STUDY ON THE UTILIZATION OF CATECHINS FROM Gambir (Uncaria Gambir Roxb) LEAVES AS ANTIOXIDANTS COOKING OIL

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ABSTRACT

Catechins are flavonoid molecules that act as antioxidants in the body. The degradation of palm oil with catechin treatment (400, 200, 100, 50, 0) was investigated in this work (ppm). The goal of this study was to see how efficient catechins are as antioxidants in cooking oil and what the optimal treatment would be for the amount of catechins added. Catechin concentration, free fatty acid, peroxide value, water content, color, and fatty acid profile are all analyzed using GC-MS. Treatment E (400 ppm) was found to be the most effective, with free fatty acid values of 0.45 percent, peroxide value of 5 meq/g, moisture content of 0.89 percent, and color of 95.95 (L*16, 11, a* -1.51, b* 14.51). Catechins can retain three fatty acids in the oil, according to GC-MS analysis: hexadecanoic acid, 9-octadecanoic acid, and heptadecanoic acid.

Keywords: catechins, degradation, oil, cooking oil, preservation

INTRODUCTION

Indonesian people in general use a lot of oil in the food processing process. One example was cooking oil. Cooking oil comes from plants that are rich in high content of unsaturated fatty acids (Marlina, 2010). Cooking oil was used as a heat conductor, adds a savory taste to food, and adds nutritional value to food ingredients (Tomagola, et al., 2016, Naufalin and Yanto, 2009). The amount of unsaturated fat in cooking oil, when left in the air, the rate of oxidation will increase with increasing temperature and will decrease with decreasing temperature. The speed of adding peroxide at a temperature of 100°C -115°C was two times higher or higher than at a temperature of 10°C (Marlina, 2010). Unsaturated fatty acids contained in cooking oil can undergo oxidation reactions and produce active peroxides which can decompose into aldehyde compounds that smell and taste rancid (Marlina, 2010). The emergence of a rancid odor was the main oil damage. The unpleasant rancid odor was caused by the formation of compounds resulting from the breakdown of hydroperoxides (Marlina, 2010). Damage to cooking oil cannot be prevented, however, the speed of the oxidation process of unsaturated fatty acids that occurs in cooking oil can be slowed by the administration of antioxidants (Tomagola, et al., 2016).
Antioxidants are generally defined as compounds that can delay, slow down and prevent the oxidation process of fats or oils. In a special sense, antioxidants are substances that can delay or prevent the occurrence of free radical oxidation reactions in the oxidation of oils or fats (Sayuti and Yenrina, 2015). In the food industry, antioxidants can be used to prevent oxidation processes that can cause damage, such as rancidity, changes in color and aroma, and other physical damage (Sayuti and Yenrina, 2015).

Based on the source, antioxidants are divided into two groups, namely synthetic antioxidants (antioxidants obtained from the synthesis of chemical reactions) and natural antioxidants (antioxidants extracted from natural ingredients) (Sayuti and Yenrina, 2015). Bioactive compounds extracted from several plants or plants are widely used as natural antioxidants, because synthetic antioxidants used in food products have received a lot of negative responses from consumers. This was due to their potential to damage or endanger health and cause tumors/cancer to grow (Taufik, 2019).

The use of synthetic antioxidants such as benzoic acid, BHA (Butylated Hydroxy Anisol), BHT (Butylated Hydroxy Toluene), TBHQ (Tertiary Butylated Hydroxy Quinone), and propyl gallate can cause side effects on body health. BHA and BHT have been studied to cause tumors in experimental animals if used for a long time, and can cause liver damage if consumed in excess (Tomagola, et al., 2016). The side effects caused by the use of synthetic antioxidants spur the development of research on natural antioxidants that are safer and more capable of reducing free radicals in the body. The selection of natural antioxidants must consider the solubility in oil. Therefore, the use of natural antioxidants that are polar, such as anthocyanins does not recommend or suggested. Compound natural antioxidants that are semipolar or non-polar, can be developed in oil or fat products, such as semi-polar catechins. Therefore, the addition of catechins in oil as antioxidants in oil can be developed. It was proven that research conducted by Marlina (2010) and Taufik (2019) regarding the use of catechins in gambir products as natural antioxidants in cooking oil found that the addition of catechins can slow down the oxidation process in oil and extend the shelf life of vegetable oils.

Gambir was one of the leading commodities in Indonesia. Currently, Indonesia was listed as the main producer and supplier of the world’s gambir needs, reaching 80% with a total production of around 18,297,760 tons/year. The markets for Indonesian gambir products are Australia, Bangladesh, Hong Kong, India, Malaysia, Nepal, Pakistan, Taiwan, Japan, Saudi Arabia, the Philippines, Thailand and Singapore (Yeni, 2015). Gambir was an agricultural product that contains a lot of flavonoid compounds. The flavonoid compounds found in gambir include catechins which have the chemical formula C15H16O64H2O and several hydroxy acids, all of which are rich in phenolic groups and can be used as food tannins. Gambir was an indigenous product as a source of catechins. In Gambir there was a dominant catechin compound (Pambayun, et al., 2007).

Gambir products can be produced from gambir plants by processing young leaves and twigs using hot water, followed by pressing, precipitation of liquids, and drying of the sediment, to obtain gambir products. Gambir leaves are known to contain phenolic compounds such as polyphenols, phenols, and catechins. Catechins are the main compounds and one of the natural antioxidants in gambir products. The use of aijans.lppm.unand.ac.id

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catechins from the solid extract of gambir was currently getting a lot of attention. But using a very long process. Therefore, ketakin from gambir leaves was used directly without a long process. Because catechins have good solubility in oil,

The use of catechins from gambir leaves as natural antioxidants in oil can be developed. In a previous study, Taufik (2019) compared the oil that was added with pure catechins from the solid extract of gambir with a synthetic antioxidant, namely TBHQ, obtaining the optimum concentration of adding 200 ppm of pure catechins was the same as the addition of 180 ppm of synthetic antioxidant TBHQ. In Taufik's research (2019) used catechins extracted from gambir products on the market. Theoretically, catechins can also be extracted directly from gambir leaves. Until now there was no information about the effectiveness of catechin antioxidants extracted directly from gambir leaves on the quality of cooking oil. Therefore, it was studied about the use of catechins from gambir leaves as antioxidants in cooking oil.

EXPERIMENTAL SECTION

A. Material

The materials used in this study consisted of raw materials and chemicals. The raw materials are gambir leaves from Pesisir Selatan Regency and Refinery Oil from PT. Incasary Raya, Padang City. The chemicals used were ethyl acetate, 2-propanol, acetic acid, n-hexane, chloroform, 0.1 N potassium hydroxide (KOH) in alcohol, sodium thiosulfate (Na$_2$S$_2$O$_3$), sodium hydroxide (NaOH), diphenyl-2-picrylhydrazil (DPPH), ethanol 96%, Sodium Sulfate (Na$_2$SO$_4$), distilled water, and other chemicals.

The instruments that used in this research are rotary evaporator (Buchi B-490), freezer (Gea AB-396-T-X), shaker waterbath (Memmert WNB 14 W/Ring) analytical balance (Denver M-X). 310), Ranchimat (Metrohm Herisau, Switzerland), Hunter lab, UV-Vis spectrophotometer (Hitachi), erlenmeyer (IWAKI), measuring cup (Pyrex), separating funnel (Pyrex), 30 cm stir bar, vacuum pump, oven, hotplate, microburette, whatman filter paper no.1, hot plate, burette, Gas Chromatography-Mass Spectroscopy (GCMS), porcelain dish, desiccator, and glassware (Pyrex) commonly used in the laboratory.

B. Method of Research

The design used in this study was a completely randomized design (CRD) with 5 treatment levels and 2 replications. Data were analyzed using the analysis of variance (Analysis of Variant or ANOVA) followed by a further test of BNT or DMRT with a 5% confidence interval. The best treatment was selected using the Multiple Attribute method. The treatment carried out in this study was the addition of the concentration of catechins from gambir leaves in 100 grams of cooking oil as follows:

- a. Treatment A (0 ppm)
- b. Treatment B (50 ppm)
- c. Treatment C (100 ppm)
- d. Treatment D (200 ppm)
e. Treatment E (400 ppm)

C. Research Implementation

Extraction of Gambir Leaves (Damanik, et al., 2014)

50 grams of fresh gambir leaves steamed for 15 minutes in water, then dissolved in 300 ml of solvent (95% ethyl acetate). The samples were then heated in heating mantles complete with a cooling circuit for 3 hours. Then filtered and the filtrate in a Rotary Vacuum Evaporator to evaporate the ethyl acetate solution to obtain a paste, at a temperature of 40°C until all the solvent has evaporated which was indicated by the solvent not dripping again within a minimum period of 5 minutes. Gambir leaf extract was obtained.

Purification of Catechins from Leaf Extract Gambir (Taufik, 2019)

1 gram of gambir leaf extract was diluted with ethyl acetate, as much as 10 mL then stored in the freezer for 24 hours. Then it was dripped with n-hexane little by little until white catechin needles were formed. Catechins are separated by filtration. Repeat work up to 10 times. Catechins dry at temperature 40°C for 24 hours until it becomes powder.

Oil Treatment (Taufik, 2019)

Sample preparation for detection of palm oil quality (Peroxide Number, Free Fatty Acid, Moisture Content, Color, and Fatty Acid Identification by GC-MS). Sample 0 ppm, 50 ppm, 100 ppm, 200 ppm, and 400 ppm of each catechin were added as antioxidants. Preparation of 400 ppm by dissolving 0.4 grams in 1 L of oil. The oil that has been added with catechin treatment was degraded at a temperature of 180°C using a Rancimat device. For each sample, the Free Fatty Acid content, Peroxide Number, Moisture Content, Color, and Fatty Acid Identification with GCMS were tested.

D. ANALYSIS PROCEDURE

Catechin Levels

a. Standard Solution

Weigh 50 mg of dry catechin standard (Ws mg), then pour into a 50 ml volumetric flask quantitatively, dissolve and dilute with ethyl acetate and squeeze (solution A); - put solution A in a water bath for 5 minutes to achieve a homogeneous solution, pipette 2 ml of solution A quantitatively into an Erlenmeyer with a 100 ml grinder and add 50 ml of ethyl acetate solvent (solution B) and place the solution in a water bath for 5 minutes. Solution B was ready for measurement.

b. Sample Solution

Weigh 50 mg of catechin powder sample (W mg), pour into a 50 ml volumetric flask, dissolve and dilute with ethyl acetate and squeeze (solution C). Put the solution C into a water bath for 5 minutes then filter, discard 15 ml of the first filtered filtrate and continue filtering, pipette 2 ml of the C solution filtrate.
quantitatively into an Erlenmeyer with a sharpening cap 100 ml and add 50 ml of ethyl acetate solvent (solution D), put solution D into a water bath for 5 minutes, solution D was ready for measurement.

c. Solution Measurement

Measurements were carried out using an ultra violet spectrophotometer at a wavelength of 279 nm and 300 nm, with the following steps: Measure the absorbance of the blank solution (ethyl acetate) = 0, measure the standard absorbance solution at a wavelength of 279 nm = Ec and 300 nm, measure absorbance of sample solution at wavelength 279 nm = Et and wavelength 300 nm

\[
\text{Absorbance of Sample Solution} = \frac{\text{Standard Solution Absorbance}}{\text{Initial weight of sample (g)}} \times 100\%
\]

**Free Fatty Acids (Taufik, 2019)**

Three grams of the oil sample was diluted with 50 mL of neutralized isopropyl alcohol. Homogenize the solution by heating it until there are bubbles. Added 3 drops of phenolphthalein indicator, then titrated with 0.1N NaOH to light pink can last at least 30 seconds. FFA levels were determined as palmitic acid with the following equation:

\[
\% \text{ALB} = \frac{mL \text{ NaOH} \times N \text{ NaOH} \times 0.256}{\text{Initial weight of sample (g)}} \times 100\%
\]

**Peroxide Number (Taufik, 2019)**

The oil sample (5 g) was put into a 250 mL Erlenmeyer flask and diluted with 30 mL of a solution of acetic acid: chloroform (3: 2) while shaking until dissolved. Saturated Potassium Iodide (Saturated KI) (0.5 mL) was added to the solution. The solution was allowed to stand for one minute and occasionally shaken, then added 30 mL of distilled water. The mixture was titrated with 0.1 N Na2S2O3 until the yellow color almost disappeared. The starch solution (1%, 0.5 mL) was added immediately and the titration was continued until the blue color just disappeared or was clear. Then note the volume used. The peroxide value was expressed in milliliters of peroxide equivalent in 1000 g of sample, and was determined using the following equation:

\[
\text{BP} = \frac{mL \text{ Na}_2\text{S}_2\text{O}_3 \times N \text{ Na}_2\text{S}_2\text{O}_3}{\text{Initial weight of sample (g)}} \times 100\%
\]

**Color**
The color of the oil was measured using the Hunterlab Colorimeter tool by placing the sample in the available container then pressing the start button and the L, a, and b values of the measured oil will appear ranging from 0 - 100. The notation "a" indicates the chromatic color of the red-red mixture. green, the value "+a" indicates red and the value "-a" indicates green. The notation "b" indicates a mixed chromatic color of yellow-blue, the value "+b" indicates yellow and the value "-b" indicates blue. While the notation "L" indicates the brightness of the color. The higher the "L" value, the brighter the color of the oil.

**Water Content**

The clean porcelain dish was heated in an oven at 105°C for 30 minutes, then cooled in a desiccator, then weighed until a constant weight of dry-empty plates was obtained. The sample of cooking oil was weighed as much as 2 g in the cup and dry sand 2 grams, then heated in the oven at 105°C for 4 hours. The sample was cooled in a desiccator for approximately 15 minutes and reweighed. Drying was carried out until a constant weight was obtained. Weight reduction was the amount of water in the oil. Determination of water content was carried out in 2 repetitions.

\[
\% \text{ Moisture Content} = \frac{\text{Initial weight of sample (g)} - (\text{final weight} - \text{empty cup (g)})}{\text{Initial weight of sample (g)}} \times 100\%
\]

**Identification of Fatty Acid Profile (GC-MS) (Yuliana, 2017)**

a. Sample preparation

The oil was put into a test tube. Added 1 mL of n-hexane and alcohol. Added 3 mL of saturated NaCl solution to clarify the separation area between the extract and alcohol. The n-hexane portion (upper phase) was transferred to the vial, anhydrous Na2SO4 was added to trap water so as to prevent the presence of water in the test material. the test sample was put into the second vial carefully so that the anhydrous Na2SO4 was not carried away. The sample was ready to be analyzed on the GC-MS instrument.

b. Identification

GC-MS was activated and all related components were adjusted until a 1 l sample was ready to be injected and ready to run. The analysis view was set. Selected sample login on the monitor while waiting for GC and MS on the monitor in the Ready state. Start was clicked on the monitor, so that the automatic injector cleans the syringe according to the setting, 1 l of the sample was injected into the autoinjector. If the graph already looks a bit flat, the GC analysis can be stopped by clicking stop on the monitor. The graph peaks are identified at each retention time from the initial peak to the final peak and are matched with references in the GCMS program by selecting the similiary search option. The identification results will show the most similar components of several components of molecular weight and high intense peak. After that, disable the GC-MS instrument.
RESULT AND DISCUSSION

Raw Material Analysis (Catechin Powder)

Catechin powder is a pure catechin produced from gambier leaves which goes through a series of processes ranging from leaf steaming, extraction, and purification. The catechin powder obtained has a slightly brownish white color which can be seen in Figure 1. The catechin powder obtained was analyzed for the levels of catechins and antioxidant IC50. The results of the analysis can be seen in table 1.

Table 1. Results of Analysis of Catechin Powder

<table>
<thead>
<tr>
<th>Catechin powder</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catechin level (%)</td>
<td>94.26 ± 0.11</td>
</tr>
<tr>
<td>Antioxidant activity</td>
<td>2.74 ± 0.08</td>
</tr>
</tbody>
</table>

The value of catechin content obtained in the analysis of catechin powder is 94.26%. This level has met the requirements of the Herbal Pharmacopoeia where the catechin content in gambier extract is of high quality should not be less than 90% (Addiena, et al.2019). This shows the catechin powder from the leaves of Uncaria gambir Roxb. used are of good quality.

Fig 1. Catechin powder produced
Observation of Degraded Oil that has been Added Catechins

a. Free Fatty Acids

Determination of free fatty acid levels aims to indicate the level of damage from the oil due to hydrolysis. The formation of free fatty acids is caused by the hydrolysis reaction of triglyceride esters (Pambayun et al, 2007). The amount of free fatty acids contained in the oil is a parameter of oil quality, where the higher the free fatty acid content, the lower the quality. The result of the average number of free fatty acids in the oil can be seen in Table 2.

Table 2. Average Value of Free Fatty Acids Degraded Oil with added Catechins

<table>
<thead>
<tr>
<th>Treatment (catechin)</th>
<th>Free fatty acids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (400 ppm)</td>
<td>0.45 ± 0.03 a</td>
</tr>
<tr>
<td>D (200 ppm)</td>
<td>0.51 ± 0.06 a b</td>
</tr>
<tr>
<td>C (100 ppm)</td>
<td>0.58 ± 0.03 a b</td>
</tr>
<tr>
<td>B (50 ppm)</td>
<td>0.64 ± 0.06 b</td>
</tr>
<tr>
<td>A (0 ppm)</td>
<td>1.19 ± 0.12 c</td>
</tr>
</tbody>
</table>

Note: The numbers in the same column followed by the same lowercase letters are not significantly different in the DNMRT test at the 5% level.

Based on the results of the free fatty acid test of the degradation oil that has been added to the resulting catechin powder, the range of values for the free fatty acid content is 0.45-1.19%, the highest acid number is 1.19% in the oil that is not treated with catechin powder (0 ppm) namely treatment A and the lowest is treatment E of 0.45%. Based on the results of the analysis of variance at the level 5% showed that the addition of catechin powder with concentrations of 0 ppm, 50 ppm, 100 ppm, 200 ppm, and 400 ppm, had a significant effect on free fatty acids.

Based on the table above, it shows that the higher the addition of catechin powder to the oil, the lower the free fatty acids produced after degradation. The addition of antioxidants such as catechins to oil can inhibit the rate of increase in free fatty acid levels. It can be seen that the oil that is not added with antioxidants (catechins) has higher free fatty acids than the oil that is added with antioxidants (catechins). The high levels of free fatty acids in the oil are followed by the higher the water content of the oil. The high water content allows a continuous hydrolysis reaction, thus causing the free fatty acid levels in the oil to increase. In addition, the unsaturated fatty acids in the oil will release unstable hydrogen. if not given antioxidants or free radical scavengers. These free radicals will react with oxygen to become active peroxides, but in the presence of antioxidants from catechins, the radicals do not bind oxygen but are catechin antioxidants (Alamsyah, et., al 2007).

b. Peroxide Number
The peroxide number is an index of the amount of fat or oil that has been oxidized. The number of peroxides is very important to be identified to determine the level of oxidation that occurs in oil. Oils containing unsaturated fatty acids can be oxidized by oxygen to produce a peroxide compound. The higher the peroxide number, the lower the quality of the oil. The results of the average number of peroxides in the oil can be seen in Table 3.

Table 3. Average Value of Oil Peroxide Numbers of The degradation that has been added Catechins

<table>
<thead>
<tr>
<th>Treatment (catechin)</th>
<th>Peroxide Number (meq O2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (400 ppm)</td>
<td>5.00 ± 1.41 a</td>
</tr>
<tr>
<td>D (200 ppm)</td>
<td>6.51 ± 0.71 a b</td>
</tr>
<tr>
<td>C (100 ppm)</td>
<td>7.00 ± 1.41 a b</td>
</tr>
<tr>
<td>B (50 ppm)</td>
<td>8.5 ± 0.71 b</td>
</tr>
<tr>
<td>A (0 ppm)</td>
<td>15.00 ± 1.41 c</td>
</tr>
</tbody>
</table>

Note: Numbers in the same row followed by the same lowercase letter does not differ significant in the DNMRT test at the 5% level

Based on the results of testing the peroxide value of the degraded oil that has been added to the resulting catechins, the range of the peroxide value is 5 - 15 meq O2/g, the highest peroxide value is 15 meq O2/g in the oil that is not treated with catechins, namely treatment A and the lowest is treatment E of 5 meq O2/g. Based on the results of analysis of variance against the degraded oil yield that has been added catechins at the level of 5% showed that the addition of catechin concentrations with percentages of 0 ppm, 50 ppm, 100 ppm, 200 ppm, and 400 ppm, has a significant effect on the peroxide value of rubber seed oil.

Based on the table above, it was found that the higher the concentration of catechins, the smaller the peroxide value produced. This is reinforced by research conducted by (Taufik, 2019), where increasing the concentration of catechins in palm oil and coconut oil also results in low peroxide values. According to SNI for cooking oil (SNI 3741:2013), the maximum peroxide value in cooking oil is 10 meq O2/g. The decrease in the peroxide value along with the increase in the concentration of catechins was caused by the phenolic groups present in the catechins themselves. The phenolic group has antioxidant activity that can inhibit the oxidation reaction. Oils that are not added with antioxidants (catechins) will oxidize faster than those added with antioxidants (catechins). According to Marlina (2010), the increase in peroxide value illustrates that the unsaturated fatty acids from the oil have become free radicals but are not yet active.

C. Moisture Content
Determination of water content in oil is important to determine the amount of water contained in oil. If there is water in the amount a lot of oil can cause a hydrolysis reaction to produce free fatty acids and glycerol in the oil, the oil can smell rancid because the oil turns into ketone compounds (Budiman, 2016). The results of the average water content in the oil can be seen in Table 4.

Table 4. Average Value of Oil Moisture Content of The degradation that has been added Catechins

<table>
<thead>
<tr>
<th>Treatment (catechin)</th>
<th>Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (400 ppm)</td>
<td>0.89 ± 0.01 a</td>
</tr>
<tr>
<td>D (200 ppm)</td>
<td>1.23 ± 0.03 b</td>
</tr>
<tr>
<td>C (100 ppm)</td>
<td>1.25 ± 0.02 b</td>
</tr>
<tr>
<td>B (50 ppm)</td>
<td>1.28 ± 0.10 b c</td>
</tr>
<tr>
<td>A (0 ppm)</td>
<td>1.39 ± 0.40 c</td>
</tr>
</tbody>
</table>

Note: The numbers in the same column followed by the same lowercase letters are not significantly different in the DNMRT test at the 5% level.

Based on the results of testing the water content of the degraded oil that has been added with catechin powder, the water content value ranges from 0.89-1.39%. The highest water content was in treatment A as a control of 1.39% and the lowest was treatment E with the addition of 400 ppm catechin powder with a water content of 0.89%. Based on the results of analysis of variance on the degradation oil yield at the level of 5%, it showed that the addition of catechin powder with percentages of 0, 50, 100, 200, and 400 ppm had a significant effect on the moisture content of the oil. Based on the table above, it shows that the higher the addition of catechin powder, the lower the water content produced from the degradation oil. The water content increases with increasing heating temperature in the oil. The possibility that evaporates in the determination of the water content is not only water but also fatty acids that are present has a boiling point below 105°C (Bahri, 2013) High water content will cause a hydrolysis reaction to the oil. The results of the hydrolysis reaction are characterized by a rancid odor and taste which is not pleasing to the product (Marlina, 2010). The hydrolysis greatly reduces the quality of the oil. Water is a reactant for the sustainability of the hydrolysis process which will reduce the quality of the oil. The presence of water in the oil causes the oil to hydrolyze into glycerol and fatty acids. The high-water content in food can encourage enzymatic reactions that result in changes in chemical composition, especially damage to active compounds that can reduce quality foodstuffs. The hydrolysis will more easily occur in oils with high water content, so the lower the water content, the better the quality of the oil. The presence of antioxidants in the oil will reduce the speed of the process of increasing water content (Marlina, 2010). This is confirmed by research conducted by Marlina (2010) on the use of gambier as a natural antioxidant. Marlina said that the higher the addition of catechin levels, the water content in the oil will decreases. One of the factors that may accelerate the process of hydrolysis of oil is the humidity of the air high levels cause hydrolysis of the fatty ester bonds so that the fatty acids volatile will be easily liberated. The addition of
antioxidants (catechins) can maintain fatty acids in the oil, so that evaporation of volatile fatty acids is slightly inhibited.

D. Color

Color test is one of the properties that can be seen as a physical property of the oil. Testing the color of the degraded oil to which catechin powder has been added can be measured using a tool, namely Hunterlab, which produces 3 color parameters with the notation L*, a*, b*. Based on analysis of variance, the addition of catechin powder significantly affected the color value of the oil produced at the level of = 5%. For this reason, it is necessary to carry out further DNMRT testing at the 5% level. The average value of the resulting viscosity can be seen in Table 5.

Table 5. Color Test Values L*, a*, b* the oil that has been added Catechins

<table>
<thead>
<tr>
<th>Treatment (catechin)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>(^\circ)Hue</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (400 ppm)</td>
<td>6.11 ± 0.01 a</td>
<td>-1.51 ± 0.03 a</td>
<td>14.51 ± 0.23 a</td>
<td>95.95 ± 0.21 a</td>
</tr>
<tr>
<td>D (200 ppm)</td>
<td>6.56 ± 0.00 b</td>
<td>-1.41 ± 0.05 b</td>
<td>16.70 ± 0.38 b</td>
<td>94.82 ± 0.28 b</td>
</tr>
<tr>
<td>C (100 ppm)</td>
<td>7.59 ± 0.01 c</td>
<td>-1.39 ± 0.03 b</td>
<td>17.98 ± 0.13 c</td>
<td>94.43 ± 0.12 c</td>
</tr>
<tr>
<td>B (50 ppm)</td>
<td>7.94 ± 0.03 c</td>
<td>-1.09 ± 0.01 c</td>
<td>19.68 ± 0.12 d</td>
<td>93.18 ± 0.02 c</td>
</tr>
<tr>
<td>A (0 ppm)</td>
<td>8.59 ± 0.34 d</td>
<td>-0.97 ± 0.01 d</td>
<td>20.58 ± 0.79 d</td>
<td>92.69 ± 0.08 d</td>
</tr>
</tbody>
</table>

Note: The numbers in the same column followed by the same lowercase letters are not significantly different in the DNMRT test at the 5% level

From Table 5, it can be seen that the L*, a*, b* values of the degradation oil have been added to the catechin powder. From the L*, a*, b* values obtained from measurements with hunterlab, it can be seen in Figure 2 the resulting color description.

![Figure 2. CIE Lab Color Space](Source: Liu, 2014)

In Figure 2, if the values of L*, a*, b* are entered in the degradation oil to which the catechin powder has been added, the resulting catechin powder is shown in table 14, then for all oil treatments it turns yellow. The L* value indicates brightness, along with the addition of the concentration of catechin powder in the oil, the lower the L* value means that the color of the oil decreases. The value of a* is divided into 2, namely +a...
indicates red color and –a indicates green color. The higher the concentration of catechin powder in the oil, the more negative a* value. The more negative the a* value, the greener the color. The value of b* is divided into 2, namely +b indicates yellow color and –b indicates blue color. The higher the concentration of catechin powder in the oil, the higher the b* value produced. The higher the b* value, the more yellow the color will be.

In Table 5 it can be seen that the a* value produced is negative but the number is close to 0 which means that the degradation oil that has been added with catechins still looks yellow and the resulting b* value is positive, which means that the degradation oil that has been added with catechins is yellowish. This can prove that the addition of catechin concentration can maintain the yellow color of the degraded oil. According to Manurung et al, (2018) heating for too long in the oil will cause a change in the color of the oil from yellow to brownish yellow. The change in the oil is caused by an oxidation reaction that produces volatile carbonyl compounds, hydroxy acids, keto acids and epoxy acids that change the color of the oil.

In Table 5 the value of °Hue obtained is in the range of 92.69 – 95.95. °Hue values range 18 – 54 Products are red, 54 – 90 Yellow red products, 90 – 126 Yellow products, 126 – 162 Yellow green products, 162 – 198 Green products, 198– 234 Blue green products, 234 – 270 Products in blue, 270 – 306 Products in blue purple, 306 – 342 Products in purple, and 342 – 18 Products are red purple.

E. Fatty Acid Profile (GC-MS)

Degraded oil that has been added with catechin powder is further tested to determine the fatty acid profile of the degraded oil using an instrument, namely GC-MS (Gas Chromatography–Mass Spectrometry). GC-MS is an analytical method in which the sample is physically separated into smaller molecules (results separation can be seen on the chromatogram). While mass spectroscopy is an analytical method in which the analyzed sample will be converted into gas ions and these ions can be measured based on the detection results in the form of a mass spectrum. The following are the 3 highest fatty acid compositions found in the degradation oil that has been added with catechin powder in table 6.

<table>
<thead>
<tr>
<th>Treatment (catechin)</th>
<th>Hexadecanoid (Area)</th>
<th>9-Octadecanoid (Area)</th>
<th>Heptadecanoid (Area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 ppm</td>
<td>61.45</td>
<td>51.63</td>
<td>18.72</td>
</tr>
<tr>
<td>200 ppm</td>
<td>57.81</td>
<td>50.76</td>
<td>17.23</td>
</tr>
<tr>
<td>100 ppm</td>
<td>54.47</td>
<td>44.18</td>
<td>16.35</td>
</tr>
<tr>
<td>0 ppm</td>
<td>44.38</td>
<td>38.22</td>
<td>12.55</td>
</tr>
<tr>
<td>BHT 100 ppm</td>
<td>60.07</td>
<td>52.34</td>
<td>14.21</td>
</tr>
</tbody>
</table>

Based on the table above, it can be seen that Hexadecanoic, 9-Octadecanoic and Heptadecanoic are the 3 most fatty acids found in degraded palm oil to which catechin powder has been added. According to
Silvana and Vera (2018), the dominant fatty acid components for palm oil are palmitic acid (C16:0) and oleic acid (C18:1). It is proven that Hexadecanoic (palmitic acid) and Octadecanoic (oleic acid) are the 2 highest fatty acid compositions identified. Based on the table it can also be shown that the higher the concentration of catechins added, the higher the fatty acids obtained or maintained during the degradation process. Catechins are flavonoid compounds that have an active group which generally functions as a catcher and inhibitor of free radical reactions. Has –OH groups and double bonds >C=C< because these groups can donate 1 molecule of hydrogen so that free radicals derived from oxygen or reactive oxygen species (ROS) become stable and new free radicals are formed which are less reactive.

In this study, a comparison was also made using a commercial antioxidant, namely BHT (Butyl Hydroxy Toluene). The permissible concentration of BHT for oil is as much as 100 ppm. Based on the table, it can be seen that the BHT antioxidant fatty acid profile is almost close to the fatty acid profile with the addition of concentration 400 ppm catechins. Therefore, it can be concluded that the concentration of 400 ppm is the best concentration in replacing commercial (synthetic) antioxidants.

CONCLUSION

Based on the research that has been done, it can be concluded that the addition of catechin powder significantly affected the Free Fatty Acid, Peroxide Number, Color and Moisture Content. Moreover, the addition of a concentration of 400 ppm catechin powder was the best treatment obtained, with a Free Fatty Acid value of 0.45%, Peroxide Number 5 meq/g, Moisture Content 0.89% and Color 95.95 (L* 16.11, a* -1.51, b* 14.51)

CONFLICT OF INTEREST

The authors had no conflict of interest

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