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ETHANOL EXTRACT OF MATOA (*Pometia pinnata*) AS NATURAL ANTIOXIDANT TO INHIBIT OXIDATION REACTION OF CRUDE PALM OIL

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ABSTRAK

Indonesia merupakan negara nomor 2 penghasil kelapa sawit terbesar di dunia. Permintaan akan CPO (*Crude Palm Oil*) meningkat di setiap tahunnya, oleh sebab itu Indonesia diharapkan mampu bersaing di tingkat industri international dalam memproduksi minyak kelapa sawit, dengan tujuan Indonesia mampu menghasilkan mutu minyak kelapa sawit yang baik diantara industri di negara lain. Permasalahan yang sering terjadi pada pabrik *C*PO adalah penurunan mutu CPO yang disebabkan oleh peningkatan Kadar *Free Fatty Acid* (FFA) dan bilangan peroksida. Antioksidan adalah zat yang dapat menunda atau mencegah terjadinya reaksi antioksidasi radikal bebas dalam oksidasi lemak atau minyak. Antioksidan alami adalah antioksidan yang diperoleh langsung dari alam. Salah satunya yaitu daun tumbuhan matoa *(Pometia pinnata).* Berdasarkan hasil penelitian ini bahwa antioksidan ekstrak etanol tumbuhan matoa dapat menurunkan kadar *FFA* dan bilangan peroksida tergantung lamanya waktu campuran antioksidan yang diberikan pada CPO. Pada penelitian ini diperoleh penurunan kadar *FFA* dan penurunan bilangan peroksida dari sampel pada hari ke - 10 dengan penambahan antioksidan 5000 ppm yaitu 2,71%. sedangkan bilangan peroksida yaitu 0,83%.

ABSTRACT

Indonesia is the 2nd largest country in the world in terms of palm oil production. The demand for Crude Palm Oil increases every year. For this reason, Indonesia is expected to be able to compete at the international industry level in producing palm oil, with the aim of being able to produce good quality palm oil among industries in other countries. The problem that often occurs in CPO factories is a decrease in the quality of CPO caused by an increase in Free Fatty Acid (FFA) levels and Peroxide Numbers. Antioxidants are substances that can delay or prevent the occurrence of free radical anti-oxidation reactions in the oxidation of fats or oils. Natural antioxidants are antioxidants that are obtained directly from nature. Natural antioxidants are antioxidants that are obtained directly from nature. One of them is the leaf of the matoa plant (Pometia pinnata). Based on the results of this study, the antioxidants of the ethanol extract of the matoa plant can reduce levels of FFA and peroxide numbers depending on the length of time the antioxidant mixture is given to CPO. In this study, a decrease in FFA levels and peroxide numbers was obtained from samples on day - 10 with the addition of 5000 ppm antioxidants, namely 2.71%. while the peroxide number is 0.83%.

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INTRODUCTION

A problem that often occurs in CPO factories is a decrease in CPO quality caused by an increase in free fatty acid (FFA) levels, acid number, and iodine number (Viarani et al., 2022). The quality and stability of palm oil are the main factors that influence its acceptability and resale value, as well as minimize the degradation process during deep frying. One of the most important indicators in maintaining oil quality is its oxidative stability (Mahmud, 2019). The oxidative stability of vegetable oils depends on temperature, light, oxygen, metals, enzymes, the presence of antioxidants, fatty acid composition, and the use of oxygen-permeable packaging (Murjana & Handayani, 2022). High levels of free fatty acids (FFA) cause rancidity and changes in the taste and color of the oil. One of the factors causing increased levels of free fatty acids (FFA) in oil is damage to morphology and microorganisms in oil palm fruit (Muarif et al., 2022). Damage to oil palm fruit is triggered by careless harvesting, transportation, and stacking of oil palm fruit (Hasibuan, 2018).

CPO quality standards are regulated through the Indonesian standards body, which is contained in SNI-01-2901-2006. In this standard, the free fatty acid (FFA) content is set at 5.0%, the maximum peroxide value is 10, and the iodine number is 50-55 (National Standardization Agency, 2006). An alternative way to slow or minimize oil oxidation is to add antioxidants. Antioxidants consist of compounds that can deactivate free radicals by donating hydrogen atoms or electrons to these molecules (Wulandari et al., 2011). In the food industry, the most commonly used synthetic antioxidants are phenolic compounds, such as Butyl Hydroxy Anisol (BHA), Butyl Hydroxy Toluene (BHT), Tertbutyl Hydro Quinone (TBHQ) and Propyl Gallate (PGA), which can regenerate acyl glycerol and interfere with the mechanism of oxidation with proton donation (Susparini et al., 2022).

However, recently, the use of synthetic antioxidants has begun to receive negative responses because they can trigger cancer in the body (Sakka & Muin, 2023). Therefore, replacing additive antioxidants with natural antioxidants is an alternative method that is safer for health. One plant that can be used as a natural antioxidant is the leaves of the matoa plant (Rossalinda et al., 2021). The Matoa plant (*Pometia Pinnata*) is known to contain alkaloids, saponins, tannins, flavonoids, phenolics, terpenoids, and vitamins A, C, and E, which can improve the immune system. Matoa (*Pometia pinnata*) belongs to the Sapindaceae family (Sidoretno et al., 2018). The matoa plant is usually used in the wood industry for its stems and consumed as food and traditional medicine for its leaves, fruit, and seeds. Even though matoa is widely known, there is not much information regarding its properties (Utoro et al., 2022).

According to Sidoretno and Fauzana (2018), matoa fruit skin has high antioxidant activity due to its phenolic compound content (Sidoretno et al., 2018). The working mechanism of antioxidants themselves is by reactive oxygen (such as hydroxyl, superoxide, and peroxy radicals) or free radicals getting electron donors/hydrogen atoms, which come from antioxidant components in the form of molecules that can prevent oxygen or cells from being oxidized (Situmeang et al., 2022). It is known that several types of food that contain antioxidants can prevent various diseases, such as carcinogenic diseases and so on (Musa et al., 2021).

METHODS

Materials

The materials used in this research were Crude Palm Oil (CPO), matoa plant leaves, ethanol, CH_3COOH, NaOH 0.1N, $Na_2S_2O_3$ 0.01N, Starch, Aquadest, Phenolphthalein indicator, saturated KI.

Tools

The tools used in this research were a beaker, Erlenmeyer, 50-mesh sieve, measuring

flask, volume pipette, drop pipette, analytical balance (Ohaus®), blender (Maspion), stir bar, ball pipette, aluminum foil, spatula, knife, thermometer, and rotary evaporator (IKA®).

Sample Preparation

Sample preparations of matoa plant leaves as samples in this study were obtained from Papua Province. The samples were cleaned of impurities and washed with running water until they were clean of dirt, then dried in the open air until dry.

Sample Extraction

A total of 1000 g was macerated with ethanol, and the sample was completely soaked. The mixture was stirred for 6 hours, then left for 3x24 hours in a tightly closed container. Then, the filtrate is filtered and concentrated using a rotary evaporator. Maceration is repeated until a clear (colorless) maceration solution is obtained. The concentration results are then collected, dried, and weighed. Next, each extract was tested qualitatively and quantitatively.

Free Fatty Acid Level Test

The CPO sample is heated at a temperature of 60 - 70°C until it melts. Then, a sample of liquid CPO was taken and weighed 3 grams, then the sample was put into a 250 mL Erlenmeyer flask, and 50 mL of Neutral Methanol was added. After that, heat it in a water bath and set the temperature at 40˚C until all the oil is dissolved. After dissolving, add 3-5 drops of PP indicator to the sample solution. Then titrated with 0.1 N NaOH solution until it reaches a pink color (Ilyas & Husin, 2023).

The % total FFA value is calculated using the following formula:

$$\%Total\ FFA\ = \frac{V_{NaOH} \times N_{NaOH} \times Mw_{acid}}{\text{sample mass}} \quad (1)$$

Peroxide value Test

Weigh a 3 g sample of liquid CPO into a closed 250 mL Erlenmeyer and then add a mixture of 30 mL of CH_3COOH: Chloroform (3:2) solution and stir until all the sample is dissolved. Add 0.5 mL of saturated Potassium iodide solution with a dropper. Then, keep it in a dark place for 3 minutes. Add 2-3 drops of starch and titrate with 0.01 N $Na_2S_2O_3$ until it reaches a white endpoint (Musa et al., 2021). The Peroxide value is calculated using the following formula:

$$Peroxide\ value = \frac{V_{titration} \times N_{thiosulfate} \times BM_{thiosulfate}}{Sample\ mass} \quad (2)$$

Addition of Natural Antioxidants

A natural antioxidant extract of 5000 ppm was made, and then CPO was added at a concentration (ratio between CPO samples and antioxidants 1:1). The mixture of CPO samples and antioxidant compounds was left for 24 hours. The mixture of these compounds forms 2 phases between antioxidants and CPO. After being left for ±24 hours, the mixture of compounds with different concentrations was put into a separating funnel to be separated. Then, the compounds below were taken, and the free fatty acid levels and peroxide values were determined again on days 2, 4, 6, 8, and 10.

RESULT AND DISCUSSION

Sample Preparation

The samples were cleaned of impurities and washed with running water until they were clean of dirt, then dried in the open air so that no water stuck to the leaf samples. The dried samples were powdered using a blender until smooth; the powder was then sieved using a 50 mesh sieve, and the sieve results were extracted by maceration over a period of 3x24 hours to get good sample results.

Sample Extraction

A total of 1000 g of powdered matoa leaf samples were macerated with 3000 mL of 95% ethanol, and the samples were completely soaked. The mixture is stirred for 6 hours, then left for 3x24 hours in a tightly closed container so that no air enters. Then, the filtrate is filtered and concentrated using a rotary evaporator. Maceration is repeated until a clear (colorless) maceration solution is obtained. The concentration results are then collected, dried, and weighed. Next, each extract was tested qualitatively and quantitatively.

Free Fatty Acid (FFA) Test

The liquid CPO sample was weighed at 3 grams then 50 mL of neutralized 95% ethanol was added. The purpose of adding 95% ethanol was to dissolve the fat or oil in the sample so that it could react with the alkaline base, namely NaOH, then heat over a water bath and set the temperature at 40°C until all the oil is dissolved, then add 3 - 5 drops of PP indicator solution and titrate with 0.1 N NaOH solution until the color changes from reddish-orange to pink TA.

Table 1. Pure CPO Free Fatty Acid Test Results

Test	Unit	Test Result	TA Color
Free Fatty Acid (FFA)	%	5,72	Pink

The research results and free fatty acid test calculations in the table above show that CPO oil does not meet the standards set by SNI 01 - 2901 - 2006, namely max. 5 %. The results of the analysis of free fatty acid levels in CPO oil showed an FFA value of 5.72%. This shows that the CPO oil sample exceeds the standards set by SNI 01 - 2901 - 2006 by 0.72%. Apart from these results, CPO that is not good can be seen from its smell and color.

Peroxide Value Test

The peroxide number is used to determine the degree of damage to oil or fat. The method is to weigh a 3 g liquid CPO sample into a closed 100 mL Erlenmeyer and then add a mixture of 30 mL of CH_3COOH: Chloroform (3:2) solution and stir until all the sample is dissolved. Add 0.5 mL of saturated Potassium iodide solution with a dropper. Then, keep it in a dark place for 3 minutes. Add 2-3 drops of starch and titrate with 0.01 N $Na_2S_2O_3$ until it reaches a white endpoint.

Table 2. Pure CPO Peroxide Number Test Results

Test	Unit	Test Result	TA Color
Peroxide Value (PV)	%	1,23	White

The research results and peroxide number test calculations in the table above show that CPO oil meets the standards set by SNI 01 – 2901 – 2006, namely max. 10 %. The results of the analysis of the peroxide value test on CPO oil showed a result of 1.23%. This shows that the CPO oil sample meets the standards set by SNI 01 – 2901 – 2006, namely max. 10 %.

Test With Added Antioxidants

The matoa plant leaf extract is made into a 5000 ppm antioxidant stock solution first. The method is to mix 1.25 g of concentrated matoa leaf extract with 250 mL of 95% ethanol. The aim is to facilitate research and find out the dose used for this research and experiment, namely 5000 ppm. The 5000 ppm antioxidant compound was then put into a 250 mL separating funnel as much as 100 grams and 100 grams of liquid CPO was also added so that the mixture of compounds formed 2 phases between antioxidants and CPO (Comparison of CPO and Antioxidant Extract 1:1), then the sample was allowed to stand for 2 days.

After 2 days, the CPO sample was taken to test the free fatty acid content, weighed 3 g, put it in a 100 mL Erlenmeyer, and added 50 mL of neutral alcohol. After that, heat it in a water bath and set the temperature at 40°C until all the oil is dissolved. After dissolving, add 3-5 drops of PP indicator to the sample solution. Then titrated with 0.1 N NaOH solution until it reached a pink color. Carry out the same treatment on days 4, 6, 8, and 10. Next is the peroxide value test, namely taking a sample of 3 g, putting it in a closed 100 mL Erlenmeyer flask, and then adding a mixture of CH3COOH: Chloroform (3:2) solution as much as possible. 30 mL and stir until all samples are dissolved. Then, add 0.5 mL of saturated Potassium iodide solution with a dropper. Then, keep it in a dark place for 3 minutes. Add 2-3 drops of starch and titrate with 0.01 N Na2S2O3 until it reaches a white endpoint. Also, do the same treatment on days 4, 6, 8, and 10.

Table 3. Test Results with Addition of Antioxidants

Days	CPO + Antioxidant 5000 ppm sample	
	FFA (%)	Peroxide value(%)
2	3,58	1,00
4	3,20	0,95
6	3,16	0,92
8	2,85	0,88
10	2,71	0,83

Test the levels of free fatty acids (FFA) in CPO after adding antioxidants

From the research results and free fatty acid (FFA) test calculations in the table above, after adding 5000 ppm of antioxidants on days 2, 4, 6, 8, and 10, CPO oil has successfully met the standards set by SNI 01 – 2901 – 2006, i.e., max. 5 %. From the research data above, the results of the analysis showed that there was a decrease in the value of free fatty acids after adding antioxidants.

The CPO oil sample, before adding antioxidants, obtained a value of 5.72%. After adding 5000 ppm of antioxidants on day 2, a value of 3.58% was obtained. This shows a decrease in free fatty acid levels of 2.14%. Then, after adding antioxidants on day 4, the free fatty acid value was 3.20%; on day 6, it was 3.16%; on day 8, it was 2.85%; and on day 10, it was 2.71%. This shows that there was a decrease in free fatty acid levels by 2.52% for day 4, 2.56% for day 6, 2.87% for day 8 and 3.01% for day 10. This proves that The longer the mixture of CPO and antioxidants, the greater the reduction in free fatty acids in CPO. This is in accordance with research conducted by Susparini et al., 2022 and Musa et al., 2021 which stated that the antioxidant content in plant extracts was able to inhibit the formation of oxidation reactions in CPO samples. The content of phenolic compounds and flavonoids is also able to kill microorganisms found in CPO oil so that oxidation reactions caused by microorganisms can be inhibited (Musa et al., 2023).

Peroxide Number Test on CPO after adding antioxidants

From the results of the research and calculation of the peroxide number test in the table above, after adding 5000 ppm of antioxidants on days 2, 4, 6, 8, and 10, CPO oil succeeded in meeting the standards set by SNI 01 – 2901 – 2006, namely max. 10 %. From the research data above, the results of the analysis showed that there was a decrease in the peroxide value after adding antioxidants.

The CPO oil sample, before adding antioxidants, obtained a value of 1.23%. After adding 5000 ppm of antioxidants on day 2, a value of 1.00% was obtained. This shows a decrease in peroxide levels of 0.23%. Then, after adding antioxidants on day 4, the peroxide value was 0.95%; on day 6, it was 0.92%; on day 8, it was 0.88%; and on day 10, it was 0.83%. This shows a decrease in peroxide levels of 0.28% for day 4, 0.31% for day 6, 0.35% for day 8 and 0.40% for day 10. This proves that the longer The mixture of CPO with antioxidants the greater the reduction in peroxide value in CPO. This is in accordance with research conducted by Hajar et al. (2021), which states that matoa plant extracts contain secondary metabolite compounds, such as flavonoids and phenolics, which are able to inhibit free radicals. The high content of antioxidant compounds in matoa extract is able to reduce free radical reactions in large amounts of CPO samples.

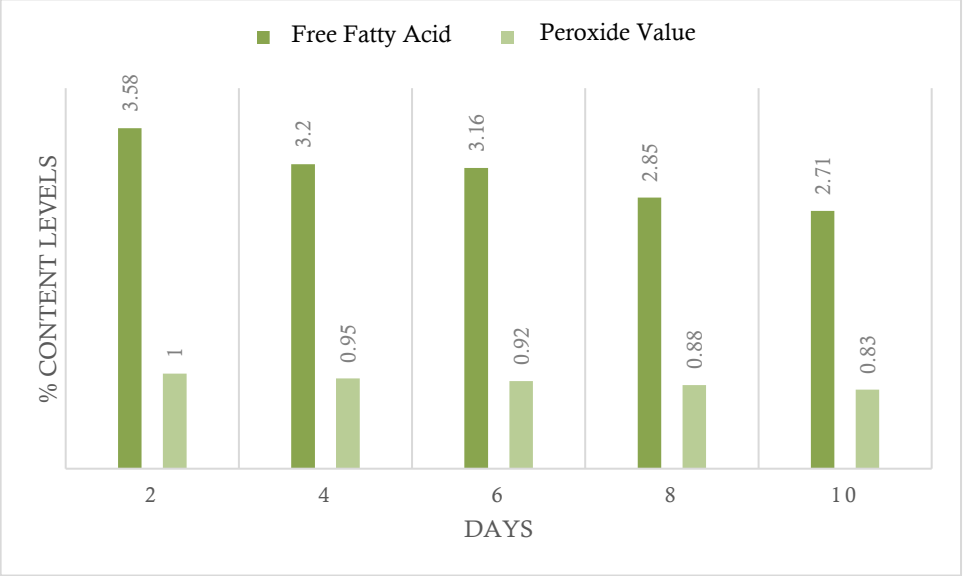

Figure 1. Diagram of free fatty acid levels and peroxide numbers after adding natural antioxidants to CPO samples

CONCLUSION

The conclusions obtained from the CPO (Crude Palm Oil) Quality Test Using Ethanol Extract of Matoa (*Pometia pinnata*) Plant Leaves were the free fatty acid test results of 3.58% - 2.71%, and the peroxide value test results of 1.00% - 0.83 %.

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