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Comparative Study of Carotenoids Content in Ripe and Unripe Oil Palm Fresh Fruit Bunches

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Abstract: Currently *Elaies Guineensis* or oil palm is the most widely planted commodity crop in Malaysia and has a very large impact to the country's economy. At the same time, the industry also produces huge amount of oil palm waste materials such as Unripe Fresh Fruit Bunche (FFB). Each year million tons of Unripe FFB could not be processed in the mill and were disposed-off and thus posed additional threats to the environment. The objective of this study was to recycle the oil from Unripe FFB and compared the carotenoids content with the Ripe FFB. Carotenoids is the natural chemical compounds which gives palm oil its orange red color. The compound is good for human health as it can strengthen body immunity system and act as antioxidant The experiment was conducted by collecting fruits from three (3) samples of Ripe FFB and Unripe FFB. The selected fruits were then sterilized, and Crude Palm Oil (CPO) was extracted. The analysis of oil samples was conducted using Near Infrared Spectroscopy Diode Array (NIRS DA) 1650. Result for the carotenoids showed that mean for the Ripe FFB was 968.07 ppm and for the Unripe FFB was 927.37 ppm. The Free Fatty Acids (FFA) were 22.08 and 14.47 respectively which indicated that the fruits were badly bruised during the processing. This study showed that the carotenoids content in Unripe FFB is comparable with the Ripe FFB and thus it can be concluded that Crude Palm Oil (CPO) from Unripe FFB can be used for carotenoids extraction instead of rejected or disposed-off to the environment.

Keywords: Unripe fresh fruit bunch, oil palm, crude palm oil, carotenoids, fee fatty acids

1. Introduction

Oil palm is a well-known tropical crop originated from west and central Africa. Owing to its many uses, it was domesticated and has been cultivated throughout the humid tropics especially in Malaysia and Indonesia. Currently, palm oil world trade is conquered by Malaysia and Indonesia [1]. Palm oil industry has grown bigger and mainly driven by these two countries and as for Malaysia it has contributed to the country's gross domestic product (GDP) over 5% [2]. Palm oil can be derived from either mesocarp, or kernel of the oil palm fruits. Extraction of oil from mesocarp and seed will produce Crude Palm Oil (CPO) and Palm Kernel Oil (PKO), respectively. Apart from the oil itself, some of the other elements found in CPO are free fatty acids, moisture, impurities and trace metals which are detrimental to the stability of the oil.

Malaysia is currently the second biggest producer and exporter of palm oil in the world after Indonesia. Currently, the most popular method of extracting CPO from oil palm fruit mesocarp is wet processing method where the oil palm Fresh Fruit Bunches (FFB) are sterilized using steam at high temperature and pressure and then the oil is extracted through series of chemical and mechanical processes as shown in Fig. 1. Unfortunately, during these processes, some of

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the phytochemicals are also partially destroyed. At the refinery, CPO also needs to undergo physical and chemical refining process to remove undesirable compounds to obtain clean and transparent oil for human consumption [3]. These processes involved vacuum and high temperature condition which also destroyed carotenoids and some other valuable components [4]. The complete process flow diagram to produce palm oil right from the plantation and the chemical and mechanical processes involved is shown in Fig. 1.

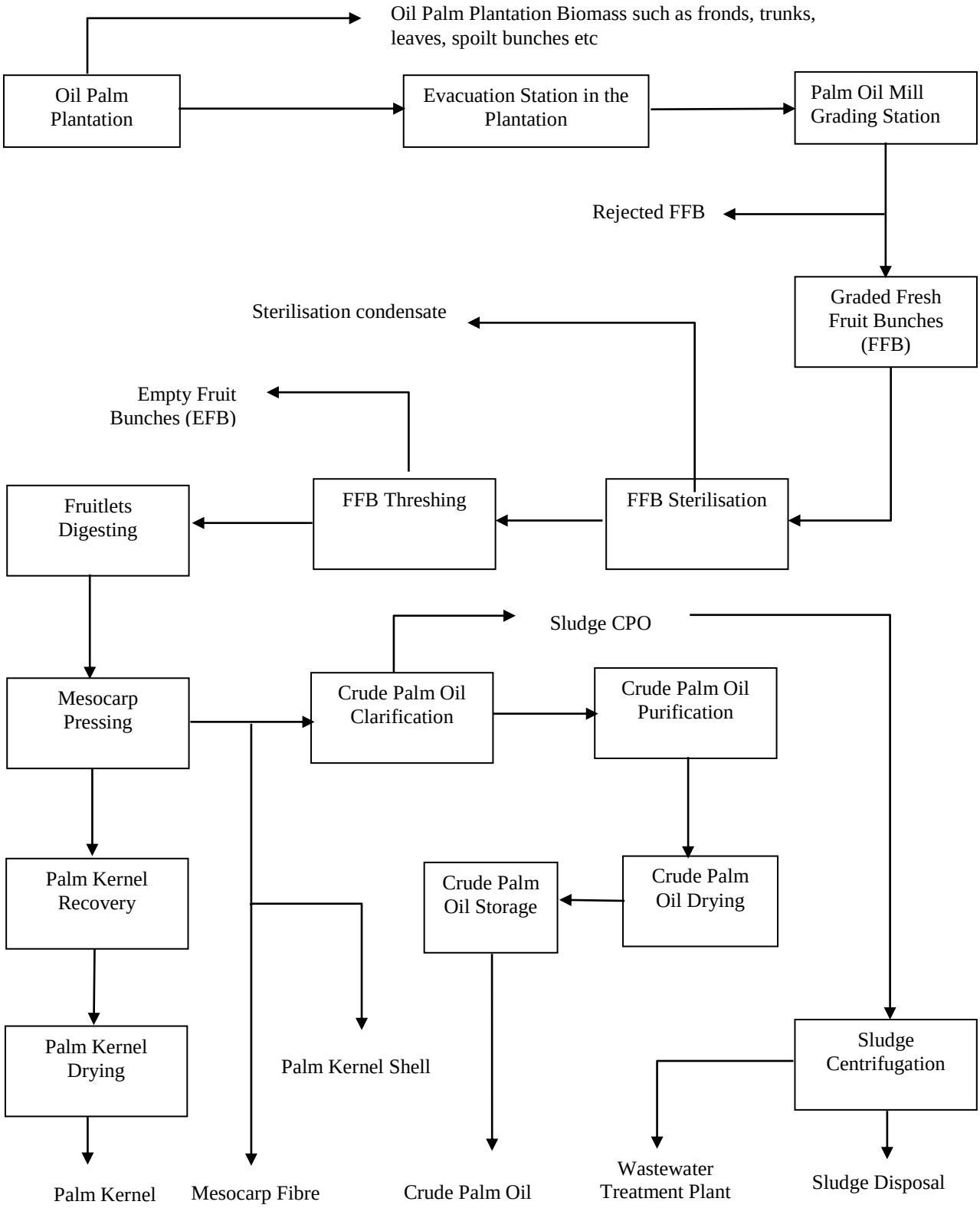

Fig. 1 – Palm Oil processing from the plantation to the mill

Apart from the existing processing technology which destroy carotenoids and some other valuable components, the industry is also facing oil palm Unripe FFB rejection at the palm oil. Unripe Bunch is black or purple-black in color and fruit mesocarp outer layer of yellowish. The FFBs have no fresh fruit socket during inspection at the refinery. Palm oil mill usually discarded the Unripe FFB because it contains less oil and will affect the Oil Extraction Rate (OER) performance of the mill. OER is the measurement of efficiency of oil extraction from a given quantity of FFB. Normally it should be in between 21-22% by including the weight of FFB. As for the fruitlets alone, for the Unripe FFB the OER can be as low as 5.9% compared to 58.3% for the Ripe FFB [5]. Fig. 2 shows the physical outlook of the Ripe and Unripe FFB. Ripe FFB sample is red-orange in colour whilst the Unripe FFB is purple-black.

(a) (b)

Fig. 2 - The physical outlook difference between (a) ripe FFB, and; (b) unripe FFB

Among the important components in the CPO is the carotenoids. Although it is available in minor quantity in parts per million (ppm), it is very important because it responsible for the occurrence of natural yellow, orange, and red pigment. Red pigment in oil palm is the main source of natural carotenoid which is also rich in vitamin A. Typically, crude palm oil contains 500–700 mg/kg of carotenoids and the major carotenoids of palm oil are α- and β-carotenes, which constitute more than 80% of the total carotenoids in palm oil [6]. Recently carotenoids from CPO has become one of the main interests in palm oil research due to the technological feasibility of extracting carotenoids from CPO. Various methods of carotenoid recovery from palm oil have been developed; these include saponification [7], adsorption [8], selective solvent extraction [8] and transesterification, followed by both phase separation and distillation of the esters [9].

As highlighted earlier in Fig. 1, Unripe FFBs are usually discarded at the grading section of the palm oil milling process. Thus, the main objective of this study is to determine and compare the carotenoids content of both Ripe and Unripe FFB so that better decision could be made to recycle and extract the oil from Unripe FFB.

2. Methodology

In this study, the Ripe and Unripe FFB samples were obtained from Pembangunan Pertanian Melaka Sdn. Bhd. (PPMSB) located in Merlimau, Malacca. Three (3) replications of Ripe and Unripe FFB samples were collected and used in this study so that simple statistical analysis could be performed. Fig. 3 simplifies the study methodology. Firstly, the samples were weighted immediately after collection. Then by using a machine, the stalks were removed from the FFB. This is a simple de-coring machine to remove the FFB stalk by using the sharp cylindrical hollow shaft. The separated oil palm fruitlets were then counted and weighed. After that, the samples were sterilized to deactivate the lipase enzyme and soften the mesocarp for oil extraction process. The mesocarps were then peeled from the nut and pressed to obtain the oil. The pressed oil was then kept in oven to remove the remaining water in the oil and ready for further analysis using near infrared machine NIRS DA1650 (Denmark). The machine was used to determine palm oil carotene concentration, free fatty acid percentage and Deterioration of Bleachability Index (DOBI).

For the Free Fatty Acids (FFA) determination, basic acid-base titration method was used as proposed in many studies. [10], [11], [12]. Exactly 5 g CPO sample was weighed in an Erlenmeyer flask and 50 ml of neutralized Isopropanol were added. The flask was then placed on a hot plate at 40°C for 3 to 5 min until the solvent reached a temperature of about 40°C. The sample was then shaken gently while titrating with sodium hydroxide (NaOH) until the first permanent pink color could be observed. For the FFA value, these recorded measurements were used in the calculation using the following equation:

$$\text{FFA}\% = \frac{25.6 \times \text{N} \times \text{V}}{\text{W}} \quad (1)$$

where FFA is the Free Fatty Acids, 25.6 is the weight of palmitic acid (palm oil and fractions), N is the normality of NaOH, V is the volume (ml) of NaOH used, and W is the weight (g) of the test portion.

For the DOBI and Carotenoids determination, spectrophotometer NIRS DA 1650 was used. In this study, absorbance of a test solution at 446 nm and 269 nm were used. In this method, 0.1 g of CPO was weighed and dissolved in 25 ml of hexane solvent. The solution sample was placed in a cuvette and absorbance measured at 446 nm (measurement of carotenoids) and at 269 nm using a spectrophotometer as proposed by earlier study [13]. The following equations were used for both DOBI and Carotenoids determination:

$$\text{DOBI} = \frac{A_{446}}{A_{269}} \tag{2}$$

where DOBI is Deterioration of Bleachability Index, A_{446} is the absorbance at 446 nm, and A_{269} is the absorbance at 269 nm.

$$\text{Carotenoids (ppm)} = \frac{383 \times A_{446} \times V}{W \times 100} \tag{3}$$

where 383 is the diffusion coefficient, V is the value of hexane (ml), W is the weight of CPO sample (g), A446 is the absorbance at 446 nm, and 100 is the constant. In this study, simple statistical analysis was performed such as mean, standard deviation and one-way Analysis of Variance (ANOVA). Three (3) samples were used for each category for replications and statistical analysis purposes.

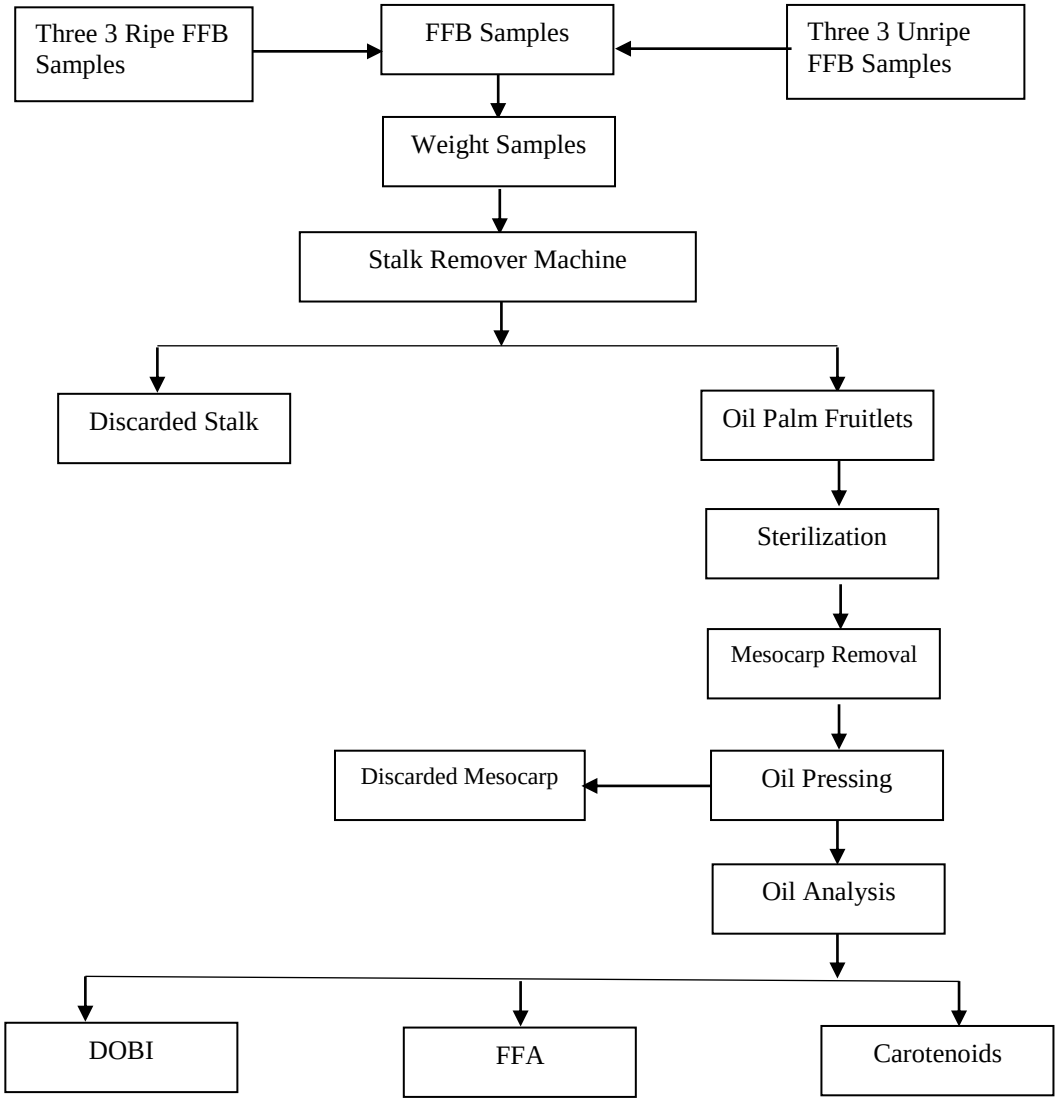

Fig. 3 - Flowchart for process study methodology

3. Results

Table 1 shows the results in table form for the DOBI, FFA and Carotenoids content of the tested samples for both Ripe FFA and Unripe FFB while Fig. 4 shows the results in histogram form for easier comparison.

Table 1 - Results for DOBI, FFA and Carotenoids for the Ripe FFB and Unripe FFB

Sample Type	Sample Number	DOBI (2.3 Minimum*)			FFA (%) (5.0% Maximum*)			Carotenoid Content (ppm)		
		Value	Mean	Std. Dev.	Value	Mean	Std. Dev.	Value	Mean	Std. Dev.
Ripe FFB	X_1	0.00	0.00	0.00	21.50	22.08	2.03	906.9	968.07	163.68
	X_2	0.00			19.94			1192		
	X_3	0.00			24.80			805.3		
Unripe FFB	Y_1	1.36	0.79	0.58	10.78	14.47	4.11	947.2	927.37	14.43
	Y_2	0.00			20.21			913.3		
	Y_3	1.02			12.43			921.6		

Std. Dev. – Standard Deviation, ppm-parts per million, FFA–free fatty acids, DOBI-Deterioration of Bleachability Index, *DOBI and FFA standard by PORAM/MPOA

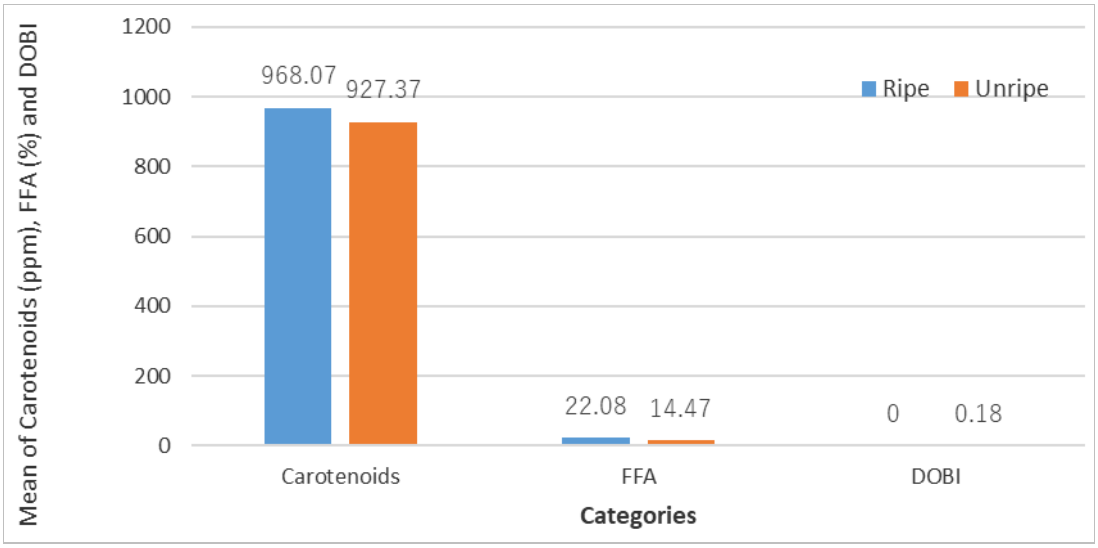

Fig. 4 - Mean value for carotenoids concentration, free fatty acid and deterioration of bleachability index

The Deterioration of Bleachability Index (DOBI) is an analytical procedure used to indicate the rate of oxidation and the ease of processing of the tested palm oil. A higher DOBI value indicates the fruit is more fresh, ripe and free of contaminates, whilst lower DOBI value shows the bad quality of CPO produced at the mill. In the CPO refinery, bleaching earth will be used to refine the oil to an acceptable color as required by users and food manufacturers. The DOBI value gives the palm oil refiner information on what type of bleaching earth to use and how much is required. As for DOBI, the results obtained showed that there was no difference between Ripe and Unripe FFB. Scientifically DOBI value decreases as storage time or handling time increases and once DOBI value reaches below 2 it indicates that the quality of CPO obtained is low and refining cannot be done effectively [14]. In this study, the handling time was too long and thus the fruitlets were badly affected.

Free fatty acids (FFA) are released naturally in crude palm oil (CPO) and can be increased by the action of lipase enzyme in the palm fruit and by microbial activity. Palm oil quality and price is dependent on the FFA content in palm oil. High content of free fatty acids in palm oil affects the quality of palm oil and leads to various health and environmental issues. The maximum free fatty acids content set by the Palm Oil Refiners Association of Malaysia in crude palm oil is 5% and < 0.1% in refined bleached deodorized oil. In this study, the value for FFA for all samples were very bad due to long handling time before sterilization. Both samples show very high FFA values of higher than

5% as allowed by the standard. This indicates that the fruitlets had been deteriorated as they were not immediately processed after stalk removal process. Also, during the cutting, the fruitlets were badly bruises as thus attacked by lipolytic enzyme and thus increases the FFA percentage and affected the oil quality. Several other studies also confirmed this finding as reported earlier [15]- [17].

Carotenoids are plant pigments responsible for yellowish to reddish hues in oil palm fruitlets. These pigments play an important role in plant health as well as and human health. Carotenoids can act as antioxidants in the human body. They have strong cancer-fighting properties and could be converted by the body to vitamin A as well anti-inflammatory and immune system benefits and associated with cardiovascular disease prevention. Based on Table 1 and Fig. 3, the result for the mean shows that Carotenoids concentration of Ripe FFB is 968.07 ppm and slightly higher than Unripe FFB at 927.37 ppm. These values are in the range mentioned by previous researcher [18]. However, based on statistical analysis using one-way ANOVA, is no significant difference between Ripe FFB and Unripe FFB in terms of Carotenoids concentration due to the significant value is $0.817 > \alpha = 0.05$. Thus, it can be concluded that there is no differences in Carotenoids concentration between different maturity level of oil palm. This is consistent with previous study [19], which showed that the ripe fruitlets had slightly higher Carotenoids compared to the unripe fruitlets.

4. Conclusions

From the findings in this study, it can be concluded that CPO of both Ripe FFB and Unripe FFB have almost same amount of Carotenoids content. The ripe fruitlets had slightly higher carotenoids than the unripe fruitlets, however it was not significant. For the FFA and DOBI although the results were not promising as compared to the standard which was basically due to longer handling time before sterilization. In the next experiment, the sample should be immediately processed after stalk removal. Since this scientific analysis has proven that the differences between two levels of maturity was not significant, it is important for the unripe bunches to be fully utilized to optimized profit. This result had strongly proven that unripe oil palm can be useful especially in extracting the Carotenoids and utilize it for health supplements product.

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