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The Effect of Light on the Oxidative Stability of Palm Olein

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Abstract

The effect of light and additives on the oxidative stability of palm olein has been studied. Acid value, peroxide value and iodine value of the oil samples at selected hours were evaluated in this study. The micro structural changes of palm olein were confirmed by using Fourier transform infrared (FTIR) spectroscopy while thermogravimetric analysis (TGA) was used in order to detect any changes in the bulk properties of palm olein. It was found that the effect of light and heat can increase the lipid oxidation. Palm olein blended with the additive Irgalube F10 showed lower acid values compared to original palm olein after 768 hours of heating. Addition of additive Irgalube F10 in oil samples is able to increase the thermal oxidation stability.

Keywords: Thermogravimetric analysis, oxidative stability, additive, palm olein, antioxidants.

1.0 Introduction

Nowadays, the environment issues created an opportunity to the lubricant industry to produce environmentally friendly lubricant. The biodegradable lubricants become a replacement of mineral oil (petroleum), especially as hydraulic fluids and engine oils [1].

In contrast to mineral oil, lubricants and hydraulic fluids based on vegetable oils are largely rapid and completely biodegradable and of low ecotoxicity. They are inherently highly effective lubricants with excellent tribological properties. However their thermal and hydrolytic stabilities are limited and need to be improved by a variety of measures. In order to compete with mineral oils, some of their inherent disadvantages must be corrected. They are sensitive to hydrolysis and oxidative attack and their low temperature behavior is partly unsatisfactory properties [2].

There are many factors that cause the lipid oxidation. Light is one of the factors towards the lipid oxidation that can lead to free-radical formation together with oxygen or high temperature. When lipid oxidation occurred, the hydroperoxides formed are tasteless, colorless and odorless and will further originate a wide range of breakdown products. So, evaluating parameters that influence lipid oxidation will help better to understand and control this chemical reaction in food [3]. Natural antioxidants which are tocopherols, tocotrienols and plastochromanoil-8 have been

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studied and the natural antioxidants play an important role in vegetables oils by inhibiting lipid oxidation [4].

In the present study, the effects of light and heat on the oxidative stability of palm olein were studied. The oil sample was prepared under two different conditions which were stored in darkness and another one set under visible light. Besides that, the effect of additive on the oxidative stability of palm olein when exposed to light also was studied. Two different temperatures were used to store the oil samples which are room temperature and 135°C (heated in oil bath) for 768 hours. Moreover, acid value, peroxide value and iodine value of the oil samples at selected hours were evaluated in this study. The micro structural changes of palm olein were confirmed by using Fourier transform infrared (FTIR) spectroscopy while thermogravimetric analysis (TGA) used to detect any changes in the bulk properties of palm olein. Furthermore, no pervious literature has been studied on the oxidative stability on the palm olein towards the effect of light.

2.0 Materials and Method

The samples were prepared under two different conditions which were stored in the darkness and another one under the exposure of visible light. Besides that, the effect of additive also was determined which without additive and additive-added. The additive Irgalube F10, 2.0% were used in this experiment. All the samples with additive-added were stirred for an hour with magnetic stirrer. The percentage of additive in liquid form calculated by the equation show below:

$$wt(add) = \frac{wt(oil) \times \%(add)}{100} \qquad (1)$$

where, *wt (add)* is weight of additive, *wt (oil)* is weight of oil and *% (add)* is percentage of additive.

The samples were stored at two different temperatures which are room temperature as the set control and another one will be heated at 135°C in oil bath for 768 hours and were analyzed at a certain period of interval preset (0, 48, 96, 192, 288, 384, 576 and 768 hours) for its iodine value (IV), peroxide value (PV), acid value (AV), iodine value (IV), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. Each of the analyses was done 3 times for each sample.

In acidity test (TAN) was conducted following AOCS method Cd 3A-63. 3 ml of sample was weighed and added into Erlenmeyer flask. Then, 25 ml of diethyl ether, 25 ml of ethanol 95% and 1 ml of phenolphthalein 1% were added into sample and titrated with 0.05 M KOH solutions. The end point is considered when the solution change to pink colour and maintain for 15 min. The acid value was calculated as follow:

$$TAN = (A - B) \times N \times 56.11 / wt$$

where, A is KOH used in titration of mixture (ml), B is KOH used in titration of blank (ml), N is normality of KOH (0.05) and wt is weight of sample (g).

Peroxide value test was conducted according to AOCS official method Cd8-53 and the iodine value test was according to AOCS method Cd 1b-87. In Fourier transform infrared (FTIR) spectroscopy analysis, a spectrum was obtained on the Perkin Elmer FTIR system spectrum GX. Firstly, sample was placed in KBr cell and was scanned at the wavelength from 370cm^{-1}, N-hexane solution was used for cell cleaning before the oil sample is located on the cell. Number of scan for the sample was 6 times. The spectra obtained are used to observe the structural bond and functional group of the samples prepared. For thermogravimetric analysis, it was performed using Perkin Elmer Pyris 6 TGA at a heating rate of 5°C/min. Sample of approximately 15mg was heated from 30°C to 450°C. The instrument was purged of nitrogen flow at a rate of 20.00 ml/min.

3.0 Results and Discussion

3.1 Effect of Additives

Unsaturated vegetable oils are more reactive than the saturated part of vegetable oils. Few factors enhanced their chemical reactivity such as exposure to air [5], heat [6], light and moisture [7]. Besides that, the oxidation is also influenced by fatty acid composition of the oils and antioxidants [8].

The total acid number (TAN) for all samples of palm olein and palm olein with additive increased rapidly after heating in the oil bath at the temperature of 135°C. Result also showed that the additive Irgalube F10 effectively act as antioxidant which can reduce the oxidation of palm olein. TAN of original palm olein increased rapidly from 0.2095 mg KOH/g to 4.8512 mg KOH/g. In contrast, the palm olein which blended with 2.0% of additive Irgalube F10 increased from 0.3164 mg KOH/g to 3.6239 mg KOH/g proportionally to the heating temperature and the exposed time (Figure 1). Palm olein blended with the additive Irgalube F10 showed lower acid

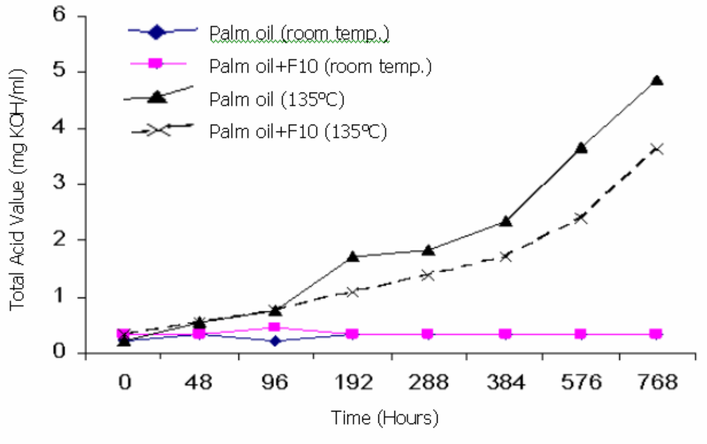

Figure 1 Variation of TAN with hours for palm olein with and without additive in the dark condition.

values compared to original palm olein after heated in the oil bath for 768 hours which indicate that Irgalube F10 were able to act as antioxidant which inhibits the thermal oxidation process.

The increasing of the TAN for all samples was found correlates with the hours of heating in the dark condition. The difference of the TAN is due to the different percentage of free fatty acid that obtained in the oils. Beside that, with the continuing heating in high temperature for a long period, also one of the factors that causing the TAN increased. This is due to the rapid formation of the first intermediate products which are the hydroperoxides of fatty acids and the further formation of secondary products such as aldehyde, ketones, acid and alcohol.

The results showed that the trend of the peroxide values is fluctuated for all samples. In the beginning of 100 hours, the peroxides value of original palm olein increased correlates with the hours of heating in the dark condition. This is due to the formation of hydroperoxides of unsaturated fatty acids that were obtained as a result of lipid oxidation (Figure 2). While the PV of the palm olein with additive-added were decreased in the beginning of 200 hours. Therefore, additive Irgalube F10 started to prevent the oil samples from the formation of hydroperoxides in the early stage.

It was observed that the trends of the peroxide values were unstable because the hydroperoxides of unsaturated fatty acids formed by lipid oxidation are very unstable and break down into a wide variety of volatile flavor compounds as well as nonvolatile products. Therefore, at the beginning the increasing of PV showed that the concentration of hydroperoxides is higher while the PV decreased when the secondary products are observed. The fluctuated of the peroxide values were due to the rapid decomposition of the peroxides that are formed during primary oxidation to secondary oxidation products [9].

The presence of additive Irgalube F10 could reduce the formation of hydroperoxides and hence the further formation of the hydroperoxides to the secondary products is slower. Therefore, the addition of additive increases the stability of the oils.

Figure 2 shows the iodine value (IV) for all samples in dark condition which heated in oil bath at 135°C from 0 hour to 768 hours. The IV decreased slowly from 0 hour to 768 hours proportionally to the heating temperature and the exposure time, showing the decreasing in double bond of the oil samples after heating treatment. Addition of additive Irgalube F10 in palm olein could prevent the decreasing of the IV and hence proved that additive can improve the oxidative stability of the palm olein towards thermal oxidation.

Decreasing of the IV is caused by the high temperature heating process which enable the molecules of the oil samples have enough energy to break the double bond in the chain. The IV is a simple fat analysis that can measure the unsaturation. Therefore, the oil samples after the heating treatment obtained the decreasing of the IV. It also means that the heating treatment will cause the unsaturated part become less while the saturated part increases.

The onset temperature for original palm olein at 0 hour is 391°C and decreased to 386°C after 768 hours of heating. This is due to the thermal decomposition of the oil that breaking down the oxygenated hydrocarbon produced the lower molecular weight components in the original palm

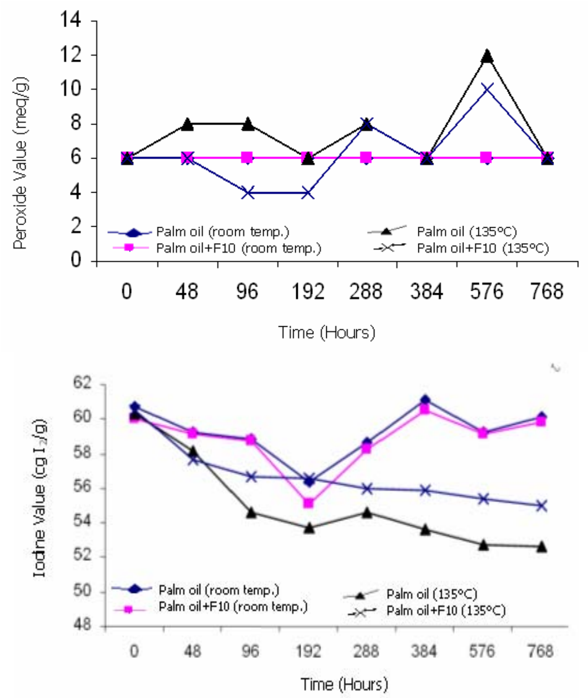

Figure 2. Summary of peroxide value and iodine value for palm olein with and without additive in the dark condition heated at 135°C.

olein [10]. Therefore, the decreasing onset temperature of the original palm olein shows that it is less thermally stable after a long period of heating time.

Meanwhile, the onset temperature for palm olein is lower (386°C) than the palm olein blended with additive after 768 hours of heating (390°C) showing that the original palm olein tends to degrade faster at a much lower temperature compared to the oil samples that blended with additive (Table 1). In the other side, both palm olein and palm olein with additive showed similar degradation temperatures which are 427°C and 429°C. The presence of 2.0% of additive Irgalube F10 still have the ability to act as antioxidant that made the oil samples become more thermally stable after a long period of heating treatment.

Table 1. Results of onset temperature and maximum degradation temperature for palm olein with and without additive in the dark condition.

Samples	Onset Temperature / °C		Maximum Degradation Temperature / °C	
	0 Hour	768 Hours	0 Hour	768 hours
Palm Oil	391	386	426	427
Palm Oil + F10	397	390	432	429

The thermogram of additive was used as a reference to determine the percentages of the additive obtained in the oil samples by compared it with the thermogram of oil samples blended with additive. Results obtain showed that there are no curve in thermogram of additive Irgalube F10 indicates that the total amount of the additive Irgalube F10 is suitable for oil samples and able to improve the physical properties of oil samples but do not influence the main components in the oil samples.

3.2 Effect of Light

TAN of the original palm olein increased slowly under the exposure of light which is 0.2151 to 0.3256 mg KOH/g. The increasing of TAN in original palm olein under the exposure of light only shows slightly difference compared to the palm olein which stored without light. In the presence of additive Irgalube F10 under the exposure of light, the TAN is increased from 0.2158 to 0.7532 mg KOH/g showed that the additives are able to act as photosensitizer under exposure of light which increased the oxidation process.

In contrast, additive Irgalube F10 are manage to prevent the oil samples from lipid oxidation showed by lower PV compared to original palm olein. Under the exposure of light, the original palm olein gave the higher increasing of peroxide value. The PV increased from an initial value of 13.9939 meq/g to 79.9244 meq/g showed that the original palm olein under the exposure of light accelerated the formation of the hydroperoxides.

Result Iodine value test showed that under the exposure of light didn't give any affect to the palm olein with or without additive-added. This indicates that there are no effects on the unsaturation of the oil samples under the light exposure.

The results of thermogravimetric analysis (TGA) not obviously showed the differences of the effect of light between the oil sample with and without exposure of light. Oil samples blended with the additive showing maximum degradation at 432°C while the oil samples without additives degrade at 428°C in the exposure of light for 768 hours. This indicates that the additives Irgalube F10 in the presence of light (after 768 hours) will cause the degradation of oil and was proved that low molecular weight components of the oil samples more easily degraded in the early stage with the exposure of light. Overall, the oil samples blended with additive can cause the lipid photo-oxidation and oil will degrade easily in the presence of light. As a result, the additive Irgalube F10 under the exposure of light will accelerate the lipid oxidation.

Table 2 Results of onset temperature and maximum degradation temperature for palm olein with and without additive in the exposure of light.

Samples	Onset Temperature / °C		Maximum Degradation Temperature / °C	
	0 Hour	768 Hours	0 Hour	768 hours
Palm Oil	392	392	426	429
Palm Oil + F10	397	394	432	428

4.0 Conclusion

Results show that 2.0% of additive Irgalube act as antioxidant and successfully reduced the rate of oxidation towards the heating and exposure of light. The oil samples with additive are higher in total acid number compared to the original palm olein under the exposure of light. It indicates that the additive Irgalube F10 acted as photosensitizer under exposure of light which believed to accelerate the lipid oxidation. The peroxide values of the oil samples blended with additives gave the lower PV in the presence of light. Therefore, additive Irgalube F10 still manages to prevent the oils from the formation of hydroperoxides. This showed that the presence of Irgalube F10 in the oil samples under the exposure of light only manage to prevent the formation of hydroperoxides but fail to prevent the formation of fatty acid. Oxidation of palm olein was affected by the heating treatment. The oil samples after the heating treatment obtained the higher acid values, a fluctuated pattern in peroxide value test and the iodine values were decreased proportionally to the heating and exposed time. While, the addition of additive Irgalube F10 in oil samples can help to stabilize the thermal oxidation. As a conclusion, the effect of light and heat indeed can increase the lipid oxidation.

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