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THE IMPACT OF TEMPERATURE AND ANTIOXIDANTS ON OXIDATION AND THE FORMATION OF TRANS FATTY ACIDS IN SEVERAL PALM OIL DERIVATIVES

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Abstract

The quality of palm oil is strongly influenced by temperature. The oxidation of palm oil can be caused by high temperatures. The higher the storage temperature, the faster oxidation occurs. In this research, the temperature significantly affects the quality of several palm oil derivative products such as Palm Olein, Palm Stearin, Palm Kernel Oil, and Palm Kernel Stearin. Antioxidants are very effective in resisting the increase in the oxidation reaction of some palm oil commodities. With the addition of tertiary butylhydroquinone (TBHQ) or butylated hydroxytoluene (BHT), the increase in peroxide value, p-anisidine values, free fatty acid, color tends to be slower than without the addition of antioxidants. For PV, BHT was the most effective antioxidant for RPKOL at a 29.75% increase, RBDOL at 9.91%, and RBDST at 5.26% but for RPKS TBHQ was the most effective increase at 19.83%. For anisidine value, TBHQ+BHT was most effective for RPKOL with a 61.62% increase, TBHQ for RPKS with 76.76%, BHT for RBDOL and RBDST with 15.37% and 14.46%. In the FFA test, BHT was effective for RPKOL and RPKS with a percentage increase of 6.48% and 6.67%, but TBHQ was effective for RBDOL and RBDST to controlled FFA with an increase of 8.41% and 3.38%. In color testing, TBHQ proved to be the effective antioxidant for RPKOL and RBDOL, resulting in percentage increases of 8.71% and 2.13%, respectively. For RPKS, the combination of TBHQ and BHT was employed, resulting in no percentage increase (0%). Additionally, BHT at 3.85% was used for RBDST. At a temperature of 130°C, an oxidation process was observed, indicating the formation of an aldehyde compound. This was evidenced by the FT-IR spectrum, showing peaks at wave numbers 1760 cm^{-1} (C=O of aldehyde) and 2900 cm^{-1} (CH on aldehyde). In this research, we can also see the formation of trans fatty acids C18:1n9t in GC-FID's peak area.

INTRODUCTION

Palm oil (Elaeis Guineensis) is currently growing rapidly in Indonesia as one of the plantation commodities that has an important role in economic activities in Indonesia. According to FAO data (2012), the plantation area in Indonesia is ranked first in the world's largest area with an area of 6.5 million hectares. Among the various types of vegetable oil-producing plants, oil palm is a plant with the highest potential for oil production. Palm oil is consumed in more than 150 countries around the world. It plays an important role in the socioeconomic development of Asia, Latin America, and Africa. In 2010, world production of oils and fats reached 172.1 million tons [1].

In a palm oil processing factory, storage is one of the most important things. During storage, the temperature of the oil must be maintained to avoid damage to the quality of the oil, and heat must be applied gradually. A sudden temperature rise must be avoided as it will damage the oil [2]. In the study [3] showed how palm oil changes when exposed to excessive temperatures. The stability of palm oil not only provides opportunities for processing to reduce operational costs but also maintains its quality. According to [2] the maximum storage temperatures for palm oil are: Palm Kernel Oil & Palm Kernel Stearin 45^0C; Palm Olein 35^0C; Palm Stearin 70^0C. Meanwhile, according to [4], the storage temperature affected the change in the percentage value of free fatty acids (FFA), peroxide value (PV), and the color of the palm cooking oil samples. The percent change in sample value is stable in the range of 18^0C - 36^0C storage temperature. In [5], cooking oil that had the best stability was stored for 2 weeks at 20^0C - 24^0C and 1 week at 28^0C - 30^0C.

Oxidation greatly affects the quality of palm oil products and if it lasts for a long time can cause

unpleasant odors and have a bad effect on the body by damaging functions in various tissues [6]. Oxidation of oil or fat can be affected by temperature, light/irradiation, availability of oxygen, and metals which are catalysts.

The classic method of looking at fat oxidation is the determination of the peroxide number (PV). Peroxide content was determined by the iodometric method. The amount of iodine (I_2) released is proportional to the concentration of peroxide present. I_2 release was assessed by titration against a standard solution of sodium thiosulphate ($Na_2S_2O_3$) using a starch indicator. Another parameter is the determination of p-Anisidine Value (p-AnV). Anisidine Value is a combined measure of most of the 2-alkenal and 2,4-dienal as well as saturated aldehydes in animal fats and vegetable oils. Anisidine value is generally used to follow the formation of aldehyde compounds in vegetable oils and correlates well with the development of off-flavors in oxidized lipids [7]. The aldehydes in the oil react with the p-anisidin reagent in an acidic environment [8]. The AOCS Cd 18-90 method has been used as the standard method for anisidine analysis. The anisidine test can also be used as a crude predictor of future fresh storage stability for refined oils [9]. According to [10] the increase in anisidine value is very significantly affected by the interaction between temperature and time.

Previous research [11] stated that FTIR spectroscopy can be used to predict the anisidine value in olein (palm oil) with satisfactory accuracy when the anisidine value is not greater than 17 and will allow a faster determination than using chemical methods.

Fat-forming fatty acids can be distinguished based on the number of C atoms (carbon), the presence or absence of double bonds, the number of double bonds, and the location of the double bonds. Based on their chemical structure, fatty acids are divided into saturated fatty acids (SFA), namely fatty acids that do not have double bonds. While fatty acids that have double bonds are referred to as unsaturated fatty acids (UFA) [12]. The results of research over the last decade indicate that the presence of trans fatty acids (TFA) in food has a negative impact on health, namely as a trigger for coronary heart disease which should not be ignored. Even according to the results of research in the last two years the effect of TFA is worse than the negative effects of saturated fatty acids and cholesterol [13,14]. A study [15] showed that fats/oils that were heated/reheated at high temperatures showed high levels of TFA and SFA at the expense of cis-UFA, which is nutritionally undesirable.

Damage to fat, namely oxidation, can be inhibited using various kinds of antioxidant compounds. Antioxidants are compounds that can inhibit or prevent the oxidation of fats, nucleic acids, and others by inhibiting the oxidation stages (initiation or propagation). Another use of antioxidants is to extend shelf life by protecting food from deterioration in quality caused by oxidation such as rancidity. According to [16,17,18] antioxidants are inhibitors that can stop oxidation reactions by preventing the occurrence of radicals or by neutralizing free radicals. Research has been done, that the addition of antioxidants to cooking oil increases the oxidative stability of the oil. TBHQ demonstrated efficiency in terms of fatty acid composition, physico-chemical properties, and sensory evaluation. When oil was added with antioxidants, it showed changes in unsaturated fatty acids/UFA and saturated fatty acids/SFA, each of which was lower than the control [19].

EXPERIMENT

This experiment requires references if the methodology is already used in a previous study. Indicate some information if the method has been modified.

Material

The materials used were refined bleached deodorized palm olein/ RBDOL, refined bleached deodorized palm stearin/ RBDPS, refined bleached deodorized palm kernel olein/ RPKOL, refined bleached deodorized palm kernel stearin/ RPKS (sample PT.CCIC Jakarta), TBHQ, BHT (Subur Kimia Jaya), sodium thiosulfate $Na_2S_2O_3$ (Merck), p-anisidine (Merck), acetic acid (Merck), isooctane (Merck), potassium bicromate $K_2Cr_2O_7$ (Merck), potassium iodide (Merck), chloride acid (Merck), potato starch (Sigma-Adrich), natrium hydroxide NaOH (Merck), potassium iodide KI (Merck), penolphtalein (Merck), ethanol 95% (Mallincrodt), chloride acid 37% (Merck), and aquades.

Instrumentation

The instrumentations used were Mettler Toledo *Analytical Balance*, Thermo *Hot Plate Stirrer*, Memmert UN-55 *Oven*, Brand *Tittrete Buret Digital*, Lovibond *Tintometer Model F*, Gay Lussac *Picnometer*, Memmert *Waterbath Circulator*, Brookfield DV1 *Viscometer With UL*

Adapter, Thermo Genesys 150 *UV VIS Spectrophometer*, Perkin Elmer Clarus 590 *GC Flame Ionization Detector (FID)*, Perkin Elmer ATR-*FTIR*.

Procedure

Sample Preparation

The samples were divided into four groups (**Figure 1**). Group I was heated without antioxidants with temperature variations: RPKOL, RPKS (0,40,50,85,130^{0}C); RBDOL (0,30,40,85,130^{0}C); RBDPS (0,65,70,85,130^{0}C). Group II was added with TBHQ 100 ppm and then heated with the same temperature variations as Group I. Group III was added with BHT 100 ppm and then heated with the same temperature variations. Group IV was added with TBHQ 50 ppm + 50 ppm BHT and then heated with the same temperature variations. The heating time for each group was carried out for 24 hours in the oven (**Figure 2**).

Figure 1. Sample preparation before treatment, from left to right : RPKOL, RPKS, RBDOL, RBDST.

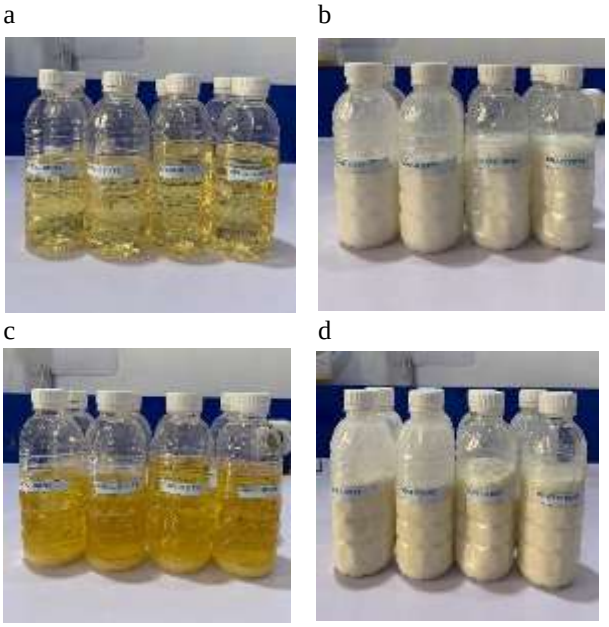


Figure 2. Sample after treatment (heating and adding antioxidant): a.RPKOL, b.RPKS, c.RBDOL, d.RBDST.

Peroxide Value Test

The sample is weighed as much as 5 g and then acetic acid reagent: isooctane (3:2). After adding 0.5 ml of saturated potassium iodide for exactly 1 minute, 50 ml of distilled water was added. Then add 0.5 ml of potato starch. Then titrated with 0.01 N sodium thiosulfate. The same thing was done for the blank. This procedure was carried out in each sample group.

$$\text{Peroxide Value} = \frac{(S-B)\ x\ N\ x\ 1000}{mass\ of\ sample} \quad (1)$$

S is sample titration volume, ml; B blank titration volume, ml; N normality of sodium hiosulfate solution [20].

Anisidine Value Test

Palm oil samples were weighed 0.5 – 4 g in a 25 ml volumetric flask. Then dissolved by adding isooctane up to the boundary mark. Then the absorbance (Ab) was measured at 350 nm with a spectrophotometer, using isooctane as a blank. Then pipette 5 ml of the dissolved oil sample into a new test tube, then add 1 ml of p-Anisidine (0.25 g/100 ml of glacial acetic acid). Then it was shaken, and after exactly 10 minutes the absorbance (As) was measured at 350 nm. As a blank, the same treatment was carried out without a sample. The anisidine value is determined by the following equation.

$$\text{Anisidine value} = \frac{25\ x\ (1.2\ As-Ab)}{m} \quad (2)$$

As is the absorbance of the oil after adding p-Anisidine reagent; Ab absorbance of the oil; m mass of sample [20].

Free Fatty Acid Test

The oil sample was weighed 56.4 g in an Erlenmeyer, then 50 ml of warm 95% ethanol was added (which had been neutralized with NaOH) and then dropped several drops of phenolphthalein indicator. Titrated with 0.1 mol/l NaOH standard solution until the end point of the titration is reached, the pink color does not change for ± 15 seconds. The determination of free fatty acids is calculated by the following equation.

$$\text{FFA} = \frac{V\ x\ 25.6\ x\ N}{m} \quad (3)$$

V volume of titration, ml; N normality of sodium hydroxide/ NaOH; m weight of the sample, g [20].

Color Lovibond Test

The oil sample was heated to $+10^0$C above the melting point. Filled sample into the Lovibond cell. The cell containing the oil sample was placed in a tintometer and the color was observed [20]. Color is an important physical indicator of oil quality [21].

Density Test

After sample heated RPKOL, RPKS (0,40,50,85,130^{0}C); RBDOL (0,30,40,85,130^{0}C); RBDPS (0,65,70,85,130^{0}C). The oil sample was melted and then put into the pycnometer where the empty weight had been weighed. Set the water bath temperature at 50^{0}C. After the temperature is stable, put the sample in the pycnometer into the water bath. Left it for 1 hour. Then removed and dried with a clean tissue. Cooled to room temperature, then weighed.

$$\text{Density (g/ml)} = \frac{m2-mo}{Vt} \quad (4)$$

m_0 empty picnometer weight; m_2 weight of the picnometer and sample after heating; Vt volume calibrated picnometer at temperature T [20].

Viscosity Test

Waterbath set at the desired temperature. Then the spindle's cover was opened. Then the Viscometer tool was turned on, autozero, replaced the spindle, and set the speed. Entered the sample 16 ml then started rotation. Then the results are on the display [22].

Trans Fatty Acid Test

Weighed 1 g of margarine sample and dissolved it with 5 ml of hexane. Stirred, then pipetted 100µl of the solution into another empty tube. Added 2.5 ml of 0.5 M methanol NaOH, cover, and stir. Heated in a water bath at ± 100^{0}C for 30 minutes. Cooled, then added 1.5 ml of 14% BF_3 in methanol, covered, and stirred. The solution was reheated in a water bath at ± 100^{0}C for 30 minutes. Cool and shake the solution until the solution temperature is around 30^{0}C. Immediately add 2 ml of hexane and 1 ml of saturated NaCl, then shake (vortex) vigorously for ± 2 minutes. Leave the solution at room temperature. When the fatty acid hexane-methyl ester layer is separated from the water phase, transfer the fatty acid hexane-methyl ester layer to a small tube containing 0.1-0.2 g anhydrous Na_2SO_4, shake, and leave for 15 minutes. Transfer another layer of fatty acid hexane-methyl ester analyte into the autosampler vial. Inject into GC-FID. Create a calibration curve with the Y-axis as the response and the X-axis as the concentration (ppm). Calculation of the trans fatty acid content (as elaidic acid) in the example [23,24,24,26].

FT-IR Test

In this research, the samples were tested with the FT-IR spectrophotometer. The samples had been heated at 130^{0}C for 24 hours. Tested using flame ionization detector (FID) and obtained peak area. This test is to identify the formation of aldehyde compounds caused by secondary oxidation in palm oil. Unsaturated aldehydes tested in the carbonyl frequency in the range 1705–1685 cm^{-1} and the peaks of C=O of hexenal and decadienal at 1697 and 1689 cm^{-1}. Also tested at the range 2820–2700 cm^{-1} for the C-H stretching region for saturated aldehydes. [7,11].

RESULT AND DISCUSSION

Peroxide Value

The results of the peroxide number test are presented in **Table 1**. Peroxide increased in yield due to an increase in temperature. The role of antioxidants in holding back the increase in peroxide value is very visible compared to samples without the addition of antioxidants. The best antioxidant effect for peroxide value is found by using butylated hydroxytoluene (BHT) for sample refined bleached deodorized palm kernel olein (RPKOL), refined bleached deodorized palm olein (RBDOL), and refined bleached deodorized palm stearin (RBDST). Only refined bleached deodorized palm kernel stearin (RPKS) showed tertiary butylhydroquinone (TBHQ) as the most effective.

Table 1. Peroxide value results for a.RPKOL; b.RPKS; c.RBDOL; d.RBDST

a. RPKOL

Temp (^{0}C)	Peroxide Value (meq/kg)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.55	0.47	0.47	0.47
40	0.55	0.49	0.51	0.50
50	0.64	0.53	0.54	0.53
85	0.79	0.66	0.65	0.66
130	0.84	0.77	0.75	0.76

b. RPKS

Temp (^{0}C)	Peroxide Value (meq/kg) Without TBHQ	BHT	TBHQ+BHT
0	0.34	0.29	0.30	0.28
40	0.41	0.31	0.32	0.31
50	0.41	0.35	0.36	0.33
85	0.43	0.33	0.36	0.36
130	0.55	0.40	0.41	0.39

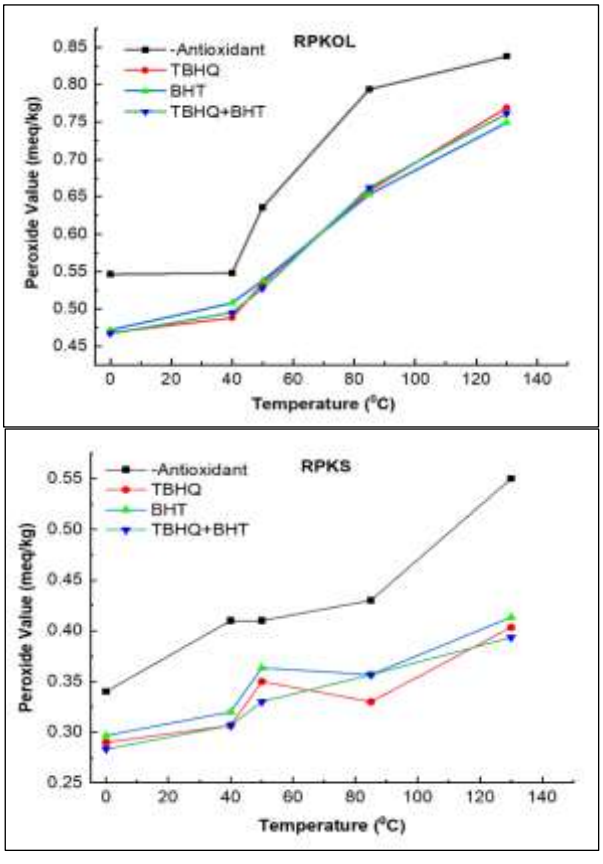
c.RBDOL

Temp (^{0}C)	Peroxide Value (meq/kg) Without TBHQ	BHT	TBHQ+BHT
0	1.53	1.46	1.46	1.45
30	1.54	1.48	1.50	1.48
40	1.62	1.52	1.53	1.52
85	1.78	1.65	1.64	1.65
130	1.83	1.76	1.74	1.75

d.RBDST

Temp (^{0}C)	Peroxide Value (meq/kg) Without TBHQ	BHT	TBHQ+BHT
0	2.74	2.67	2.67	2.66
65	2.75	2.69	2.71	2.69
70	2.83	2.73	2.74	2.73
85	2.99	2.86	2.85	2.86
130	3.04	2.97	2.95	2.96

The graph of temperature effect on the increase in peroxide number and the effect of adding antioxidants to palm oil samples, RPKOL, RPKS, RBDOL, RBDST can be shown in **Figure 3.**



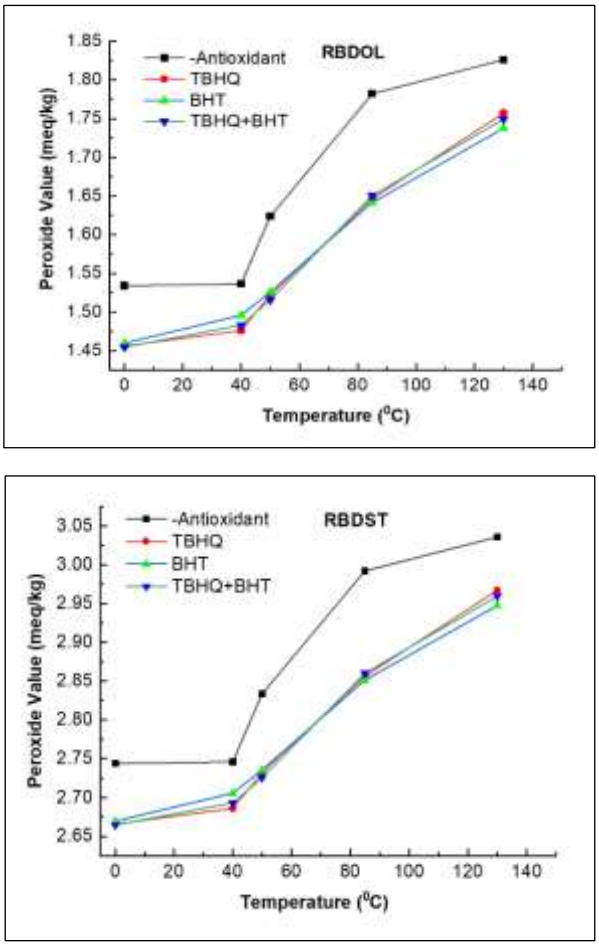


Figure 3. Graph of the effect of temperature and antioxidants for peroxide value.

From the statistical results of the Anova variant analysis on RPKOL, RPKS, and RBDOL, was found that there were changes due to increasing temperature and the addition of antioxidants to the increase in peroxide value. For RBDST, the difference was only due to temperature, but the addition of antioxidants had no effect. Percentage of increase PV for each treatment were: RPKOL (28.92, 30.84, 29.75, 31.04); RPKS (32.35, 19.83, 22.47, 22.35); RBDOL (10.29, 9.91, 9.61, 9.96); RBDST (5.75, 5.41, 5.26, 5.44). The research results showed that the addition of BHT was the lowest increase for all commodities. except RPKS showed TBHQ was the most effective.

Anisidine Value

The results of the anisidine value showed an increase due to an increase in temperature. There were significant differences in results with or without the addition of antioxidants. It is presented in **Table 2**.

Table 2. Anisidine value results for a.RPKOL; b.RPKS ; c.RBDOL ; d.RBDST.

a. RPKOL

Temp (^{0}C)	Anisidine Value (meq/kg)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.23	0.21	0.15	0.21
40	0.23	0.24	0.18	0.25
50	0.32	0.28	0.22	0.28
85	0.47	0.35	0.38	0.37
130	0.52	0.48	0.44	0.46

b. RPKS

Temp (^{0}C)	Anisidine Value (meq/kg)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.12	0.07	0.08	0.06
40	0.19	0.08	0.10	0.08
50	0.19	0.13	0.14	0.11
85	0.21	0.11	0.13	0.13
130	0.33	0.18	0.19	0.17

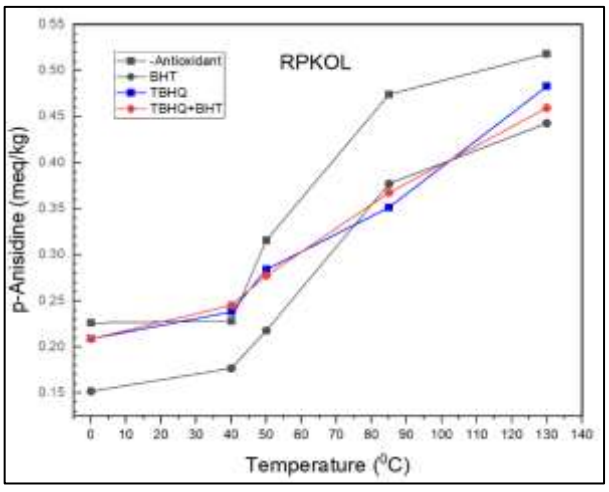
c. RBDOL

Temp (^{0}C)	Anisidine Value (meq/kg)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.88	0.81	0.81	0.80
30	0.87	0.81	0.83	0.82
40	0.96	0.86	0.87	0.85
85	1.11	0.98	0.97	0.98
130	1.15	1.08	1.06	1.08

d. RBDST

Temp (^{0}C)	Anisidine Value (meq/kg)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.50	0.42	0.42	0.42
65	0.45	0.39	0.41	0.40
70	0.46	0.36	0.36	0.35
85	0.69	0.57	0.56	0.57
130	0.71	0.62	0.60	0.61

The graph of the effect of temperature and antioxidants on increasing anisidine value in palm oil samples, RPKOL, RPKS, RBDOL, and RBDST can be shown in **Figure 4**.



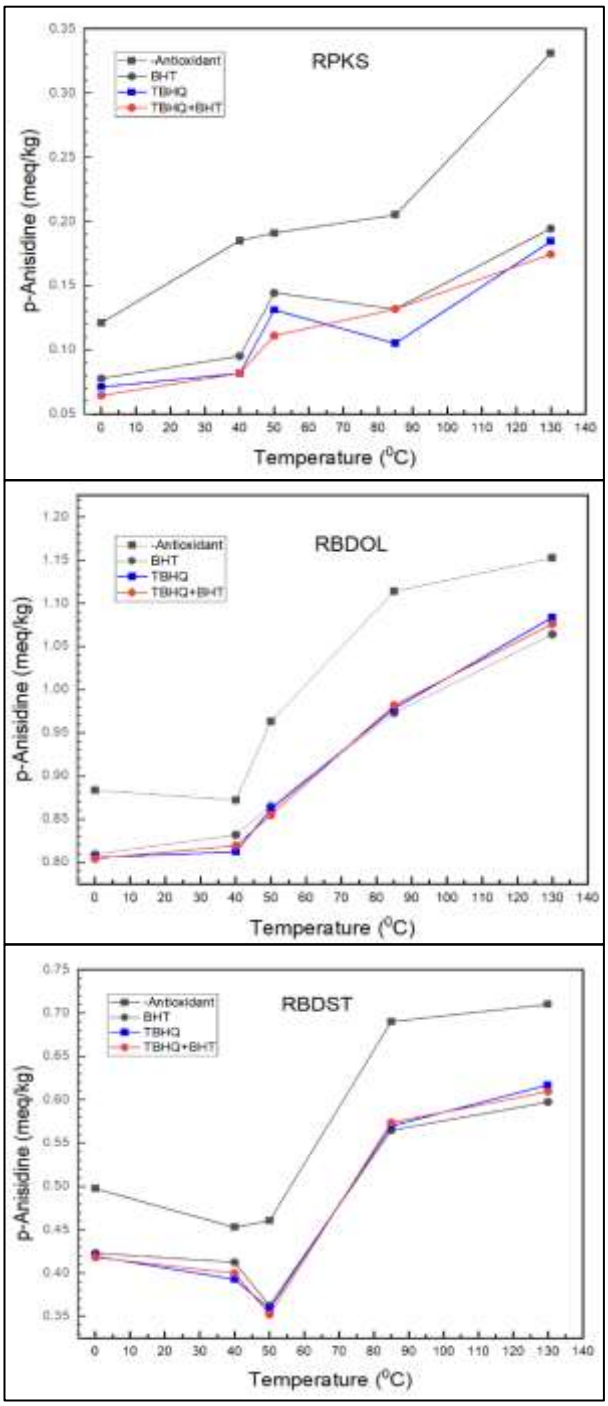


Figure 4. Graph of the effect of temperature and antioxidants for anisidine value.

From the statistical results of ANOVA, analysis of the samples (RPKOL, RPKS, RBDOL, RBDST), there were differences due to the increase in temperature and the addition of antioxidants for anisidine value. The increasing percentage for anisidine: RPKOL (69.87, 62.46, 100.11, 61.62); RPKS (88.43, 76.76, 81.97, 93.78); RBDOL (16.07, 15.94, 15.37, 16.03); RBDST (16.27, 15.54, 14.46, 15.71). From the results, for RPKOL the most effective antioxidant was a combination of TBHQ+BHT, for RPKS was TBHQ, but for

RBDOL and RBDST was BHT. So the antioxidants that we used in this research were very effective in controlling anisidine value.

Free Fatty Acid (FFA)

The results of the FFA test also showed an increase in yield due to an increase in temperature. The role of antioxidants is very visible compared to samples without the addition of antioxidants. The results are shown in **Table 3**.

Table 3. Free fatty acid results for a.RPKOL; b.RPKS; c.RBDOL ; d.RBDST.

a. RPKOL

Temp	Free Fatty Acid (%)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	0.093	0.092	0.093	0.092
40	0.093	0.093	0.093	0.093
50	0.094	0.093	0.094	0.093
85	0.096	0.096	0.096	0.095
130	0.107	0.104	0.105	0.104

b. RPKS

Temp	Free Fatty Acid (%)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	0.045	0.044	0.045	0.043
40	0.047	0.046	0.046	0.044
50	0.047	0.046	0.046	0.045
85	0.049	0.048	0.047	0.046
130	0.057	0.051	0.052	0.049

c. RBDOL

Temp	Free Fatty Acid (%)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	0.112	0.110	0.110	0.109
30	0.117	0.112	0.112	0.112
40	0.117	0.112	0.111	0.113
85	0.125	0.119	0.120	0.119
130	0.153	0.134	0.133	0.131

d. RBDST

Temp	Free Fatty Acid (%)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	0.151	0.148	0.148	0.147
65	0.152	0.149	0.149	0.149
70	0.154	0.149	0.149	0.148
85	0.159	0.156	0.158	0.157
130	0.160	0.158	0.159	0.157

The statistical results of Anova analysis of variance in the RPKS, RBDOL, and RBDST samples showed that there was a difference in yield due to the increase in temperature and the addition of antioxidants to the increase in FFA. The percentage increase is RPKOL (10.56, 7.95, 6.48, 8.01); RPKS (11.11, 8.14, 6.67, 8.20); RBDOL (14.51, 8.41, 8.51, 8.87); RBDST (3.48, 3.38, 4.06, 3.91). BHT is effective for RPKOL and RPKS, but TBHQ is effective for RBDOL and RBDST to control FFA. The graph effect of temperature and the addition of antioxidants on the increased FFA in palm oil samples is shown in **Figure 5**.

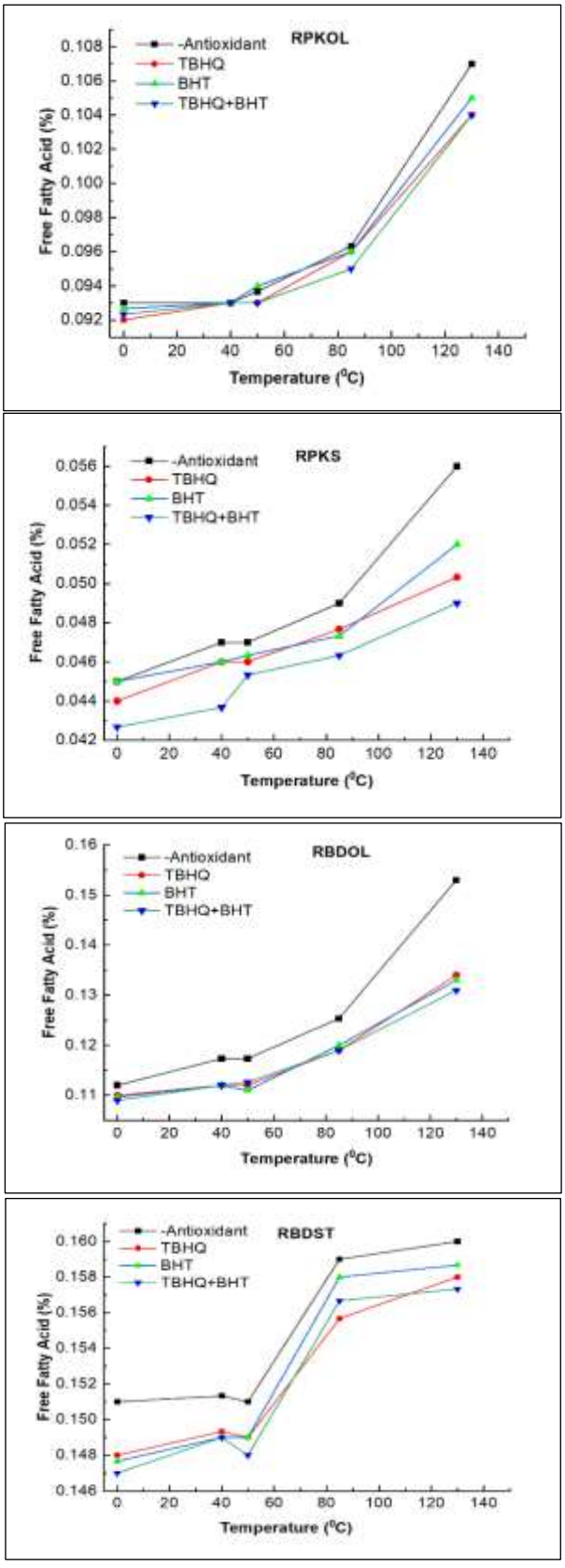


Figure 5. Graph of the effect of temperature and addition of antioxidants on the increase in FFA.

Color Lovibond

The results of the color test also showed a change in yield due to the increase in temperature and the antioxidants. The results are shown in **Table 4**.

Table 4. Color Lovibond results for a.RPKOL; b.RPKS; c.RBDOL ; d.RBDST.

a.RPKOL

Temp	Color Lovibond (Red)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	1.1	1.0	1.0	1.0
40	1.1	1.1	1.1	1.1
50	1.1	1.1	1.2	1.1
85	1.2	1.1	1.2	1.1
130	1.2	1.1	1.2	1.1

b.RPKS

Temp	Color Lovibond (Red)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	0.6	0.5	0.5	0.5
40	0.6	0.5	0.5	0.5
50	0.6	0.5	0.5	0.5
85	0.6	0.5	0.5	0.5
130	0.8	0.6	0.6	0.5

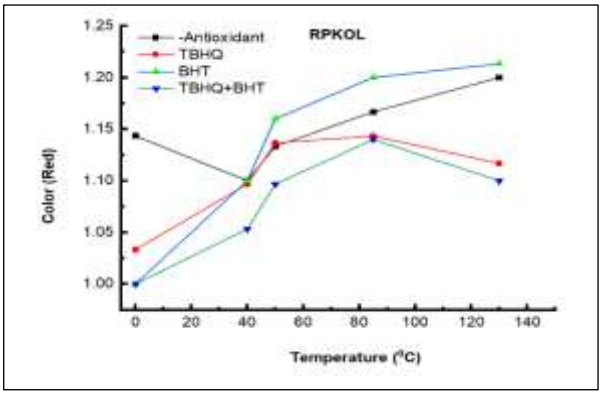
c.RBDOL

Temp	Color Lovibond (Red)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	2.9	2.7	2.7	2.6
30	2.9	2.8	2.8	2.7
40	2.9	2.8	2.8	2.7
85	3.0	2.8	2.8	2.7
130	3.1	2.9	2.8	2.7

d.RBDST

Temp	Color Lovibond (Red)			
(^{0}C)	Without	TBHQ	BHT	TBHQ+BHT
0	2.5	2.3	2.2	2.2
65	2.5	2.3	2.3	2.3
70	2.5	2.3	2.3	2.3
85	2.6	2.4	2.3	2.3
130	2.6	2.4	2.3	2.4

The effect of temperature and the addition of antioxidants on color in palm oil samples (RPKOL, RPKS, RBDOL, RBDST) is shown in **Figure 6**.



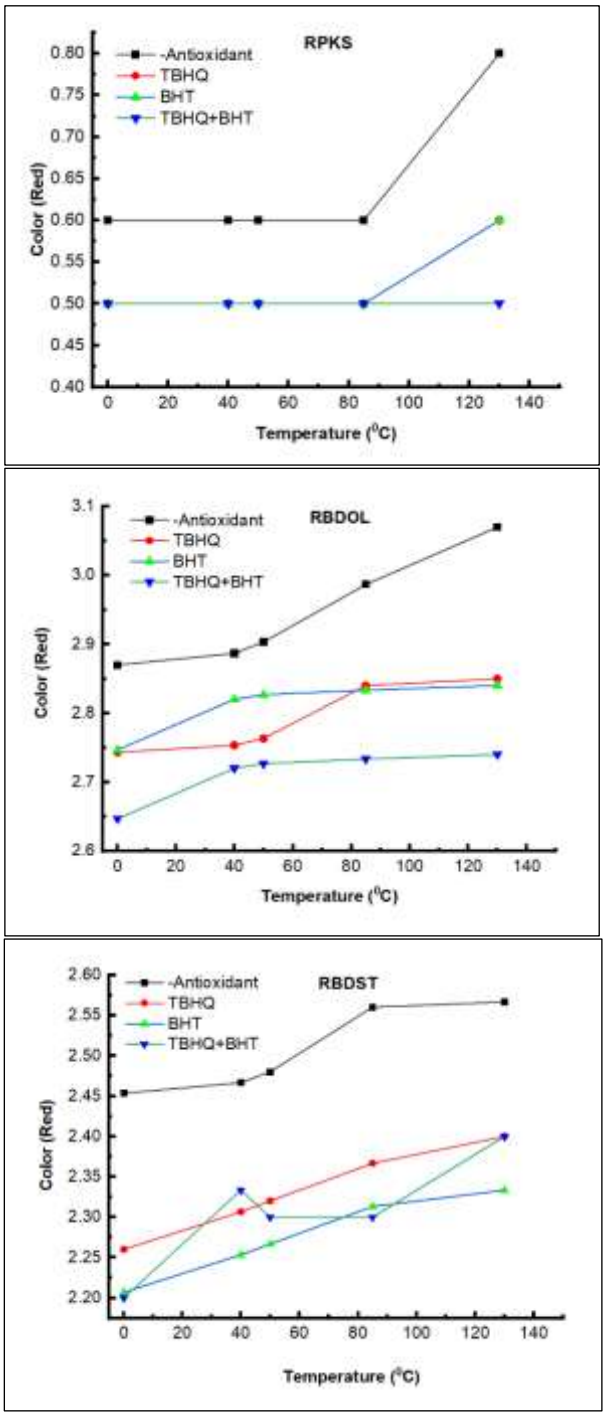


Figure 6. Graph of the effect of temperature and the addition of antioxidants on color changes.

From statistical results of ANOVA analysis of the samples (RPKOL, RPKS, RBDOL, RBDST) showed that there was a difference due to the increase in temperature and the addition of antioxidants to changes in color. For increase percentage was obtained: RPKOL (0.58, 8.71, 16.83, 9.75); RPKS (8.33, 5.00, 5.00, 0.00); RBDOL (3.19, 2.13, 3.03, 3.15); RBDST (2.65, 3.91, 3.85, 6.06). The effective antioxidant for RPKOL, and RBDOL was TBHQ; for RPKS it was TBHQ+BHT, and for RBDST was BHT.

Density

The results of the density test are presented in **Table 5**. There was no significant difference in yield due to the increase in temperature and the addition of antioxidants to changes in density.

Table 5. Density results for a.RPKOL; b.RPKS; c.RBDOL ; d.RBDST.

a. RPKOL

Temp (^{0}C)	Density at 50^{0}C (g/ml)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.093	0.092	0.093	0.092
40	0.093	0.093	0.093	0.093
50	0.094	0.093	0.094	0.093
85	0.096	0.096	0.096	0.095
130	0.107	0.104	0.105	0.104

b. RPKS

Temp (^{0}C)	Density at 50^{0}C (g/ml)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.045	0.044	0.045	0.043
40	0.047	0.046	0.046	0.044
50	0.047	0.046	0.046	0.045
85	0.049	0.048	0.047	0.046
130	0.056	0.050	0.052	0.049

c. RBDOL

Temp (^{0}C)	Density at 50^{0}C (g/ml)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.112	0.110	0.110	0.109
30	0.117	0.112	0.112	0.112
40	0.117	0.112	0.111	0.113
85	0.125	0.119	0.120	0.119
130	0.153	0.134	0.133	0.131

d. RBDST

Temp (^{0}C)	Density at 50^{0}C (g/ml)			
	Without	TBHQ	BHT	TBHQ+BHT
0	0.151	0.148	0.148	0.147
65	0.151	0.149	0.149	0.149
70	0.151	0.149	0.149	0.148
85	0.159	0.156	0.158	0.157
130	0.160	0.158	0.159	0.157

Viscosity

This research did not found a difference in yield due to the addition of antioxidants to viscosity. The increase in temperature affected the Viscosity for RPKOL, RPKS, and RBDOL but for the RBDST sample, had no significant effect. The results for viscosity are presented in **Table 6**.

Table 6. Viscosity results for a.RPKOL; b.RPKS; c.RBDOL ; d.RBDST.

a. RPKOL

Temp (^{0}C)	Viscosity at 40^{0}C (cP)			
	Without	TBHQ	BHT	TBHQ+BHT
0	28.20	28.31	28.28	28.28
40	28.44	28.36	28.41	28.41
50	28.36	28.43	28.31	28.31
85	28.20	28.20	28.32	28.32
130	28.56	28.52	28.56	28.44

b. RPKS

Temp (^{0}C)	Viscosity at 40^{0}C (cP)			
	Without	TBHQ	BHT	TBHQ+BHT
0	28.56	28.12	28.56	28.43
40	28.56	28.17	28.56	28.12
50	28.66	28.59	28.66	28.40
85	27.90	28.12	27.90	28.63
130	27.98	28.21	27.98	28.12

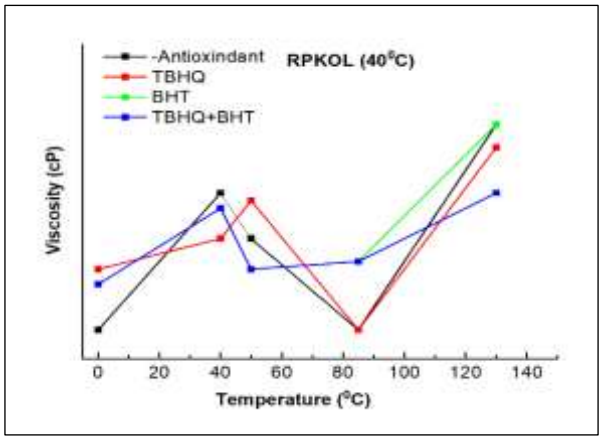
c. RBDOL

Temp (^{0}C)	Viscosity at 40^{0}C (cP)			
	Without	TBHQ	BHT	TBHQ+BHT
0	38.04	37.96	38.00	38.24
30	38.12	38.47	38.29	38.09
40	38.44	38.17	38.31	38.33
85	37.92	38.05	37.99	38.16
130	38.64	38.33	38.64	38.57

d. RBDST

Temp (^{0}C)	Viscosity at 60^{0}C (cP)			
	Without	TBHQ	BHT	TBHQ+BHT
0	20.96	20.92	20.96	20.97
65	20.91	20.93	20.91	20.91
70	20.95	20.93	20.95	20.95
85	20.92	20.95	20.92	20.96
130	20.97	20.96	20.97	20.96

The effect of temperature and the addition of antioxidants on the viscosity is shown in **Figure 8.**



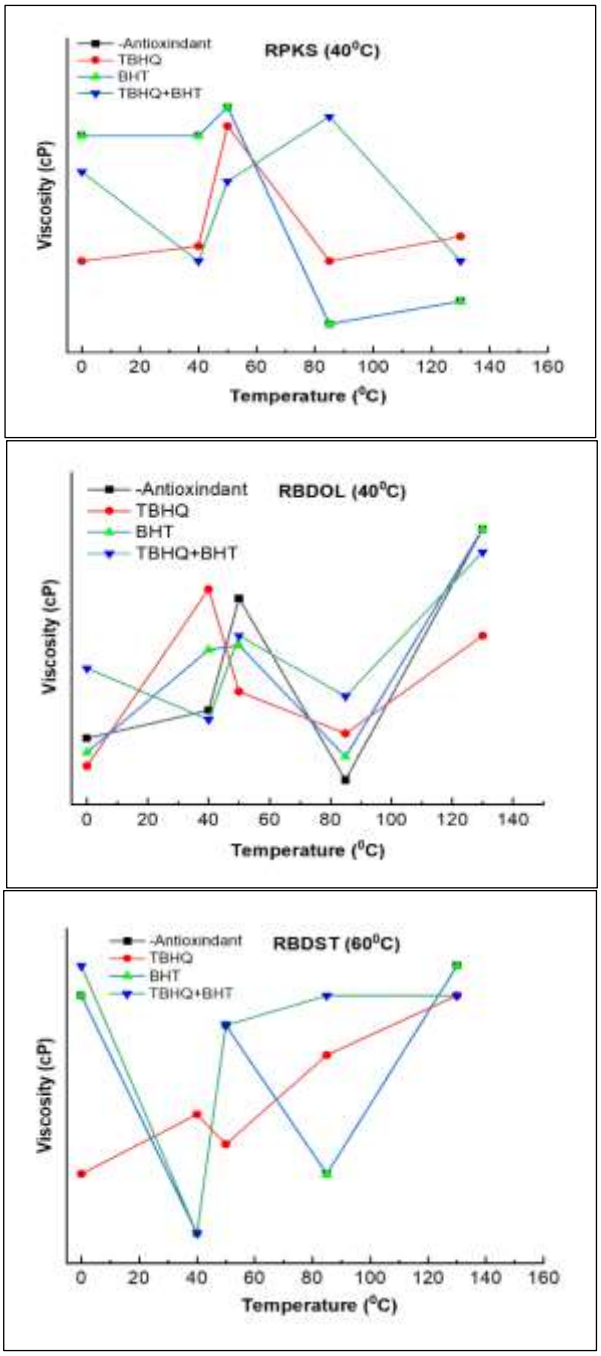


Figure 8. Viscosity's Graph of the temperature and antioxidants effects.

Trans Fatty Acid

In the Trans Fatty Acid (TFA) test using a GC Clarus 590 Perkin Elmer GC flame ionization detector (FID), peak area data was obtained, and the fatty acid composition (FAC) response after 130^{0}C heating treatment for each addition of antioxidants. In the fatty acid composition can be seen that the formation of trans fatty acid (TFA) in C18:1n9t (trans 9-octadecanoic) or elaidic acid in RPKOL, RPKS, RBDOL, RBDST palm oil samples can be seen in **Figure 9.**

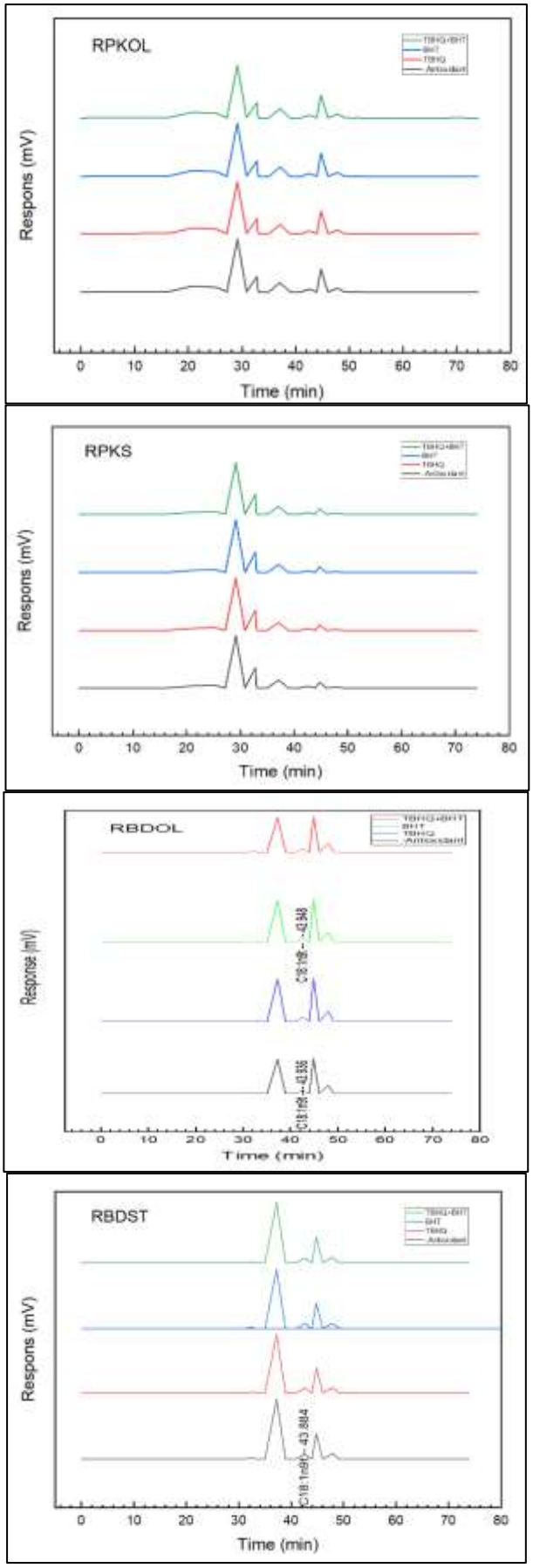
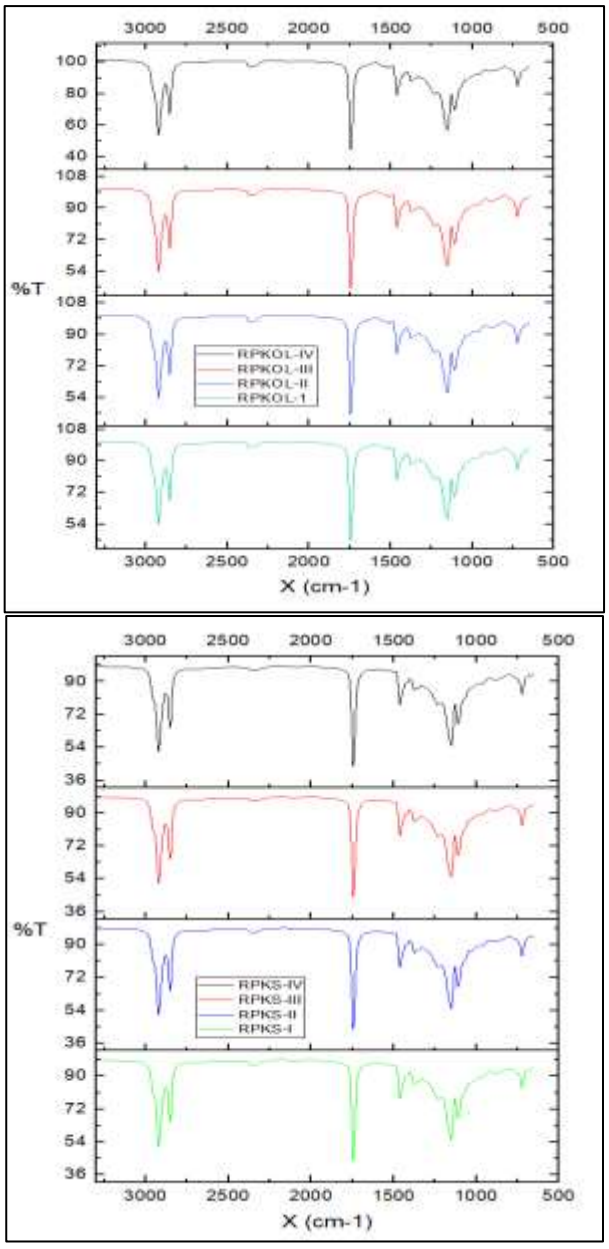


Figure 9. The response of the GC for the Peak Area where C18:1n9t appears.

The GC's response to the palm oil samples found that in RBDOL, TFA C18:1n9t was formed in the treatment without antioxidants (43,936 min) and in the addition of BHT (43,948 min). In RBDST, TFA C18:1n9t was formed in the treatment without antioxidants (43,834 min). But for RPKOL and RPKS samples there were no trans fatty acids formed. The response of the TFA signal to the fatty acid composition (FAC) indicates that the palm oil has been oxidized and trans fatty acids are also formed which are known to be harmful for human consumption.

Fourier Transform Infrared (FT-IR)

The results of FT-IR testing using ATR-FTIR Perkin Elmer obtained spectrum/wave numbers as shown in **Figure 10**.



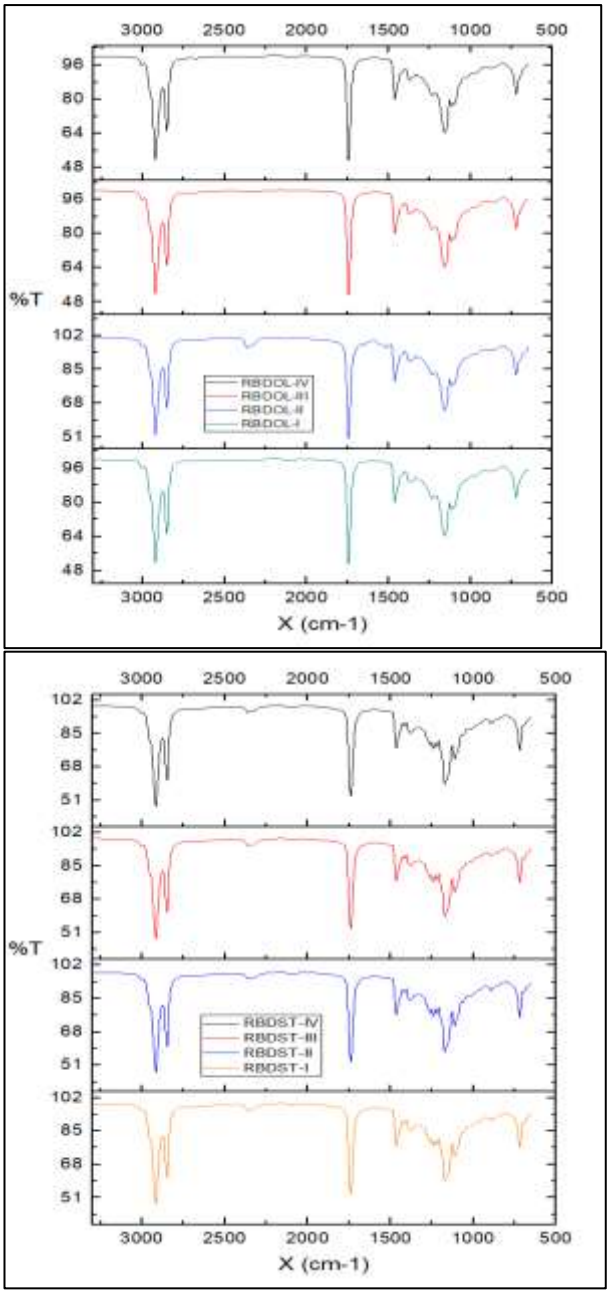


Figure 10. FT-IR spectrum of palm oil samples after heating at 130^0C for 24 hours.

From the results of the FT-IR test on palm oil samples at 130^0C without antioxidants, the spectrum showed the presence of carboxyl groups and the presence of aldehydes at wave numbers 1760 cm^{-1} (C=O aldehyde bonds) and 2900 cm^{-1} (CH bonds in aldehydes) [7,11]. So from the IR spectrum, it identified aldehyde compounds. The formation of aldehyde compounds causes an unpleasant or rancid odor in the oil.

CONCLUSION

Heating induces oxidation in palm oil products, leading to a deterioration in quality, as

evidenced by elevated peroxide value, anisidine value, free fatty acids (FFA), and color. The peroxide value (PV) results indicated that the addition of BHT was most effective for RPKOL, RBDOL, and RBDST products. However, for RPKS, TBHQ was found to be the most effective antioxidant. Regarding the anisidine value, the combination of TBHQ and BHT proved most effective for RPKOL, TBHQ alone was effective for RPKS, and BHT was effective for both RBDOL and RBDST. It can be concluded that antioxidants in this research were very effective in reducing anisidine value.

In the FFA test, BHT is effective for RPKOL and RPKS, whereas TBHQ is effective for controlling FFA in RBDOL and RBDST. In color testing, TBHQ emerged as the most effective antioxidant for RPKOL and RBDOL, while TBHQ+BHT was effective for RPKS, and BHT was effective for RBDST. Density was not influenced by temperature or antioxidants. In viscosity results, temperature had an impact on RPKOL, RPKS, and RBDOL, but not on RBDST. Both RBDOL and RBDST exhibited the presence of trans fatty acids after being subjected to the highest temperature.

From the GC analysis, it was determined that in RBDOL, TFA C18:1n9t was formed in treatments without antioxidants and with the addition of BH. For RBDST, TFA C18:1n9t was formed in treatments without antioxidants. Aldehydes were detected at wave numbers 1760 cm^{-1} (C=O aldehyde bonds) and 2900 cm^{-1} (CH bonds in aldehydes) in all palm oil products in this study. Therefore, the IR spectrum identified the presence of aldehyde compounds. The formation of these compounds leads to an unpleasant or rancid odor in the oil.

Controlling the heating temperature of palm oil is crucial to prevent rapid oxidation and maintain the quality of the palm oil properly. Tests for palm oil oxidation can be further developed by exploring additional parameters and monitoring changes in fatty acid composition. The use of antioxidants proves highly effective in inhibiting oxidation in palm oil; however, careful attention to the level or concentration of their application is essential

Further research on the increase in oxidation in palm oil commodities can be continued or expanded by exploring variables such as temperature, antioxidant concentration, and types of environmentally friendly and safe natural antioxidants for human health.

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