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Critical Chemical-Quality Assessment for the Oxidative Stability of Bulk Palm Oil in Indonesia

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ABSTRACT

The main objective of this study was to assess the quality of bulk palm oil from the point of production (and its distributors) using the critical factors of vitamin A stability and carotenoids (expressed as beta-carotene) in Indonesia. The specific objectives were to analyze the peroxide value (PV), acid value of free fatty acid (FFA) and carotenoids (expressed as beta-carotene) content of unfortified bulk palm oil in Indonesia. The study showed that the quality of initial bulk palm cooking oil, both at the level of manufacturers and distributors, was inconsistent; however, it was still in compliance with the Indonesian standard for cooking oil (SNI 7709-2012). The PV and FFA range of bulk palm cooking oil analyzed was 0-8.94 meq O_2 kg^{-1} and 0.06-0.23% respectively, and the range of carotenoids content (expressed as beta-carotene) was quite low, only 1.2-3.05 ppm, respectively. The results of this study could be used as the basis of vitamin A fortification in palm oil, since the stability of the fortificant in the oil would be affected by the initial chemical quality, especially its FFA and PV content.

Keywords: carotenoid content, free fatty acid, peroxide value, bulk palm oil

INTRODUCTION

Vitamin A fortification of cooking oil (vegetable oil) is currently an important strategy to lower the burden of vitamin A deficiency (VAD). Based on data from the food and agriculture organization of the united nations (FAO) it can be estimated that all cooking oil consumed in 75 developing countries is fortified to a level of 60 IU g^{-1} retinyl palmitate.

The Indonesian government has recently started to implement this strategy to address VAD in Indonesia. Cooking oil is potentially and possibly the best vehicle for vitamin A fortification in Indonesia because it is the second most consumed commodity after rice by more than 90% of the population. Theaverage consumption is >23 g cap^{-1} day^{-1} (more than 10 g of the minimum amount for fortification) and the average household usage for

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frying is 1-3 times (Martianto *et al*. 2005). Considering that the most common type of cooking oil purchased by both poor and non-poor households is bulk palm oil, this commodity was consequently determined as a vehicle for vitamin A fortification in Indonesia.

Although vitamin A can be uniformly distributed in oil and is easily absorbed from oil, the effectiveness of cooking oil fortified by vitamin A is affected by various factors. Among the most important factors is the stability of vitamin A in cooking oil during storage and the cooking process. A limited study was done in Makassar City during the pilot project of palm oil fortification under the KFI-JFPR project. The major findings of the study indicate that the turnover of oil from the producers to the household is relatively short, rangeing from 3-4 weeks; vitamin A retention in sub distributors was found to be 96.8% (after 1 week), in retailers 95.5% (after 3 weeks), and in households 93.6% (after 3-4 weeks). The Makassar study also found that different cooking conditions resulted in different vitamin A retention. For instance, vitamin A retention after three times of cooking of various snacks such as roti lasuna, roti kambu, jalangkote, and fried fish, were 63%, 58%, 51% and 60% respectively. On the other hand, stir fried kangkong and stringbeans caused much lower retention, as low as 37.3% and 31.0%, respectively (Martianto *et al*. 2007).

Other important factors which can affect vitamin A stability are the quality of initial cooking oil; especially its carotenoids content (expressed as beta-carotene); peroxide and acid values. These factors were absent in the Makassar study. In addition, besides its function as antioxidants protecting vitamin A, carotenoids have been known as pro-vitamin A. Consequently, the supply of vitamin A may also be provided by carotenoids; especially beta-carotene.

The specific objectives of this study were to analyze the peroxide value, acid value and carotenoids (expressed as beta-carotene) content of unfortified bulk palm oil in Indonesia. The results are expected to provide information for decision making related to the implementation of vitamin A fortification in palm oil in Indonesia.

MATERIALS AND METHODS

The materials used to analyze the chemical characteristics of bulk palm oil were glacial acetic acid p.a, chloroform p.a, potassium iodide p.a, starch indicator, natrium tiosulfate p.a, ethanol p.a, phenolphthalein indicator p.a, sodium hydroxide p.a, hexane p.a (Merck KGaA, Darmstadt, Germany) and distilled water. Laboratory tools for analysis were an analytical balance, a UV/VIS 2450 spectrophotometer (Shimadzu Corporation, Tokyo, Japan), micro pipettes, burettes, flasks, volumetric flasks, cuvettes and other glassware.

Sampling of Bulk Palm Oil

The analysis of chemical characteristics of bulk palm oil was done by collecting samples from producers (refineries) and main distributors located in Java (Jakarta, Bogor, Depok, Tangerang, Bekasi and Surabaya) and Sumatera (some regencies of North Sumatera, Padang-West Sumatera and Dumai-Riau).

In refineries, sampling of bulk palm oil was carried out at least 3 times, i.e. after production from three different batches and/or from the taps of storage tanks to the tanks of distribution trucks. Meanwhile, sampling at the main distributors was carried out maximum 2 days after

delivery from the producers. A total of 109 samples of bulk palm oil were collected once from producers and main distributors (Table 1).

Table 1 Sampling location and number of bulk palm oil samples

Sampling location	Number of samples
Producers in Java	12
Producers in Sumatera	44
Main distributors in Java	25
Main distributors in Sumatera	28
Total	109

Analysis of the Chemical Characteristics of Bulk Palm Oil

The parameters used to analyze the chemical characteristics of bulk palm oil are free fatty acid (FFA), peroxide value (PV) and carotenoid content (expressed as β-carotene).

Free Fatty Acid (AOCS 2003a)

The percentage of FFA in each sample was determined by the titration method. Briefly, 10 g of sample was poured into a flask and then mixed with 50 mL of 95% ethanol and 1% phenolphthalein indicator. The mixture solution was heated at maximum 22 °C on a steam bath for 3 minutes and 2-3 drops of 1% phenolphthalein indicator was added. The solution was then titrated against sodium hydroxide solution (0.01 N) until a permanent pink color persisted for at least 30 s. The FFA was calculated using the following formula:

$$\text{FFA (\%)} = \frac{\text{V X N NaOH X 25.6}}{\text{W}}$$

where:
V, volume NaOH (mL);
N, normality of standard NaOH;
W, sample weight (g).

Peroxide Value (AOCS 2003b)

The peroxide value in each oil sample was determined by using the titration method. 5±0.5 g of the sample was weighed and poured into a 250 mL erlenmeyer flask and 30 mL of glacial acetic acid-chloroform solution (2:3) was added and gently shaken. 0.5 mL saturated potassium iodide and 30 mL of distilled water were added into the mixture solution, shaken and kept in a dark room for 15 minutes. 2-3 drops of 1% starch indicator were added to the solution and was titrated by using sodium thiosulfate solution 0.05 N. The peroxide value of the sample was calculated using the following formula:

$$\text{Peroxide value (meq kg}^{-1}) = \frac{(V1-V0) \times N \times 1000}{m}$$

where:
V_1, volume sodium thiosulfate solution for oil sample (mL);
V_0, volume sodium thiosulfate solution for blank (mL);
N, normality of standard sodium thiosulfate;
m, oil weight (g).

Carotenoids (expressed as β-carotene)

The determination of β-carotenes was according Lin *et al.* (1995). A 10 g of sample was dissolved in hexane in a 25 mL volumetric flask and diluted to the mark. The solution was then transferred to a 1 mm cuvette and absorbance at 446 was measured using a Shimadzu 2450 UV/VIS Spectrometer that had been calibrated previously. The carotene content was expressed as ppm β–carotene and was calculated using the following formula:

$$\text{β-carotene (ppm)} = \frac{25 \times 383\ (a_s)}{100W}$$

where:
a_s, absorbance of the sample;
W, weight of the sample in gr;
Blank, hexane.

Processing and analysis of the palm oil data obtained were conducted using

descriptive quantitative statistics by describing or depicting the collected data.

RESULTS AND DISCUSSION

The PV and FFA range of bulk palm cooking oil analyzed was 0-8.94 meq O_2 kg^{-1} and 0.06-0.23% respectively, and the range of carotenoids content (expressed as beta-carotene) was quite low, i.e. only 1.2-3.05 ppm. In general, the quality characteristics of bulk palm oil measured in this study still met the requirement of the Indonesian standard for cooking oil (SNI 7709-2012) and Codex standard 210-199 (CODEX STAN, 2011). However, both values did not meet the recommended analytical standard for fresh frying oil (Refined-Bleached-Deodorised or RBD oil) (Gupta 2005) (Table 2). The profile of chemical characteristics (PV, FFA, carotenoids) of bulk palm oil of producers and distributors analyzed in this study are described below.

Peroxide Value of Bulk Palm Oil in Distribution Channels

Overall, the bulk palm oil samples of producers and distributors were consistent. The bulk palm oil of producers (n=56) had more varied PV than that of distributors (n=53). Samples obtained from producers in Java (n=12) contributed significantly to the wide PV distribution range of bulk palm oil of producers (Figure 1). It indicates that the quality of bulk palm oil of producers in Java was more consistent compared to that in Sumatera. This may be due to the inconsistent initial quality of crude palm oil (CPO) of producers (refineries) in Java. The freshness of CPO in the bulk tanks of producers in Java was varied. It is likely that the CPO goes through prolonged storage for as we know refineries of cooking palm oil in Java bring in the raw material of CPO from outside of Java. Prolonged storage or high temperature storage of crude oil can greatly affect the quality of the refined oil. Long-term storage of CPO can increase oxidation, free fatty acids, and nonhydratable phospholipids in the crude oil, resulting in poor-quality refined oil. Crude oil with a high peroxide value can be refined to meet the fresh oil analytical standards but can oxidize very rapidly during frying. Hydroperoxides in refined oil are very unstable and decompose into a series of aldehydes, ketones, hydrocarbons, alcohols and many more reaction products as the oil oxidation process continues. In reality, these reactions can continue during storage of the packaged product, as the oil in the product continues to break down via autoxidation and develops oxidized or a rancid flavor in the product (Gupta 2005).

Although it has a wide PV distribution range, the mean PV of bulk palm oil of producers in Java was significantly different than that of producers in Sumatera ($p<0.05$). The mean PV of bulk palm oil of producers in Java (1.14 meq O_2 kg^{-1}) was much lower than that of producers in Sumatera (3.33 meq O_2 kg^{-1}). Similar results were obtained for distributors in Java and Sumatera where the mean PV of bulk palm oil of distributors in Java (1.68 meq O_2 kg^{-1}) was lower than that of distributors in Sumatera

Table 2 The standard quality characteristics for fresh cooking oil

Quality characteristic	Maximum level		
	SNI 7709-2012	CODEX STAN 210	Analytical standard
Peroxide value	max. 10 meq O_2 kg^{-1}	up to 10 meq O_2 kg^{-1}	0.1 meq O_2 kg^{-1}
Free fatty acid	max. 0.3%	not defined	0.05%

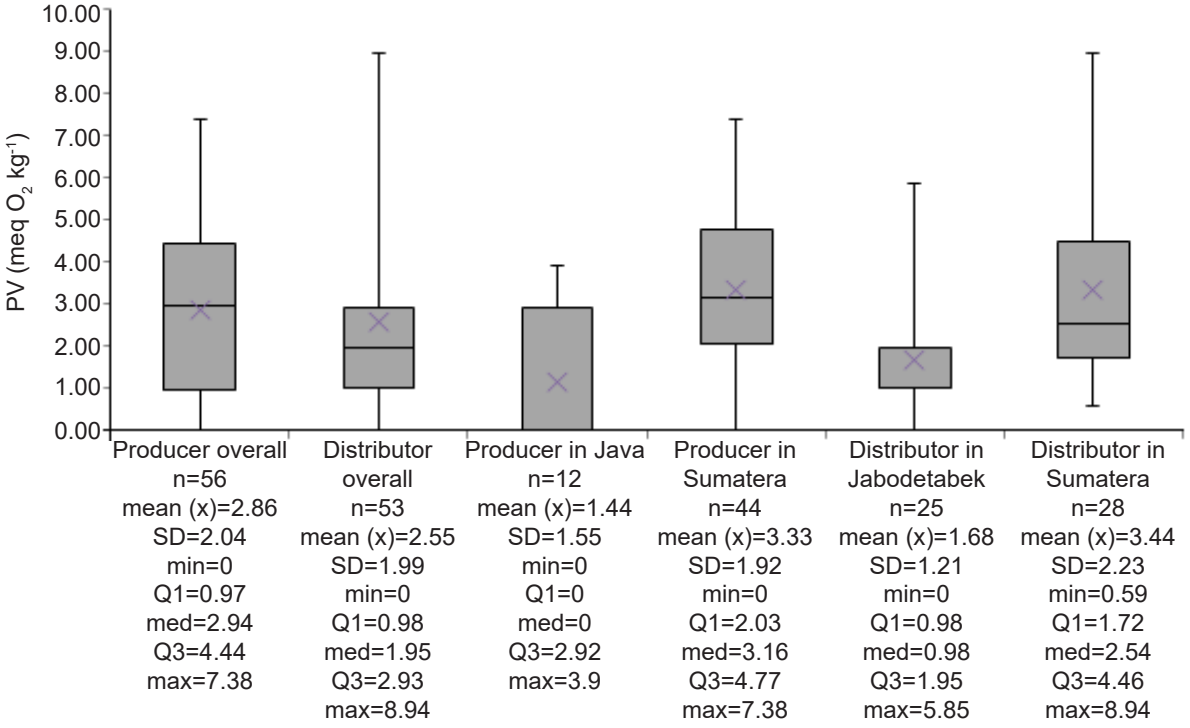

Figure 1 Profile of peroxide value of bulk palm oil in distribution channels.

(3.34 meq O_2 kg^{-1}). There was no significant difference between the mean PV of bulk palm oil of producers in Java and that of distributors in Java. The same t-test results were also obtained for the Sumatera area (Figure 1).

The PV range of bulk palm oil samples of producers and distributors was 0-7.38 and 0-8.94 meq O_2 kg^{-1} respectively. Both met the requirements of the Indonesian standard for cooking oil (SNI 7709-2012) and Codex standard for named vegetable oils (CODEX STAN 210-199), i.e. up to 10 meq O_2 kg^{-1}, but did not meet the recommended analytical standard (<1 meq O_2 kg^{-1}). If the oil contains high levels of PV>1, it will oxidize rapidly in the fryer (Gupta 2005). Even though the PV range of all bulk palm oil samples met the standard, the quality of vegetable oil (assessed by PV) prior to fortification has been shown to have a dramatic effect on the stability of retinyl palmitate (Andarwulan *et al*. 2014). Research has shown that when vegetable oil is oxidized through elevated levels of peroxides, it will significantly cause a loss of vitamin A (Andarwulan *et al*. 2014). Because of those reasons, a PV level of <2 meq kg^{-1} has been proposed as a key parameter at the time of production (Laillou *et al*. 2012). A low PV does not indicate that the oil is good; it only gives an indication (sometimes misleading) of the current state of oxidation of an oil sample and does not indicate the potential for oxidation (Frank *et al*. 2011).

Free Fatty Acid of Bulk Palm Oil in Distribution Channels

Overall, the bulk palm oil samples of distributors (n=53) had more FFA than that of producers (n=56). Half FFA value of samples of producers in Java had a wider range (0.09-0.18%) compared to that in Sumatera (0.06-0.12%). Yet again, it confirms that the initial quality of CPO of bulk palm oil production of producers in Java was varied compared to that in Sumatera.

The mean FFA of bulk palm oil of producers in Java was significantly different than that in Sumatera ($p<0.05$), which was higher in Java (0.12%) than that of producers in Sumatera (0.09%) (Figure 2). However, there was no significant difference between the mean FFA of bulk palm oil of distributors (0.14%) in Java and that of distributors (0.12%) in Sumatera ($p>0.05$). The mean FFA of bulk palm oil of producers in Sumatera was significantly different than that of distributors in Sumatera ($p<0.05$).

Overall, the FFA of bulk palm oil analyzed both of producers and distributors met the requirements of the Indonesia standard for cooking oil (SNI 7709-2012) and specifications set by PORLA, i.e. 0.25%. However, it did not meet the recommended analytical standard for frying oil (<0.05%). Cooking oil with FFA >0.05% indicates that it is produced from poor quality crude oil and the oil is not processed properly. The FFA of all palm oil samples met the standard and during the storage of palm oil, the rate of FFA formation is influenced by the amount of initial PV in the oil (Andarwulan *et al*. 2016). In this regard, PV is the critical quality factor for palm oil stability during storage.

Carotenoids of Bulk Palm Oil in Distribution Channels

Palm oil is the world's richest source of natural plant carotenoids in terms of equivalent retinol (pro-vitamin A) (Rodrigues-Amaya 1999; Edem 2002; Sudram *et al*. 2003). The mean carotenes of bulk palm oil of producers in Java (1.2 ppm) was not significantly different than that of producers (1.2 ppm) in Sumatera ($p>0.05$). In contrast, the mean carotene of bulk palm oil of distributors in Java was significantly different than that in Sumatera ($p<0.05$) i.e. the mean carotenes of bulk palm oil of distributors (1.33 ppm) in Java was lower than that of distributors (1.81 ppm) in Sumatera. A study on antioxidant composition including beta carotene in some vegetable oils also showed that

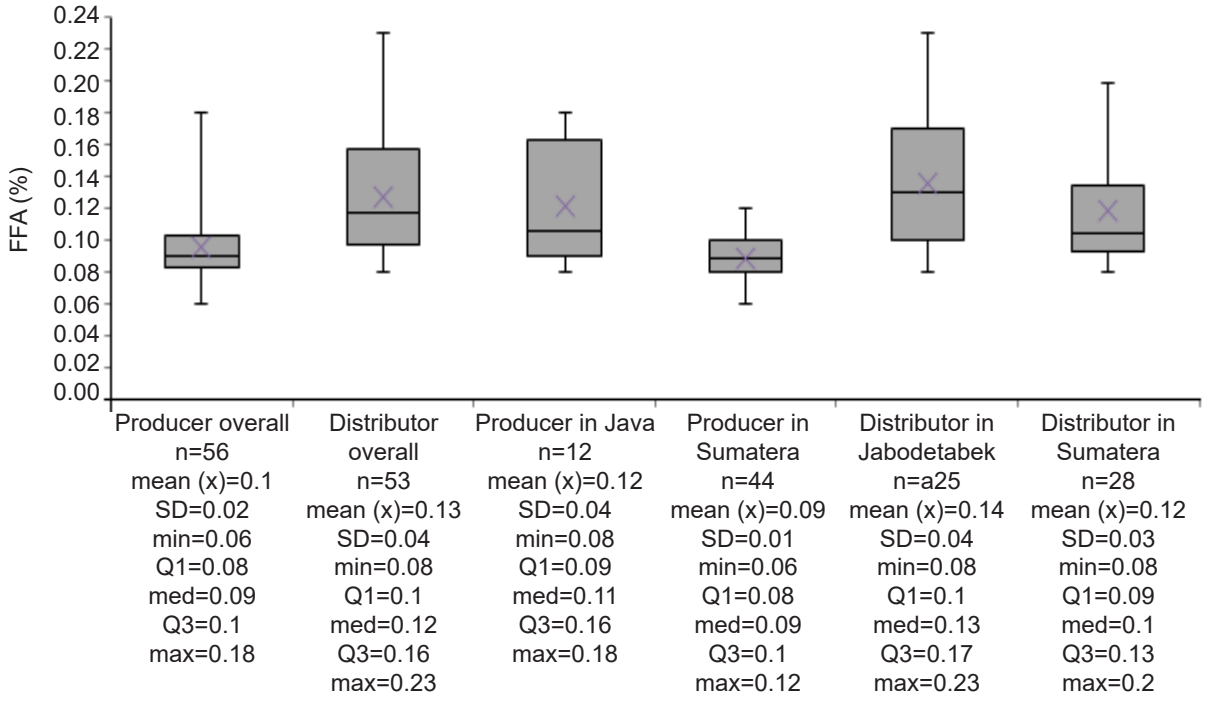

Figure 2 Profile of free fatty acid of bulk palm oil in distribution channels.

palm olein did not contain beta carotene (Dauqan *et al*. 2011). The low concentration of carotenes in bulk palm oil is due to the processing steps in palm oil refining (Figure 3).

The mean carotenes of bulk palm oil of producers was significantly different than that of distributors ($p<0.05$). Also, there were no significant difference between mean carotenes of bulk palm oil of producers in Java and distributors in Sumatera ($p<0.05$); the mean carotenes of bulk palm oil of distributors was slightly higher than that of producers. The similar t-test result was also obtained for the Sumatera area. Based on this result, the very low level of carotenoids in palm oil could not be used as a pro-vitamin A source.

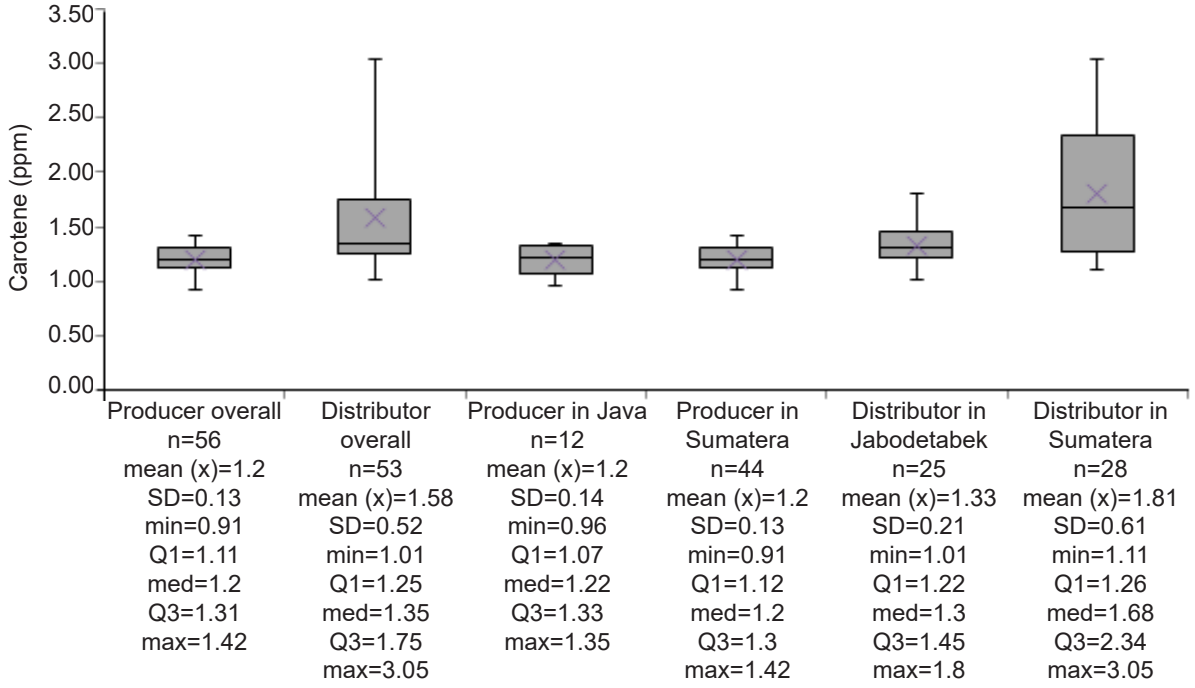

Figure 3 Profile of bulk palm oil in distribution channels.

CONCLUSION

The quality of bulk palm oil in Indonesia showed that the quality of initial bulk palm cooking oil, both of manufacturers and distributors had no clear pattern; however, it still complied with the Indonesian standard for cooking oil (SNI 7709-2012). The PV and FFA range of bulk palm cooking oil analyzed was 0-8.94 meq O_2 kg^{-1} and 0.06-0.23% respectively, and the range of carotenoids content (expressed as beta-carotene) was quite low, i.e. only 1.2-3.05 ppm.

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