

## Modified ganyong (*Canna edulis* Kerr.) starch prospective as wheat flour alternative

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### Abstract

Ganyong tuber (*Canna edulis* Kerr.) had high carbohydrate content and has potential to be used as starch. However, the starch obtained was low quality, characterized by brownish color and limited functional properties. The main aim of this work was to obtain the optimum process to transform canna starch into commercial wheat flour SNI 3751:2009 by oxidizing with food grade hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The raw material used was white canna tuber from Samarinda, East Kalimantan which have high carbohydrate content. Initially, the starch was oxidized by 35% H<sub>2</sub>O<sub>2</sub> food grade to form 1%, 2%, 3% concentration, slurry ratio of 10%, 20%, 30% and time of oxidation was 30, 60, 90 and 120 mins. The ganyong tuber starch was then subjected to modification process by optimizing the slurry ratio and H<sub>2</sub>O<sub>2</sub> oxidation time. The assessment was based on basic functional properties, swelling power and water solubility. The process was conducted using a mini-propeller chamber, and data were collected in triplicates for accuracy. The optimum result was achieved with a 60-min oxidation time, 10% slurry concentration and 2% H<sub>2</sub>O<sub>2</sub> concentration. The swelling power value reached 2.9 g/g, and water solubility was measured at 6.09 g/g. Upon proximate analysis, the canna starch contained 85.956% carbohydrates, 2.365% protein, 11.425% water and 0.254% ash content. The color analysis indicated a white degree with brightness of 91.95. Despite the improvements achieved through the process, the functional and other properties of ganyong starch were still considerably below of wheat flour standard.

## 1. Introduction

The number of imports continues to increase in line with population growth which is not followed by an increase in food production (Hidayat *et al.*, 2022). Changes in consumption patterns occur. Bread is a food product made from wheat flour and popular in the community. The Central Statistics Agency (BPS) recorded that the import value of Indonesian wheat and meslin was US\$3.45 billion with a volume of 11.17 million tons in 2021. The import value of these commodities increased 31.68% compared to the previous year which was US\$2.62 billion with a volume of 10.29 million tons (BPS, 2022). Wheat flour cannot be planted in Indonesia; hence it is imported from another country. To reduce the high import costs, it is expected that there will be an alternative raw material that can reduce the use of wheat flour (Yaqin *et al.*, 2019).

Indonesia has various sources of carbohydrates, one

of them is tubers. According to Retnowati *et al.* (2018), the tubers crop can be stored for an extended period. Furthermore, tubers can grow in marginal area and were utilized in various ways for fulfil the needs and food requirements. One type of tuber that is quite abundant in Indonesia is canna tuber (*Canna edulis* Kerr.). It has advantages in terms of the number of edible tubers, possess 68% higher amount of fiber and mineral content than others, but have not been utilized optimally. The existence of canna tubers in East Kalimantan is quite abundant, reaching approximately 700 tons/year spread over various areas in Indonesia. It has a high carbohydrate content (84.34%), as well as the mineral content of calcium, phosphorus and iron. However, currently its use is still limited in the form of fresh boiled or steamed (Munfarida and Hidayat, 2023).

Starch was the main impurity of the flour (Wardhani *et al.*, 2019). In general, starch produced from tubers is

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brown (Retnowati *et al.*, 2018). This is due to the browning process during the flour manufacturing process. With the processing and treatment methods given in the production of canna starch so far, the canna starch produced has poor quality. The resulting starch has a brownish colour, and low solubility and swelling power. So that the use of canna starch in the community is still very rare, especially to replace flour. The quality of canna starch is not only determined by the degree of whiteness and nutritional content that meets the quality standard of SNI 3751: 2018 (BSN, 2018). In addition, it is necessary to increase the swelling power and solubility. Low swelling power and solubility of starch will be difficult to applied. According to Yaruro Cáceres *et al.* (2021), the oxidation of Bogor taro flour using hydrogen peroxide as an oxidizing agent affects the swelling power and water solubility as the functional properties of starch. Rahma *et al.* (2017) said that the modification process by means of oxidation using a solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can improve the quality of starch. Thus, further research is needed to determine the optimum conditions for producing canna starch so that it meets the quality standards according to SNI 3751:2018 on wheat flour.

The main aim of this work is to examine the optimum conditions for the oxidation process of canna starch with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Some of the analyses carried out were water content, ash content, carbohydrates, fats, proteins, carboxyl groups, whiteness, swelling power, and water solubility of canna starch produced according to the variables. The aim of this research is to analyze the influence of slurry and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) concentration on the ganyong starch modification by oxidation reaction.

## 2. Materials and methods

### 2.1 Ganyong

Indonesia has two varieties of Ganyong tuber (*Canna edulis* Kerr.), red and white canna. White canna was used in this study because it has a higher starch than the red one. The canna was obtained from Samarinda, East Kalimantan.

### 2.2 Variable and control

In this study, the control variables were the type of Canna tuber (from Samarinda), sedimentation time (10 hrs), sieving diameter (80 mesh), drying method (sun drying), drying method after oxidation process (oven in 50°C) and drying time (4 hrs). The response variables were swelling power, water solubility, proximate analysis and color degree. Whereas, the independent variables were canna starch concentration in water, hydrogen peroxide concentration in water and oxidation

time. Water is used as extraction media and hydrogen peroxide solvent. Hydrogen peroxide was the bleaching agent to improve the appearance of canna starch. The research variables are shown in Table 1.

Table 1. Experimental variables.

Run	Variables	Details
1	Starch concentration in water	10, 20, 30% weight of starch
2	Hydrogen peroxide concentration in water	1, 2, 3 % weight of starch
3	Oxidation time	0, 30, 60, 90, 120 mins

### 2.3 Canna starch production

Canna tuber underwent pre-treatment procedure before it was process to be canna starch. The pre-treatment started with the peeling and washing process. To extract the starch, canna tubers was cut and blend until smooth. The squeezing process is carried out to separate the canna starch. Thereafter, the filtration process is required to separate the pulp from the filtrate. The pulp was left in the cloth and the filtrate which contain starch escape. The filtration process was repeated by adding water until the filtrate appears clear. The filtrate is kept for 10 hrs, allowing starch to settle at the bottom layer, later on ready for separation. The wet starch is dried by oven then ground to obtain fine particle. The yield of the starch is obtained by weighing the final product formed after the sieving process using an 80-mesh size.

### 2.4 Canna starch modification

Modification process of canna starch was started by weighing 25 g of canna starch then dispersed in distilled water to obtain a suspension. The oxidation process was conducted at 30°C with continuous stirring, following the method described by Yaruro Cáceres *et al.* (2021). During the process, 35% hydrogen peroxide solution was added drop by drop until the desired variable concentration was achieved. After the oxidation, the starch obtained was washed four times with distilled water. The wet modified starch was dried using an oven at 50°C. The last step involved grinding and sieving the dried starch through 80-mesh size. The product was stored in airtight plastic container at 28±2°C for further analysis.

### 2.5 Responses

The modified starch underwent various analysis to study the physicochemical characteristics that consist of swelling power, water solubility, proximate analysis, whiteness and carboxyl content. Swelling power and water solubility were measured using a centrifuge based on Senanayake *et al.* (2013) method. Proximate analysis

included determining the content of carbohydrate, fat, protein, water and ash according to the method described by Latimer (2016). The whiteness was assessed using the Judd-Hunter method with chromameter to determine color parameter (Kumoro and Hidayat, 2018). The carboxyl group content is measured using the method described by Kumoro and Hidayat (2018) method.

### 3. Results and discussion

#### 3.1 Analysis of canna bulbs and starch raw materials

The results of the proximate analysis of canna tubers and starch are listed in Table 2. From Table 2, it can be seen that the carbohydrate content is quite high in canna starch, reaching 80.052%. The water content (11.45%) and ash content (1.29%), reach the standards for wheat flour consumed in Indonesia. While the protein content of canna starch (5.676%) is still below the specified standard, which is at least 7%. The results of the proximate analysis indicate the potential of canna starch to be used as an alternative food ingredient to replace wheat flour. To expand its application, modifications is needed to improve the functional properties of canna starch, such as swelling power and water solubility. Swelling power shows information about the amount of water that can be absorbed by 1 gram of rice grain if it is in an excessive amount of water at high temperatures. With high swelling power, starch will also have high water solubility (Kumoro and Hidayat, 2018).

Table 2. Nutrient content of canna bulbs and starch.

Parameter	Canna Bulbs (%)	Canna Starch (%)	Wheat SNI (3751:2009)
Carbohydrate	22.60	80.052	-
Protein	1	5.676	Min. 7
Fat	0.11	3.562	-
Water	75	11.450	Max. 14.5
Ash	1.29	1.253	Max. 7

#### 3.2 Effect of starch concentration

The variables studied were the ratio of flour to water (10%, 20% and 30%). Oxidation was carried out with  $H_2O_2$  with a concentration of 2% at room temperature and the oxidation time was 30-120 mins. The research data on the effect of the ratio of flour to water in suspension on the value of swelling power and water solubility are presented in Figure 1 and Figure 2.

The oxidation process initiates with the formation of hydroxyl canna starch oxidation ( $HO\bullet$ ) from hydrogen peroxide. This leads to the cleavage of amylose molecular chain bonds, resulting in shorter chains. In general, during the first 60 mins of oxidation, there is a tendency for increasing the swelling power. Similar phenomena were observed in the oxidation of corn starch by Wei *et al.* (2022). Additionally, Aryanti *et al.* (2017)

reported that the concentration of amylose in starch can reduce the value of swelling power, while a high concentration of amylopectin can increase it. During the first 30-60 mins of oxidation, hydroxyl radical ( $HO\bullet$ ) depolymerize the amylose molecules, which form the outermost layer of starch structure and have a high degree of crystallinity. Simultaneously, the amylopectin molecules contribute to the increase in the swelling power value of the starch. Swelling power is expressed as grams of water retained per gram of the sample (Kumoro and Hidayat, 2018). These findings highlight the dynamic changes in the starch structure and functional properties during the oxidation process.

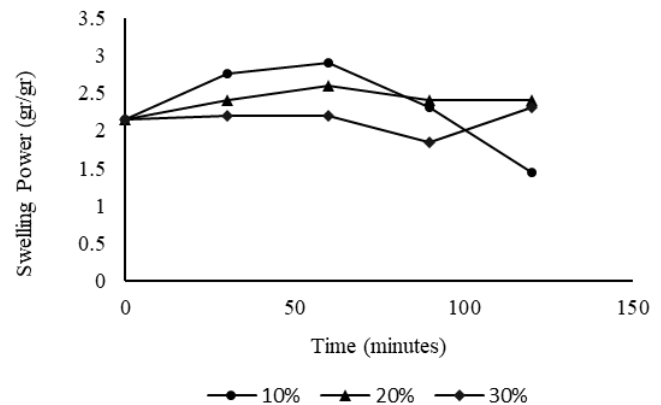


Figure 1. Effect of starch concentration on modified canna starch's swelling power with 2%  $H_2O_2$  solution.

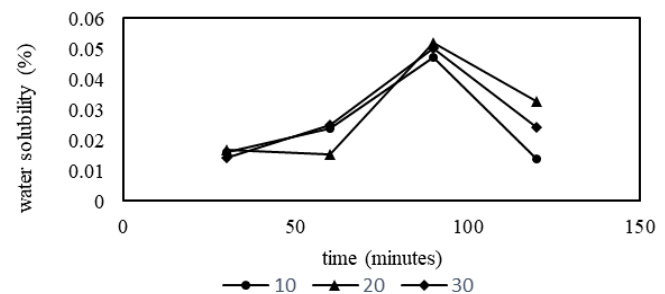


Figure 2. Effect starch concentration on modified canna starch's water solubility with 2%  $H_2O_2$  solution.

Further depolymerization occurs after 60 mins, it causes the amylopectin molecule to be depolymerized. The absence of amylopectin molecules in the starch structure causes no more molecules that can absorb and trap water molecules so that it is associated with a decrease in the value of swelling power (Zhou *et al.*, 2015). The percentage of slurry indicates the variation of starch content (amylose and amylopectin) in the starch solution oxidized. The 10% slurry percentage in this study was the composition that produced the highest swelling power value, which was 2.9 g/g at an oxidation time of 60 mins. At 10% slurry percentage, the amount of amylose and amylopectin was clearly lower than that of 20 and 30%. However, this is the optimum condition for amylopectin. The presence of amylopectin molecules in the starch structure causes the molecules to absorb

more and trap water molecules (Kumoro *et al.*, 2022), thus it can increase the value of swelling power. Meanwhile, 20% and 30% slurry percentages resulted in lower swelling power values. Fonseca *et al.* (2015), increase the rate of the oxidation reaction by increasing starch concentration in the slurry. Therefore, theoretically the swelling power of oxidized canna starch obtained will decrease with increasing slurry percentage and time. Furthermore, the concentration of oxidizing agents can also influence the swelling power. When there is a mismatch in the concentration of oxidizing agents, a large number of amylose molecules may be present in the starch structure, which can inhibit the access of water molecules to amylopectin. This can result in a lower swelling power value as compared to the optimal condition where the right balance of oxidizing agents allows for proper depolymerization and swelling of the starch molecules. Therefore, controlling the concentration of oxidizing agents is crucial in achieving the desired functional properties in the modified starch.

At the beginning of the oxidation process, amylose depolymerization occurs. Amylose molecules that are depolymerized into short chain molecules begin to dissolve in water which causes the water solubility value of flour in water to also increase significantly. This is in accordance with the statement made by Senanayake *et al.* (2013) which suggest that water solubility is influenced by the release of the amylose fraction from the starch chain. After 90 mins of oxidation, there is a decrease in solubility due to further depolymerization, which also decrease in swelling power. The proportional relationship between the solubility and swelling power values causes the decreasing water solubility after being oxidized for more than 90 mins. As the starch undergoes further modification and depolymerization in functional properties, such as solubility and swelling power. These may be affected, leading to changes in its behavior and properties in various applications.

### 3.3 The effect of oxidizing $H_2O_2$ amount on swelling power and solubility

The variables studied were the concentration of  $H_2O_2$  (1%, 2% and 3%). Oxidation was carried out at a suspension ratio of 10%, a temperature of 30°C and an oxidation time of 60 mins. The results of the research on the effect of the amount of oxidizing agent on the swelling power and water solubility values are presented in Figure 3.

Figure 3 shows that the swelling power and water solubility values in the three variables tend to fluctuate. Both showed the same tendency, at concentration of 1% to 2% there was an increase in both the value of swelling

power and water solubility. However, at a concentration of 3% there was a decrease in both values. The mechanism of oxidation with  $H_2O_2$  begins with the formation of free radicals ( $-OH$ ) which act as oxidizing agents. The  $-OH$  is very reactive with carbohydrates. Furthermore, these free radicals will oxidize the hydroxyl groups in starch and turn them into carbonyl and carboxyl groups. In this oxidation, the main product expected is a carbonyl group. Further oxidation of the carbonyl group will become a carboxyl group (Kumoro and Hidayat, 2018). The conversion of carbonyl to carboxyl group occurs rapidly. Carboxyl groups are prone to forming cross-linkages, which can inhibit the water absorption process by amylopectin, resulting in lower swelling power values (Blok *et al.*, 2023). This phenomenon was observed when using  $H_2O_2$  at 3% concentration. High levels of oxidation, with concentration of 3%  $H_2O_2$  cause excessive formation of bonds between intra-molecular starch, thus affecting its functional properties. Using  $H_2O_2$  in 3% concentration for oxidation is considered suboptimal. Besides lowering the values of swelling power and water solubility, it also brings the  $H_2O_2$  level close to the maximum permissible limit in food (4%). Therefore, controlling the concentration of oxidizing agents is vital in obtaining the desired modified starch properties while adhering to safety and regulatory standards for food applications.

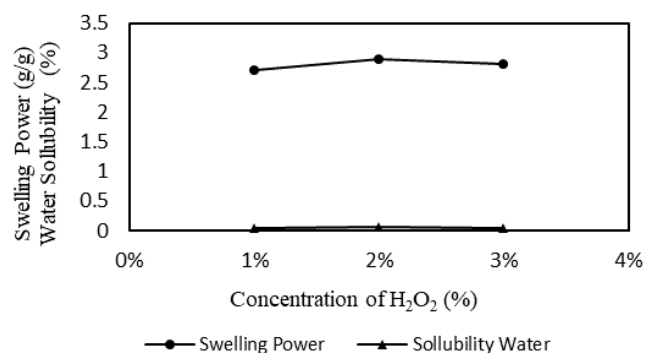


Figure 3. The effect of oxidizing agent quantity on the modified canna starch's swelling power and solubility by water ratio 10% at 60 mins time oxidation.

As for the use of  $H_2O_2$  at low concentrations, the oxidizing agent will have difficulty penetrating the starch granule structure (Suzihaque *et al.*, 2022). Presumably, this causes the reaction to proceed slowly as happened in the use of an oxidizing agent with a concentration of 1%. The absence of amylopectin molecules in the starch structure causes no more molecules that can absorb and trap water molecules so that it is associated with low swelling power values (Kumoro *et al.*, 2020). The groups formed as a result of the further depolymerization process are also susceptible to the formation of cross-linking between their intra-molecules. This bond is thought to inhibit the release of amylose which has been cut from the starch chain (trapped), so that the solubility

value of flour in water becomes lower (Senanayake *et al.*, 2013; Rahma *et al.*, 2017; Hidayat *et al.*, 2022).

### 3.4 Analysis of modified canna starch carboxyl groups

Oxidation is a method of starch modification that changes the functional groups of starch by polymer depolymerization. To determine changes in the functional groups of starch, the carboxyl value of starch without modification (native) and with modifications was analyzed. The modified canna starch analyzed was the one with the best results (the highest swelling power and water solubility values among all variables). In this study, it was observed that the maximum values of water solubility and swelling power were found in different variables. The water solubility was obtained relatively lower than swelling power and it still did not meet the standard requirement. Due to this, the analysis focused solely on selecting variables based on the highest swelling power value. The aimed for optimizing the swelling power property of the modified starch, which is a crucial functional characteristic for various industrial applications. By prioritizing the variable that resulted in the highest swelling power, the researchers aimed to enhance the starch functionality for specific uses while acknowledging that the water solubility values did not meet the desired standard.

From the results of the analysis, the value of the carboxyl group in native canna starch was 0.081%, while the modified canna starch was 0.102%. This is in accordance with Kumoro and Hidayat (2018), who reported on the oxidation process from carbonyl and carboxyl groups from hydroxyl groups occurs.

### 3.5 Nutritional content of modified canna starch compared to wheat flour

Based on the research result, it is evident that the operation conditions with a starch-to-water ratio of 10%, an oxidizing concentration of 2%, and reaction time along 60 mins are the most optimum. These conditions led to flour production with the highest solubility value among all the variables. By identifying and applying these specific conditions, the water solubility of the modified starch was successful increased, making it potentially more suitable for certain applications that require higher water solubility. Changes in the functional

Table 3. Functional properties of canna starch and wheat flour.

Flour	Swelling Power (g/g)	Water Solubility (g/100 g)
Non-modified canna starch <sup>a</sup>	2.15	0.0137
Modified canna starch <sup>a</sup>	2.9	0.0609
American wheat <sup>b</sup>	6.8-7.9	6.3-7.3

<sup>a</sup>This research results, <sup>b</sup>Chung *et al.* (2001).

properties of canna starch before and after modification can be seen in Table 3.

Based on Table 3, it is known that modified canna starch has low swelling power and water solubility values. Indeed, the water solubility value obtained for the modified canna starch was significantly lower. Therefore, it can be concluded that the modified canna starch may not be feasible as a complete replacement for wheat flour in certain applications that require similar solubility properties. Post-oxidation changes also have an impact on the nutritional content of flour which can be seen in Table 4.

The decrease of fat and protein content in starch was caused by structural damage to both during the oxidation process. Amino acids in proteins are broken down when they react with hydrogen peroxide or carbonyl compounds. Meanwhile, the increase in carbohydrate content is caused by the breakdown of long and complex chains in starch (Zhou *et al.*, 2015). The decrease in ash content is thought to be caused by the enlargement of the post-oxidation granule structure which causes a decrease in the number of small particles such as ash. While the decrease in water content is considered not too significant.

### 3.6 Color degree analysis of modified canna starch

Color is one of the important indicators in choosing a product by consumers. Color and appearance are considered as the dominant factor for food quality (Ifa *et al.*, 2021). Color parameters measured in color analysis include the level of brightness (lightness) and chromaticness. In this study, color analysis uses the Judd-Hunter Lab method, where the brightness level is expressed by the L value, while the chromatic color is expressed by the a and b values (Hidayat *et al.*, 2022). The degree of whiteness,  $L^*$  is measured on a scale ranging from 0 (black) to 100 (white) The  $a^*$  value indicates the degree of redness if positive or greenishness if negative, while the  $b^*$  value indicates the degree of yellowness if positive or bluishness if negative (Table 5). These color parameters are determined using a digital chromameter (Apple, USA) on a Machintosh platform. The samples that have undergone treatment are placed under the camera, and measurements are directed at the samples. The resulting color parameter values are displayed on the screen. By analyzing the color parameter value, it could assess the characteristics of modified canna starch. This information is essential for understanding the color properties of the starch and its potential applications in any industries, as well as food, cosmetics, and pharmaceuticals.

It is shown in the table that modified canna starch

Table 4. Nutrient content of non-modified modified canna starch.

No	Flour	Water (%)	Ash (%)	Protein (%)	Fat (%)	Carbohydrate (%)
1	Non-modified canna starch <sup>a</sup>	11.450	1.253	5.676	3.562	80.052
2	Modified canna starch	11.425	0.254	2.365	0	85.956
3	SNI wheat flour standard	Max 14.5	Max 7	Min 7	-	-

<sup>a</sup>This research results.

Table 5. Unmodified and modified canna starch color test results.

Flour	L = brightness (0 - 100)	a (greenish - redness)	b (yellowish - bluish)
Non-modified canna starch	85.21	1.61	9.1
Modified canna starch	91.95	0.51	6.63

gives a better whiteness than non-modifies. It is indicated by an increase in the degree of brightness. The high value of the whiteness value greatly affects the brightness (Kumoro *et al.*, 2019). In addition, the results showed a decrease in positive a and b values, which means that starch after modification showed lower greenish and yellowish colors than without modification. Derardja *et al.* (2022) reported that this is due to the oxidation reaction, some pigments and proteins are oxidized before the glucose unit so that these compounds will be partially lost, eventually resulting in whiter starch and more intensive in reducing the intensity of the yellow and green colors in flour. H<sub>2</sub>O<sub>2</sub> as oxidizing agent has oxidized colored pigments into oxidized pigments. Higher water absorption led to lower L\* value and greater darkening over time ( $\Delta L^*$ ). The parameters a\* and b\* were in some reports not significantly affected (Hidayat *et al.*, 2022), whereas at other result a\* and/or b\* value increased with higher water absorption.

#### 4. Conclusion

This study depicted that modification of *Canna edulis* Kerr. starch by oxidation of hydrogen peroxide insignificantly changed the functional properties of starch, such as swelling power and water solubility. Since the modified canna starch from this study still have low swelling power and water solubility value, it was still possible to used them for certain applications, such as cookies where high swelling power is not critical requirement.

#### Conflict of interest

The authors declare no conflict of interest.

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