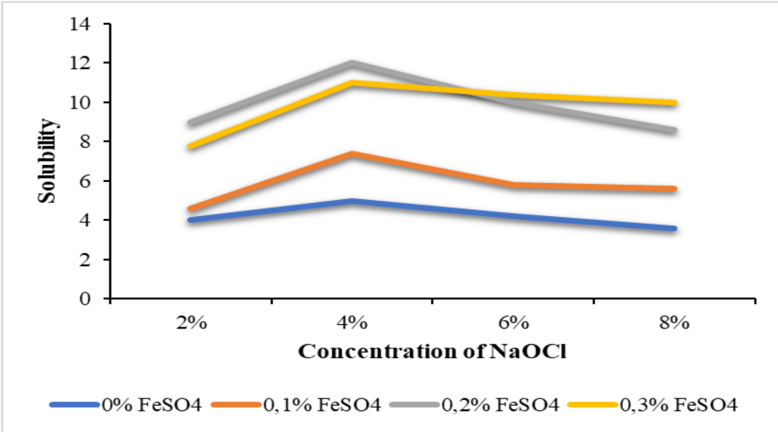

Figure 2. Graph of the relationship between NaOCl concentration and the solubility of modified starch at various concentrations of FeSO4

Based on Figure 2, it can be seen that the solubility value of lindur starch tends to increase but decrease in the oxidation treatment with a NaOCl concentration of more than 4%. The increase in starch solubility then decreases with increasing NaOCl concentration in line with research conducted by Fitria et al. (2018). This increase in starch solubility was caused by the depolymerization of starch molecules and the weak internal structure of the starch granules which caused the amylose and amylopectin fractions to dissolve in water (Garrido et al., 2012; Gumul et al., 2013; Fitria et al., 2018). According to Zavareze et al. (2012), increasing the solubility of starch is beneficial in the encapsulation of food products and food additives.

The decrease in the solubility of modified starch on the addition of more than 4% NaOCl occurred because the greater the concentration of the added oxidizing agent, the further oxidation would occur, namely the conversion of the formyl group (-CHO) to a carboxyl group (-COOH) which is susceptible to cross-linking formation in the intramolecular. This bond is thought to inhibit the development of granules and inhibit the depolymerization of starch, so that the value of the solubility of starch in water becomes lower (Chan et al., 2009; Tethool et al., 2012; Ariyanti et al., 2014).

From Figure 2 it can also be seen that the solubility of oxidized starch increased and then decreased after the use of 0.2% FeSO4 catalyst. The increase in the solubility value of modified starch can occur because the greater the number of catalysts, the more depolymerization reactions due to oxidation by NaOCl occur and produce starch molecules with short chains that are easily soluble in water (modified starch solubility increases). While the decrease in the solubility of starch in the use of catalysts > 0.2%, it is possible because the more catalyst will trigger further reactions from formyl groups to carboxyl groups that can be cross-linked within the intra molecule. As a result, short modified starch chains that form cross-linking will reduce or reduce solubility (Ariyanti et al., 2014).

Effect of Oxidizing and Catalyst Concentration on Swelling Power

Figure 3 presents the swelling power value of modified starch at various concentrations of NaOCl oxidizing agent and FeSO4 catalyst concentration. The value of swelling power increased with increasing the concentration of NaOCl added. The higher the concentration of NaOCl solution used, it means that the amylose in the modified starch granules will be less so that the swelling power of amylopectin will increase.

Higher NaOCl concentrations (6 and 8%) actually decreased the swelling power value. This is caused by the occurrence of further oxidation, namely the conversion of the hydroxyl group of the amylose and amylopectin molecules into a carbonyl group and then into a carboxyl group. As previously explained, the reduction in amylopectin molecules in the starch structure causes a decrease in starch molecules that can absorb and trap water molecules. This is indicated by the low value of swelling power (Lawal, 2004).

The increase in the swelling power value of oxidized modified starch then decreased with increasing oxidizing concentration in line with the results of research by Budiyati et al. (2016). According to Budiyati et al. (2016), the decrease in starch swelling power at higher oxidizing concentrations was due to further oxidation which caused starch degradation into fragments with shorter carbon chains. The group formed as a result of the further depolymerization process is also susceptible to cross-linking between the intra-molecules. This bond is thought to inhibit the release of amylose which has been cut from the starch chain (trapped), so that the value of water solubility is lower (Wang & Wang, 2003; Budiyati et al. 2016).

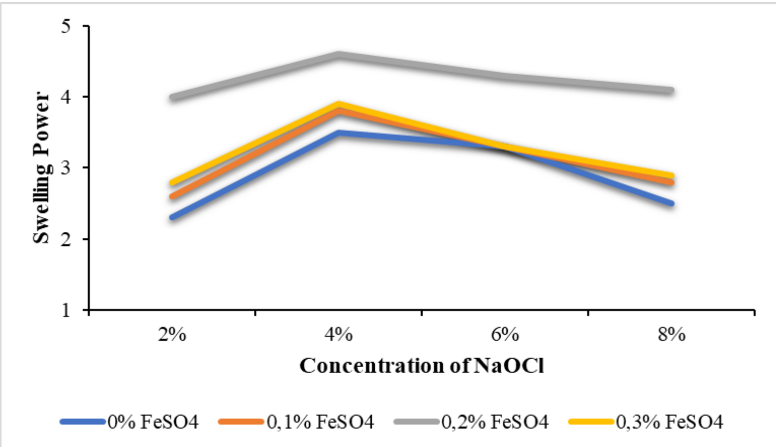

Figure 3. Graph of the relationship between NaOCl concentration and swelling power of modified lindur starch at various concentrations of FeSO4

From Figure 3, it can be seen that the higher the amount of FeSO4 catalyst, the swelling power of modified lindur starch was greater at all concentrations of NaOCl up to the use of 0.2% catalyst. An increase of 0.2% catalyst can increase the swelling power from 3.3 g/g to 4.6 g/g. After that, the swelling power of starch modified starch on increasing the amount of catalyst tends to decrease. These results are in line with the research conducted by Ariyanti et al. (2014).

In a system with a 0.3% catalyst, it is estimated that the oxidation reaction occurs faster and allows further oxidation to occur, namely the conversion of the carbonyl group to a carboxyl group which is susceptible to the formation of cross-linking between intra-molecules (Tolvanen et al., 2013; Ariyanti et al., 2014). This bond is thought to inhibit the process of water absorption by amylopectin so that the swelling power value tends to decrease (Wang and Wang, 2003).

CONCLUSION

The oxidation of lindur fruit starch using NaOCl as an oxidizing agent and ferrous sulfate catalyst affects the functional properties of starch, namely carboxyl content, solubility, and swelling power. The use of 4% NaOCl concentration and 0.2% FeSO4 catalyst concentration in starch oxidation was able to produce the best values for carboxyl content, water solubility, and swelling power.

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