

## Oxidation of Oven-Dried Cassava Starch Using Hydrogen Peroxide and UV-C Irradiation to Improve Frying Expansion

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**Abstract:** Native cassava starch usually has low volume expansion. Some modifications were developed to change its physical and chemical characteristic, i.e. hydrogen peroxide addition and UV-C irradiation. The objectives of this study were to determine UV-C intensity, oxidation time, and concentration of hydrogen peroxide addition which resulted in the highest frying expansion of oven-dried cassava starch. Oxidation was conducted with acidification of cassava starch using 1% (w/w) lactic acid, the addition of hydrogen peroxide, and irradiation of UV-C in a tumbler. Combination of UV-C intensity, oxidation time, and hydrogen peroxide concentration were adjusted by Box-Behnken design. Optimization of cassava starch was determined by Response Surface Methodology (RSM), with frying expansion as a main response. Oxidized cassava starch was analyzed for physical and chemical characteristics. The result of this study showed that the oxidation of cassava starch increased the frying expansion, carbonyl and carboxyl content, amylose content, solubility, and decreased the swelling power. The optimum condition of oven-dried cassava starch oxidation was reached at 40 watt UV-C intensity, oxidation time 2,281 minutes, and hydrogen peroxide concentration 1% (w/w), with the percentage of frying expansion 347,26%.

**Keywords:** modified starch, volume expansion, UV-C intensity, oxidation time, concentration of hydrogen peroxide

### INTRODUCTION

Cassava is one kind of agricultural commodities in Indonesia whose existence is abundant and potential for diversification in an effort to development. One of cassava products is cassava starch. One way to enhance the economic value of cassava is processing cassava starch. Cassava starch types that often found on the market are oven-dried cassava starch, commercial cassava starch, and sun-dried fermented cassava starch. Sour cassava starch is used in the manufacture of biscuit and “cheese bread” in which it is irreplaceable due to its characteristic flavor and functional properties, mainly those of expansion. The biscuits have high specific volumes, alveolar structure and crispness, similar to extruded snacks (Plata-Oviedo and Camargo, 1998).

Cassava starch especially oven-dried cassava starch and commercial cassava starch have low volume expansion. It can be a problem if using that kind of cassava starch in food stuff which need high volume expansion. Baking expansion analysis of cassava starch only illustrate the oxidized cassava starch when applied to baked products such as bread or bakery products. While cassava starch can be used more widely, for example for the development of products that require large volumes of the frying process, such as crackers, nuts and pilus atoms. Relatively few studies on starch oxidation by hydrogen peroxide are available in the literature.

Some modification was developed to improve volume expansion of cassava starch. Starch modification by oxidation process is one of the method to solve this problem. Chemical oxidation with an oxidizing agent and physical

oxidation by UV-irradiation can improve the characteristic of oxidized cassava starch. Hydrogen peroxide is widely used as an oxidizer in the oxidation reaction because it is economical and environmentally friendly. The use of H<sub>2</sub>O<sub>2</sub> in the oxidation of starch and cassava flour has been investigated by Parovuori et al. (1995), Sangseethong et al. (2010), Tavares et al. (2010), and Dias et al. (2011). Baking expansion of sour cassava starch that was oxidized with H<sub>2</sub>O<sub>2</sub> was affected by the H<sub>2</sub>O<sub>2</sub> concentration, pH and temperature of the reaction (Dias et al., 2011).

Solar ultraviolet (UV) radiation can be classified into UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (100–280 nm), the short wavelengths of less than 290 nm undergoing significant absorption by the atmosphere at the ozone layer (Nee, 1996). Effect of UV irradiation to modify the starch has been investigated by Bertolini et al. (2000), Fiedorowicz et al. (1999), and Vatanasuchart et al. (2005). UV irradiation on the oxidative degradation of starch is affected by light intensity and length of exposure time. Previous study (Vatanasuchart et al., 2005) showed that cassava starches modified by 1% lactic acid hydrolysis and exposure to UV-C irradiation had effective baking expansion compared to UV-B irradiation.

The objectives of this study were to determine the effect of UV-C intensity, time of oxidation and H<sub>2</sub>O<sub>2</sub> concentration to the characteristics of oxidized oven cassava starch and commercial cassava starch, and to find optimum conditions of oxidation process using Response Surface Methodology.

## MATERIALS AND METHODS

### Materials

Oven-dried cassava starch was obtained from industrial facilities in Lampung, Indonesia (PT. Sinar Pematang Mulia). Sun-dried fermented cassava starch was obtained from traditional industry in Yogyakarta, Indonesia. Chemical that was used was pro analysis.

### Preparation of cassava starch oxidation

In making oxidized cassava starch, cassava starch was acidified with lactic acid 1% (w/w), addition of H<sub>2</sub>O<sub>2</sub> (w/w) then irradiated by UV-C in tumbler mixer. The moisture content of cassava starch was adjust at 20% before rotating in the tumbler. The combination parameter between the intensity of UV-C lamp, time of oxidation, and H<sub>2</sub>O<sub>2</sub> concentration were adjusted with Box Behnken Design (Table 1) with frying expansion as the main response. Oxidized cassava starch was dried in cabinet dryer at 50°C, size reduction and sieved (60 mesh). Oxidized cassava starch was analyzed for physical and chemical characteristics.

Table 1

A 2 <sup>3</sup> factorial design with three central points			
Variables	Level		
	-1	0	+1
I (watt) <sup>a</sup>	20	40	60
T (minute) <sup>b</sup>	1	2	3
C (g/100 g) <sup>c</sup>	1	2	3

<sup>a</sup> I: intensity of UV-C lamp (watt)

<sup>b</sup> T: time of oxidation (minute)

<sup>c</sup> C: concentration of hydrogen peroxide (g H<sub>2</sub>O<sub>2</sub>/100 g cassava starch, d.b.)

### Frying expansion

Weighing 10 g of cassava starch, then retrieved 0.5 grams to gelatinization by adding 8 mL of boiling water into 0.5 g of starch, then heated until translucent. Gelatinized starch mixed with residual starch (9.5 g) is formed into a smooth dough. Weighing 0.5 g of dough, formed spheres, determined volume V<sub>1</sub>. Then the dough fried in a deep fryer with a temperature of 110°C initial cooking oil. After 3 minutes, the temperature was raised to 130°C. In the 4th minute, the temperature was lowered to 110°C. After 8 minutes, the temperature is raised again to 150°C until 10<sup>th</sup> minutes and then drained. During the process of frying, stirr continuously. Fried starch dough has a hard surface, so that the water tends to be difficult to penetrate its surface. The volume of frying expansion was measured by dipping quickly into a graduated cylinder until all parts submerged, calculated large increase in volume, recorded as V<sub>2</sub>. The percentage of frying expansion was calculated using Eq. (1)

$$\text{Frying expansion} = \frac{V_2 - V_1}{V_1} \times 100\% \quad (1)$$

### Carbonyl content

Carbonyl content was determined as described by Smith (1967). Dry starch (4 g) was resuspended in distilled water (100 mL) and heated in a boiling water bath for 30 min

with continuous stirring until completely gelatinized and then stored at 40°C. The pH was adjusted to 3.2 with 0.1 mol/L HCl; hydroxylamine chloride solution (15 mL) was then added to the solution (prepared by dissolving 25 g of reagent grade hydroxylamine chloride in water, adding 100 mL of 0.5 mol/L NaOH and bringing the final volume to 500 mL). Samples were covered with plastic film and put into a 38°C oven for 4 h and rapidly titrated to pH 3.2 with 0.1 mol/L HCl. The carbonyl content was expressed as the quantity of carbonyl groups per 100 glucose units (CO/100 GU), as calculated by Eq. (2)

$$\text{CO/100 GU} = \frac{(V_b - V_s) \times M \times 0.028 \times 100}{W} \quad (2)$$

where V<sub>b</sub> is the volume of HCl used for the blank (mL), V<sub>s</sub> is the volume of HCl required for the sample (mL), M is the molarity of HCl and W is the sample weight (d.b.).

### Carboxyl content

The carboxyl content was determined as previously described (Parovuori, et al., 1995). Dry starch (5 g) was resuspended in distilled water (25 mL), stirred for 30 minutes. Sample was centrifuged, washed with distilled water, and resuspended in 300 mL of distilled water. The resuspended samples were heated in a boiling waterbath with continuous stirring for 30 minutes to achieve complete gelatinization. The heated samples were then titrated to pH 8.2 with 0.01 mol/L NaOH. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COO/100 GU), as calculated by Eq. (3)

$$\text{COOH/100 GU} = \frac{(V_s - V_b) \times M \times 0.045 \times 100}{W} \quad (3)$$

Where V<sub>s</sub> is the volume of NaOH required for the sample (mL), V<sub>b</sub> is the volume of NaOH used to test the blank (mL), M is the molarity of NaOH and W is the weight of sample (d.b.)

### Amylose content

Amylose content was determined using AOAC method Ed 14<sup>th</sup> (1984). 100 mg sample was added with 1 mL ethanol 95% and 1N NaOH 9 mL, heated 10 minutes in boiled water. After cooled, suspension diluted to 100 mL. 5 mL of suspension was diluted up to 100 mL added with 1 mL acetic acid 1N, and 2 mL iodine 0,2%, and diluted up to 100 mL. The intensity of blue was measure with spectrophotometer at λ=625 nm.

### Swelling power

Swelling power was determined as described by Leach (1959). The 0.1 g sample is heated in 10 mL distilled water in waterbath at 60°C for 30 minutes with constant mixing. The samples were centrifuged at 1600 rpm for 15 minutes. The precipitated part was weighted and calculated using Eq. (4).

### Solubility

The solubility of the starch was determined as described by Kainuma (1967). The 0.5 g samples are heated in 10 mL distilled waterbath at 60°C for 30 minutes without mixing. The samples were centrifuged at 1600 rpm for 10

minutes. 5 mL supernatant was separated, dried, weighted and calculated using Eq. (5).

$$\text{Solubility (\%)} = \frac{\text{weight of sedimental paste (g)}}{\text{weight of the sample (d.b.) (g)}} \quad (4)$$

## RESULT AND DISCUSSION

### *Frying expansion*

Frying expansion is shown in Table 2. Frying expansion is the increasing percentage in the volume of starch dough when fried. Starch oxidation results showed a greater development of volume when fried. Oxidized oven dried cassava starch showed greater frying expansion than its native. The presence of high carboxyl groups will provide a great expand power (Demiate et al., 2000). Wang and Wang (2003) suggested that the increasing of specific volume is associated with the formation of carbonyl and carboxyl during the oxidation process that lead to improving hydration of the oxidized starch molecules. The

increasing hydrating ability effects on the rising of starch water binding in starch molecules that would increase the internal pressure and the pressure of water evaporation during the baking or frying process. Sun-dried fermented cassava starch showed greater frying expansion than native oven-dried and commercial cassava starches. It is due to fermentation and UV-C radiation during manufacturing (Camargo et al., 1988; Plata-Oviedo and Camargo, 1998). Starch oxidation with hydrogen peroxide under alkaline and neutral condition leads to decreasing of specific volume (Dias et al., 2011). Lactic acidification together with sufficient UV energy resulted in partial depolymerization of the cassava starch molecules. Thus, when the starch paste was heated, the modified starch molecules more readily took up water molecules, resulting in a higher peak viscosity of the UV-B irradiated samples than those treated with the UV-C irradiation or hot air drying which provided too much starch depolymerization (Vatanasuchart et al., 2005).

Table 2

Frying expansion, carbonyl and carboxyl content of oven-dried cassava starch oxidized with hydrogen peroxide and UV-C irradiation

Treatment	I (watt)	t (minute)	C (g/100 g)	Frying expansion (%)	Carbonyl content (CO/100 GU)	Carboxyl content (COOH/100 GU)
1	20	1	2	166.67	0.403	0.452
2	60	1	2	183.33	0.406	0.642
3	20	3	2	291.67	0.430	0.719
4	60	3	2	200	0.403	0.515
5	20	2	1	250	0.348	0.544
6	60	2	1	300	0.354	0.459
7	20	2	3	266.67	0.462	0.505
8	60	2	3	450	0.630	0.435
9	40	1	1	275	0.344	0.383
10	40	3	1	316.67	0.479	0.514
11	40	1	3	283.33	0.493	0.483
12	40	3	3	300	0.540	0.902
13	40	2	2	308.33	0.325	0.736
14	40	2	2	333.33	0.325	0.740
15	40	2	2	325	0.325	0.741
Native cassava starch				50	0.062	0.149
Sun-dried fermented cassava starch				200	0.064	0.271

### *Carbonyl and carboxyl content*

Both of carbonyl and carboxyl content, which represents of total oxidation of starch, are presented in Table 2. The result shows that carbonyl and carboxyl content of oxidized cassava starch is higher than its native. Schmorak et al. (1963) suggested that the type and amount of functional groups on the starch molecules are formed depending on the pH of the reaction. Formation of carbonyl group will be more intense in acidic condition, however the number of carboxyl increases with the same manner as the pH. The high number of carboxyl in this study, may occur due to the carbonyl group changed to carboxyl group. Conversion of hydroxyl groups to carbonyl takes place slowly, whereas carbonyl changes to carboxyl take place quickly (Sangseethong et al., 2010). The high carboxyl content of the modified starch could be directly related with

the molecular fragmentation due to the oxidative treatment (Takizawa et al., 2004).

### *Amylose content*

The result of amylose content is presented in Table 3. Oxidation of oven-dried cassava starch increases amylose content of oxidized cassava starch greater than its native. An increasing of amylose content in oxidized starch was investigated by some studies (Fortuna et al., 2002). Berski et al. (2011) and Pereira et al. (2017) were reported that the variation of amylose content of oat starch might be due to a varietal differences and the method used for determination. Oxidation did not affect the amylose content of the oat starches. The oxidation level of oat starch was low and so there was not probably a strong depolymerization of the chains of amylose and amylopectin.

Amorphous structure of amylopectin facilitates the oxidator into the starch molecules. Oxidation process occurs in amorphous area, shown by no changes in the pattern of X-ray and its intensity on the oxidation products (Kuakpetoon and Wang, 2001). The differences in amylose contents of oxidized cassava starch are influenced by UV-C intensity, oxidation time, dan hydrogen peroxide concentration. Fermentation and sun drying of cassava starch can increase amylose content, as resulted in the rising of amylose content of sun-dried fermented cassava starch than native cassava starch.

### Swelling power

Based on study result, the swelling power of oxidized cassava starch is lower than its native (Table 3). The decreasing of swelling power might be due to photocrosslinking during oxidation (Wang and Wang, 2003; Lorlowhakarn and Naivikul, 2005). This evidence possibly related to crystallization of amylose and amylopectin in the starch granule as reported in previous studies (Vatanasuchart *et al.*, 2005; Wang and Wang, 2001). The reduction in the swelling power after oxidation may be attributed to structural disintegration within the granules of the starch during the process of modification (Lawal, 2004).

### Solubility

The solubility is a consequence of the leaching of amylose which leads to decreasing of the solubility as the time increased, indicate the increasing of the interactions between amylose and amylopectin molecules, or between

amylopectin molecules (forming a more stable structure), impending to the leaching out of the granules (Gomes *et al.*, 2005). The solubility of oxidized cassava starch is greater than its native (Table 3) which caused by the depolymerization of starch structure and hydrogen bonds which weakness in the oxidized starch. The weakening of the hydrogen bonds makes oxidator easier to penetrate into starch granules, result to form some short chain amylose fraction which is soluble in liquid. All independent variables in this study affect the solubility of oxidized cassava starch.

Sun-dried fermented cassava starch has a higher solubility than native cassava starch. The manufacture of this kind of cassava starch similiar with the manufacture of polvilho azedo. The polvilho azedo is a hydrolyzed starch by fermentation process, resulting to weaker bonds, which facilitated the water penetration in the amorphous zones and the leaching of amylose from the granules during the heating process, mainly close to its gelatinization temperature (Camargo *et al.*, 1988).

### Optimization of oxidation process

Equations relationships between the frying expansion (Y) with UV-C intensity ( $X_1$ ), oxidation time ( $X_2$ ), and hydrogen peroxide concentration ( $X_3$ ) are:

$$Y = -308,595 + 18,441 X_1 + 256,106 X_2 - 6,184 X_3 - 0,177 X_1^2 - 41,110 X_2^2 + 12,640 X_3^2 - 1,354 X_1 X_2 - 0,958 X_1 X_3 - 6,250 X_2 X_3$$

Table 3

Amylose content, swelling power, and solubility of oven-dried cassava starch oxidized with hydrogen peroxide and UV-C irradiation

Treatment	I (watt)	t (minute)	C (g/100 g)	Amylose content (%)	Swelling power (g/g)	Solubility (%)
1	20	1	2	30.24	0.456	2.22
2	60	1	2	30.35	0.289	2.16
3	20	3	2	32.98	0.529	2.06
4	60	3	2	31.21	0.580	2.16
5	20	2	1	32.28	0.603	2.08
6	60	2	1	34.18	0.419	2.40
7	20	2	3	32.61	0.379	2.09
8	60	2	3	35.59	0.445	2.08
9	40	1	1	32.47	0.490	2.23
10	40	3	1	34.21	0.301	2.07
11	40	1	3	31.84	0.388	2.02
12	40	3	3	33.37	0.401	2.01
13	40	2	2	33.73	0.370	2.24
14	40	2	2	33.61	0.369	2.13
15	40	2	2	33.32	0.365	2.24
Native cassava starch				29.67	1.453	1.79
Sun-dried fermented cassava starch				33.33	1.102	1.91

From the calculation results, optimum condition on oxidized oven-dried cassava starch with  $H_2O_2$  and catalyzed by UV-C irradiation got on UV-C intensity 40 watt, oxidation time 2,281 minutes, and hydrogen peroxide concentration 1% with frying expansion 347,26% and desirability 0,63738. Contour curve of frying expansion of

sun-dried cassava starch oxidized with hydrogen peroxide and UV-C irradiation are shown in Figure 1.



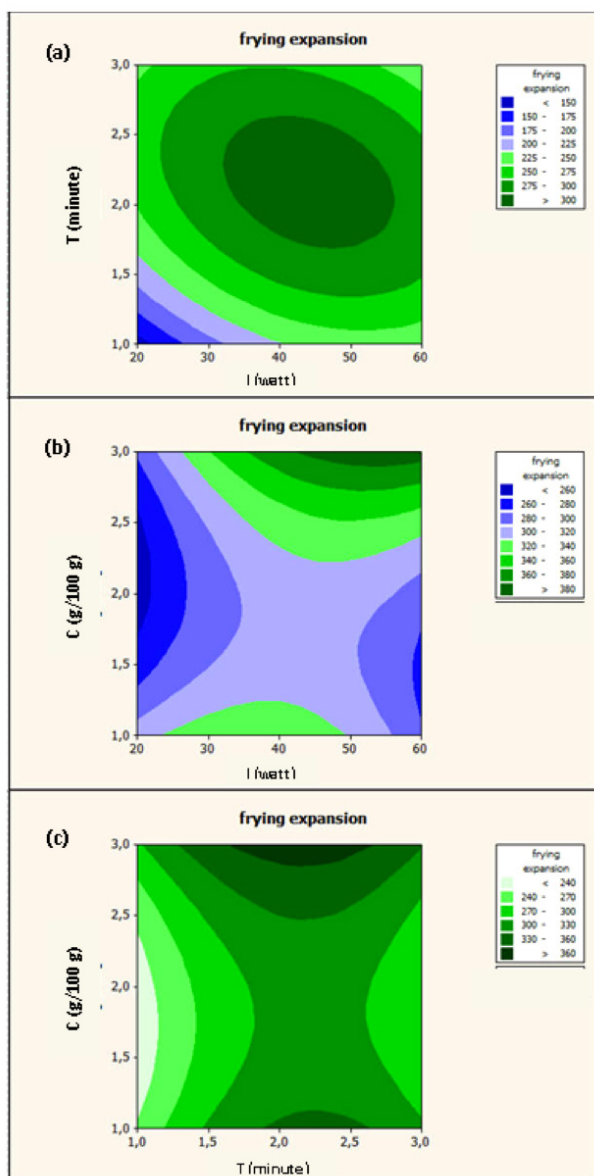


Figure 1. Contour curve of frying expansion of sun-dried cassava starch oxidized with hydrogen peroxide and UV-C irradiation as a function of UV-C intensity and time of oxidation (a), UV-C intensity and concentration of hydrogen peroxide (b), time of oxidation and concentration of hydrogen peroxide (c)

## CONCLUSION

Oxidation of cassava starch with  $H_2O_2$  and catalyzed by UV-C produced a greater number of the frying expansion, carbonyl content, carboxyl content, amylose content, solubility, greater than cassava starch without oxidation (native), and havelower swelling power. The optimum condition on oven-dried cassava starch oxidation with  $H_2O_2$  and catalyzed by UV-C got on UV-C intensity 40 watt, oxidation time 2,281 minutes, and hydrogen peroxide concentration 1% with frying expansion 347,26%.

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