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The Utilization of Ozone As an Alternatif Chlorine Substitution to Increase Quality of Arenga Starch *(Arenga pinnata)*

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Abstract

This study was aimed to determine the optimum conditions of flour bleaching with ozonation techniques and compare the effect of chlorination results. The process of bleaching flour with ozonation process is carried out in batch system. The research procedure is to vary the time 0, 30, 60, 90, 120, 150, and 180 minutes. Variation in pH 4, 6, native pH of flour, 8, 10 and 1: 3 (b / v) concentration of flour against water. Ozone concentration 0.325 g ozone / hour. The effect of the addition of chlorine is soaked for 180 minutes with the concentration of chlorine to the flour of 0.325% (w / w) and the concentration of flour to water that is 1: 3. The results obtained were carried out by means of data sampling on purpose and were carried out by white degree analysis, organoleptic test, chlorine content test and protein content test. The results of the research that has been done, that the optimum conditions for the bleaching process of flour using ozone are pH 4 with 180 minutes obtained the value of Brightness L* = 93.32, b* = 5.10. Organoleptic results give results that respondents prefer the results of the ozonation process with the classification of odor, color and texture in a row is 9; 8.5; 8.6. The results of a positive, and quantitative qualitative chlorine content test with an Argentometric Mohr titration produced 0.01% (w / w) per 10 g of palm sugar.

Keywords: Chlorination, Ozonation, Bleaching, pH, Palm Flour,

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1. Introduction

Aren or sugar palm (*Arenga pinata)* is a plant that easy to adapt in various climate conditions. Total areas of sugar palm plantation in Indonesia reaches 24,476 ha [1]. The sugar palm part that can be used as sugar production is stem pith. It contains 10.5-36.7% of starch and 0.10% of protein. The average yield of flour production is 60-70 kg [2]. In Indonesia, standard quality criteria Aren's starch mentions in SNI 3729-2008 standards [3]. However, in fact, the starch natural color is yellowish, because of its carotenoids content inside. The yellowish starch has low cheap cost. Therefore, bleaching process is needed to improve the selling quality of palm flour.

At the present, an effort to bleach Aren's starch uses hazardous chemicals calcium hypochlorite ($Ca(ClO)_2$) [4]. Chlorine is a carcinogenic substance that increases cancer probability when consumed, continuously. In other hand, waste products of Aren's starch from the chemical bleaching process is very dangerous, because of its high ability to bind with organic compounds [5]. Therefore, a healthier and eco-friendlier process is needed to whiten the palm sugar. Ozone is the solution to replace chlorine and reduce environment pollution. Ozone is a strong oxidizing agent that safe and able to oxidize carotenoid without leaving harmful residues [6]. This study aimed to understand the comparison of the effect of ozone on the whiteness of palm sugar and the effect of chlorine on the white degree of palm sugar.

2. Method

2.1. Ozonation process

For the first process, 3 kg of flour was dissolved in 1 L of aquadest, then same solution was used to create variations treatments on pH using CH_3COOH and NaOH. After that, the solution was aerated using O_3 gas using ozonator and stired at 400 rpm. Data collection for 0, 30, 60, 90, 120, 150, and 180 minutes then flour in the oven for 2 hours at 70°C.

2.2. Chlorination process

The Aren flour was soaked with chlorine solution for 180 minutes. Concentration of chlorine solution to flour was 0.325% (w / w) and the concentration of flour to water was 1: 3 (w / v). The process was carried out in a glass beaker with a stirring process of 400 rpm and then flour in the oven for 2 hours at 70°C.

2.3. Research analysis

This study was used a white degree test using Chroma meter, chlorine test qualitatively and quantitatively and organoleptic test.

3. Result and Discussion

Aren flour was obtained from home industries of flour in Ngabean-Kendal Village. The flour was brownish with white degree value of 66.65%. The results of the preliminary analysis of the of palm sugar content before treatment were presented in table 1.

Table 1: The results of the preliminary analysis of palm sugar flour before treatment [6].

Type	Value	Analisys
Protein	0,39 %	proximate analysis, SNI 06-2856-1998
Amilum	81,61 %	
Fat	0,32 %	
Moisture	16,26 %	
pH	7	pH digital

In the Table 1 shows that white degree is very low at 66.65% and the protein content is 0.39%. Even though, the standard good flour has white degree above 80 [7]. The level of white degree is also regulated in SNI 3729-2008 which states that the white color of flour is pure white.

3.1. Flour bleaching process using pH variations

Measurement process of white flour level was conducted using Chroma meter test tool which is obtained by three-dimensional color values, namely L* a* b*. Three components of Chroma meter is L* for luminance (lighting) starting from 0 to 100, a* represents colors dimension from green to red and then component b* for colors dimensions from blue to yellow, where each starts from -120 to +120. When, a* value closer to 0, then the white level value is higher, means whiter [8].

Overall, the bleaching process using ozonation was increase white score at first 30 minutes, then at the 30-180 minutes, the white degrees were not significantly changed. It may be influenced by pH factor. On acidic pH the oxidation reaction occurs directly [9]. Increasing the acidity of the water, ozone easily decomposes O2 and HO p*, ozone is more reactive in acidic conditions. Therefore ozone in an acidic environment is very strong in degrading carotenoid bonds and has highest white degree value of 93.32%, where acidification carried out with the addition of organic material oxalic acid aims to reduce carbohydrate degradation by radicals formed on decomposition ozone [9].

In the original pH conditions, ozonation occurs directly and indirectly [10]. In these conditions ozone works without special treatment. It can be seen in Figure 1 that the original pH of flour or without the addition of other substrates has a significant increase

in white degrees. Ozone has been shown to improve the quality of palm sugar flour which initially has a L* from 66,65% to 93,20% at 30 minutes. In these conditions ozone focuses on breaking the double bonds of carotenoids. As the final result of oxidation process only carbon dioxide and water will be obtained [11].

At alkaline pH conditions, the oxidation reaction that occurs is indirect oxidation. Ozone will react with sodium hydrogen decomposed to produce HO_2^* compounds in the form of free radicals hydrogen peroxide thereby reducing ozone performance in degrading carotenoid substances in palm sugar. Decomposition of ozone can be initiated by OH^- ions. In alkaline conditions the number of OH ions that initiate decomposition of ozone to OH- is greater than pH 4, the original pH of flour and pH 6, as a result the amount of OH-formed also more and the ozonation reaction indirectly increases also at pH 10 which finally produces saturated compounds which cannot be further oxidized by ozone so that it is oxidized by indirectly attacking hydroxyl radicals and forming oxidized free radicals. Oxidation of hydroxyl compounds with ozone is often imperfect oxidation and rarely produces CO2 [12, 13]. In the other side, OH- can oxidize most organic compounds quickly because it has an oxidation potential (2.8 volt) greater than ozone (2.07 vol) and less selective [13]. Increasingly alkaline atmosphere causes ozone decomposition become radical hydroxyl faster and more numerous [14]. In Figure 1, it can be seen that pH 10 has a very significant enhancement in white degree at the 180^{th} minute, resulting in a white degree up to 88,13%, where the white degree is not all the result of the ozonation process because ozone stability was interrupted by the process of addition organic hydrogen sodium material.

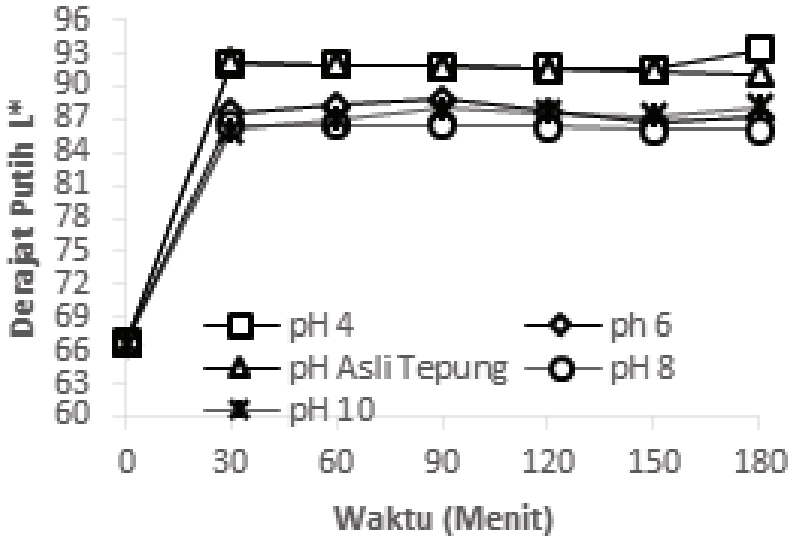

Figure 1: Relationship Between White Levels of Palm Flour, Variations in pH and White Degrees.

The A* data analysis cannot be taken into consideration in this study because the basic color of the carotenoids is yellow while a* has the effect of green and red. Then it can be seen in Figure 2 a* data is unstable and volatile. Figure 2 shows the effect of bleaching time and pH on the value of a* at pH 4, pH 6, the original pH of flour, pH 8 and pH 10.

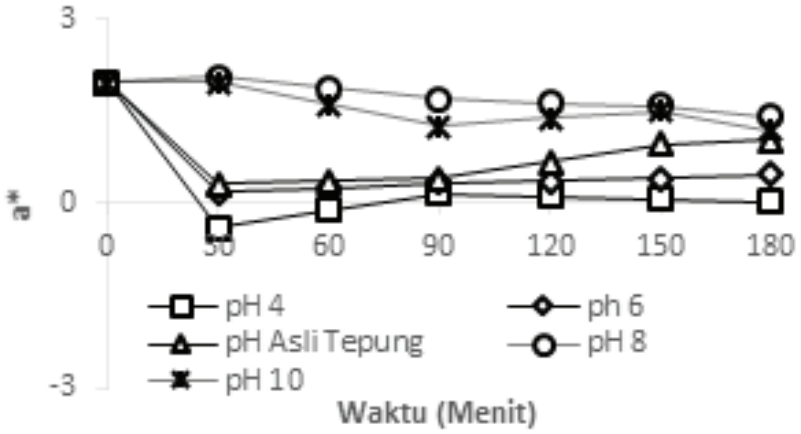

Figure 2: Effect of bleaching time and pH with a*.

The effect of the time and pH of the bleaching on the b * value at pH 4, pH 6, original pH, pH 8 and pH 10. In the bleaching process there is a b* that states a yellowish and bluish color. This b* value shows the color intensity of the carotenoid substance which has a yellow base. In flour before being bleached the color of the flour is more creamy with a b* value was 9.9 due to the effect of carotenoid substances. The ozonation process provides significant results on palm flour that the results in Figure 3 have a significant decrease from the first 0-30 minutes. At 30 - 180 minutes it can be seen that the change in b* value is not too significant. This result is because carotenoids have been oxidized by ozone [4]. Figure 3 obtained the optimum conditions that is at 150 minutes and pH 10 with b * 4.00.

The optimal conditions in the treatment under pH 4 conditions with 180 minutes ozonation time can be used as a comparison of chlorination process because it has a white degree value of L* of 93.32% and b* value was 5.10%.

3.2. Comparison of results of white ozonation with chlorination

The ozonation and chlorinassi process with variations with the same concentration is 0.325 g / L and stirred for 180 minutes at a speed of 400 rpm, the concentration of flour to water is 1: 3 (b / v). So the results obtained in table 2 are as follows:

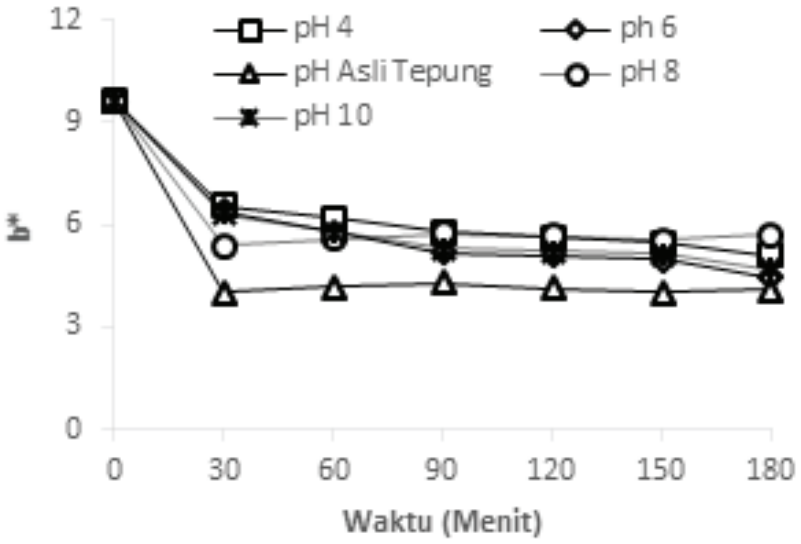

Figure 3: Effect of bleaching time and pH with b*.

Table 2: Comparison of White Degrees from Ozonation and Chlorination.

Process	pH Process	pH Final	White Degrees (L*)	b*
Whitout Treatment	7,2	7,2	66,65	9,64
Ozonation	4,1	7.1	93,32	5,10
Chlorination	10	7,8	94,42	6,52

The results of analysis of variance from table 1 states that the concentration of chlorine solution with stirring duration has a very significant effect on the pH value of the suspension. The high concentration of chlorine and soaking time given will increase the pH value of the solution because chlorine solution is an alkaline salt that dissolved in water, where if it react with water. it will broke down into calcium ions and hypochlorite ions. The hypochlorite ion is hydrolyzed by producing OH- [16]. Therefore, chlorine Ca (ClO) 2 solution can increase the pH value.

The higher the chlorine concentration produced, the higher the white degree value of palm sugar flour, but this is directly proportional to the increase in chlorine content which is still included in palm sugar. Feasibility tests can be carried out to analyze the chlorine content that is still present in dried palm flour by organoleptic test (odor, color, and texture) and test the chlorine content in a skinative and quantitative manner.

3.3. Organoleptic test results of palm flour with chlorination process

Organoleptic test used is a test of hedoik scale or preference for color and odor [17]. Organoleptic test is used to determine the extent to which consumer acceptance of sago starch is bleached with chlorine solution or with ozone. Then an organoleptic test with a hedonic scale was carried out. 10 panelists from all ages and different background were gave value for each sample of flours that, based on their preferences.

The results of the analysis of various organoleptic tests in Figure 4 overall show that panelists prefer to smell and texture from palm flour with the ozonation process but for color assessment it appears that panelists prefer palm sugar flour bleached using chlorine compared to flour with ozonation process. This test is subjective because each panelists were gave values to the palm starch they like. It may affected on their selves condition, emotional, and environment when a panelist assesses the sample.

The results of organoleptic test on odor showed that the treatment on the bleaching process of palm sugar using ozone was higher. This higher value was caused by ozone gas that has no odor and ozone does not eliminate the distinctive aroma of palm sugar. Unlike palm sugar which is bleached with chlorination because it has a typical chlorine odor, the chlorine odor must be removed by washing several times with clean water until the smell of chlorine is lost. In addition, the chlorination process also has an effect on removing the distinctive aroma of palm sugar and the average panelist does not like it.

The results of organoleptic tests on color showed that the treatment of the bleaching process of palm flour using chlorine was higher. This higher value is due to the results of bleaching with chlorine resulting in a shiny white flour so attractive to the panelists. The addition of palm sugar which is bleached with ozone produces a slightly dull white color that is not attractive to panelists.

The organoleptic test results on texture showed that the treatment of the bleaching process of palm sugar using ozone was higher. This higher value is because ozone reduces moisture content in flour and produces flour that has a dry and soft texture. By ozonation, the moisture was reduced and gave more protection against decomposer mold and bacteria. Conversely, if the water content is too low, it can change the shape, physical and chemical properties of a material. Unlike palm sugar which is bleached with chlorine which produces a slightly moist texture.

So from this explanation, it can be concluded that palm flour with the bleaching process using ozone can be accepted by the community. The results of the variance in

organoleptic tests can be seen in Figure 4 Results of Assessment of Organoleptic Tests (odor, color and texture)

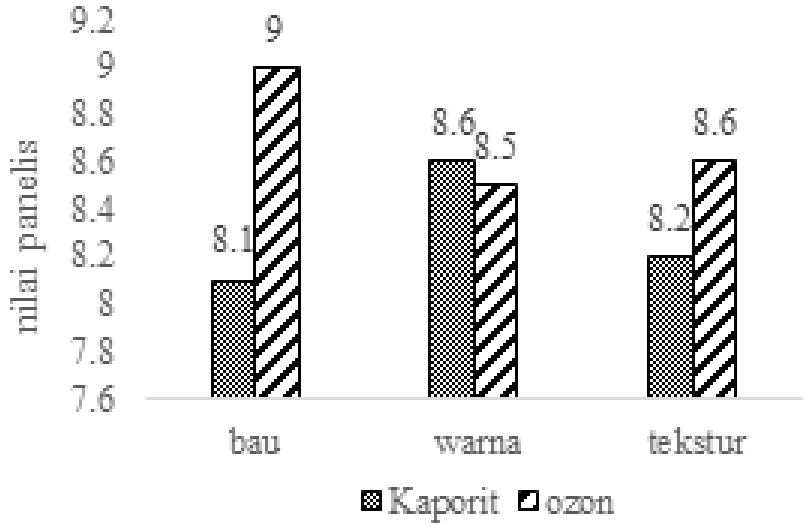

Figure 4: Results of Organoleptic Test ssessment (odor, color and texture).

3.4. Qualitative and quantitative tests of chlorine levels in flour

3.4.1. Qualitative test

From Figure 5 it turns out that the flour that is bleached with chlorine positive contains chlorine which is still dissolved in water. This fact was proofed by white deposits at the bottom of the tube. The precipitate formed according to the reaction:

$$Ag^{+} + Cl^{-} \; AgCl \downarrow \text{(white precipitate)} \quad (1)$$

In reaction (1) the Ag^{+} ion contained in $AgNO_3$ reacts with Cl^{-} ion found in $Ca(ClO)_2$ and then precipitates white AgCl crystals [18].

In the color change test it turns out that the flour is bleached with positive chlorine containing chlorine which is still dissolved in the water. This fact is evidenced by the change in color of the sample filtrate which initially has a clear color then changes to blue after being reacted with iodine.

3.4.2. Quantitative test

Quantitative analysis was carried out to determine the level of chlorine bleach in palm flour which has positive chlorine content. The method used is Argentometry Mohr was

Figure 5: A white precipitate is formed at the bottom of the test tube in the chlorine test.

(a) (b)

Figure 6: Color changes in flour sample filtrate. (a) the filtrate before treatment, no color changes have occurred, (b) positive samples contain chlorine, turn into blue.

conducted by titration process. The principle of Argentometry Mohr is a sedimentation reaction where chloride compounds are neutral or slightly alkaline with a standard solution of silver nitrate ($AgNO_3$) and potassium chromate indicator solution (K_2CrO_4) at the beginning of the titration will occur silver chloride deposits and after the equivalence point, the addition of a little silver nitrate will react with chromate to form a brownish red chromate precipitate. The addition of the potassium chromate indicator (K2CrO4) aims to determine the color of the endpoint of the titration [19]. Here are the reactions that occur in Argentometry Mohr analysis:

$$Ag^{+} + Cl^{-} \; AgCl \downarrow \text{(white precipitate)} \tag{2}$$

$$2Ag^{+} + CrO_4\ Ag_2CrO_4 \text{ (turn into red)} \quad (3)$$

Based on the quantitative examination that has been carried out, the average level of chlorine in the flour that is bleached with chlorine is 0.1 mg / L or 0.01% by weight of chlorine in mg per 10 g of palm sugar.

So in this study it can be concluded that the palm sugar that was bleached with chlorine and washed repeatedly until there is no odor and the pH value becomes neutral. After testing with several methods the results given are chlorine-positive although with a very low concentration but still dangerous to be consumed continuously, regarding of chlorine is not recommended as an addictive compound added in the flour and flour bleach prcessing [20].

3.5. Test pH variations in protein Proximat Ozonasi, chlorination and the degree of white

The samples tested i.e. flour without flour, treatment with the process ozonasi acid pH variations; the original pH of flour; the pH is basa and flour bleached with a process of chlorination process at the time of 180 minutes. Comparison of concentrations of flour with water namely 1:3 (b/b). Concentrations of ozone output i.e. 0.325 g/hour. Concentrations of chlorine with flour namely 0325 (b/b). Proksimat protein test results can be seen in Table 3:

Table 3: Proksimat protein test results against ozonasi and chlorination pH variation as well as the degree of white.

Perlakuan	kadar protein %	Derajat Putih
The Original flour	0,40	66,65
Acid Ozonation	0,39	93,32
Neutral Ozonation	0,40	91,22
Alkaline Ozonation	0,40	88.13
Chlorination	0,39	94.42

Table 3 looks that the influence of bleaching flour aren semi-hereditary process chlorination and pH variations with ozonasi keduaya protein levels delivering results is not significant. The data sessuai with the research of wang et al, (2017) stating that the substance and the substances of chlorine O3 did not change the components of the protein in flour aren. Table 3 that protein flour aren about 0.39%-0.40% as described by Prayudi (2001).

4. Conclusion

The results of the research that has been done, that the optimum conditions for the bleaching process of flour using ozone are pH 4 with 180 minutes obtained the value of Brightness L * = 93.32, b * = 5.10. Organoleptic results give results that respondents prefer the results of the ozonation process with the classification of the value of odor, color and successive textures are 9; 8.5; 8.6. The results of a positive, and quantitative qualitative chlorine content test with an Argentometric Mohr titration produced 0.01% (w / w) per 10 g of palm sugar.

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References

[1] Effendi, D.S. (2010). Prospek pengembangan tanaman aren (*Arenga pinnata Merr*) mendukung kebutuhan bioetanol di Indonesia, *Prespektif Biologi*, 9, 36-46.

[2] Adawiyah, D.R., Sasaki, T.,dan Kohyama, K. (2013). *Characterization of arengan starch in comparison with sago starch*, 102-104. Elsevier: Carbohydrate Polymers.

[3] Tim Badan Standardisasi Nasional. (2008). Surat Keputusan Mentri perindustrian menetapkan SNI 3729-2008, Kode panggil, : 633.6 TEP, No. Induk Buku : 5867 / 2008. Jakarta: Badan Standardisasi Nasional.

[4] Chittrakorn, S., Earls, D., dan MacRitchie, F. (2014). *Ozonation as an alternative to chlorination for soft wheat flours*, 203-206.

[5] Hasan, A. (2008). *Dampak penggunaan klorin. Teknik Lingkungan*. P3TL-BPPT. 7. (1):90-96.

[6] Tim Badan Standardisasi Nasional. (2008). Surat Keputusan Mentri perindustrian menetapkan SNI 06-2856-1998, Kode panggil, : 433.6 TEP, No. Induk Buku : 5867 / 2008. Jakarta: Badan Standardisasi Nasional.

[7] Yam, K. L., & Papadakis, S. (2009). A Simple Digital Imaging Method for Measuring and Analyzing Color of Food Surfaces. *Journal of Food Engineering*, 61, 137–142

[8] Keenan, C.W., Kleinfelter, D.C., dan Wood. J.H. (2011). *Ilmu Kimia Untuk Universitas*. Jilid 2. Penerbit Erlangga. Jakarta.

[9] Beltran F.J. (2004). *Ozone Reaction Kinetics for Water and Wastewater System*. Florida: Lewis Publishers.

[10] Hill A.G., dan Rice R.G. (2010). Handbook of Ozone Technology and Applications, Vol. 1, *Ann Arbor*, pp. 1–37. MI: Ann Arbor Science Publishers

[11] Langlais Bruno, David. Reckhow, Deborah.. Brink. (1991). *Ozonein Water Treatment Application Engineering*. Florida: Lewis Publishing.

[12] Sang-Kuk, H., Kazuhiro, I., and Utsumi, H., (2012), *Quantitative analysis for the anchancement o hydroxyl radical generation by phenols during ozonaton of water.* Hongkong: Sun Publishing.

[13] Putra, G. H. (2012). Pembuatan Beras Analog Berbasis Tepung Pisang Goroho (Musa Acuminate) Dengan Bahan Pengikat Carboxymethyl Celluloce (CMC). *Jurnal Agritech*. hal.1-9

[14] Nur, M.A., et. al. (2008). *Kimia Dasar II*. Jurusan Kimia, FMIPA-IPB, Bogor

[15] Soekarto, S.T. (2016). Penilaian organoleptik untuk indrustri pangan dan pertanian. Jakarta: Bhratara Karya Aksara.

[16] Marsini. (2013). Penentuan Kadar Residu Klorin Pada Beras Di Pasaran. Analis Kesehatan. Thesis Fakultas Ilmu Kesehatan, Universitas Setia Budi : Surakarta

[17] Sudjadi. (2013). *Kimia Farmasi Analisis. Pustaka Pelajar*. Yogyakarta. Hal : 146

[18] Anonim. (2008). Peraturan Menteri Kesehatan Republik Indonesia No.772/Menkes/Per/XI/88 tentang Bahan Tambahan Pangan. Departemen Kesehatan Republik Indonesia. Jakarta.