Food quality assurance of crude palm oil: a review on toxic ester feedstock

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Abstract – Palm oil, the commodity produced mainly in Indonesia and Malaysia, is widely used for deep-frying of fast food and food derivatives. European and American markets of palm oil are affected by the concern of the toxicity potential from monochloropropanediol esters (MCPDE) and glycidyl ester (GE) that are undesirably produced from monoacylglycerol (MAG), diacylglycerol (DAG) and chlorine in refineries. Improvement of oil palm plantation, fruit harvest and oil extraction process in palm oil mills is necessary before the refinery process so that hydrolysis reactions that produce MAG and DAG and chlorine contamination can be minimized in crude palm oil (CPO). This review focuses on the quality control currently employed in the mills especially in managing free fatty acid (FFA) formation as the indicator of the hydrolysis reactions along with other quality control parameters and the reduction of chlorine content.

Keywords: monochloropropanediol / glycidyl esters / crude palm oil / food quality / food contaminant

1 Introduction

Palm oil industry is one of the sectors that contribute to the economy of many tropical countries. Two species of palm trees (Genus: Elaeis) are known: Elaeis guineensis and Elaeis oleifera. E. guineensis was mainly found in West Africa and was cultivated in Malaysia by British in 1870’s as an ornamental plant before being developed for commercial purposes in the earlier 19th century (Keong, 2017; Supriyono, 2018; MPOC, 2021). Meanwhile, E. oleifera is native to South and Central America. Indonesia, as the largest palm oil producer, supplied 57% of world palm oil production in 2019, followed by Malaysia (27%), Thailand (4%), Colombia (2%), Nigeria (1%) and others (8%) (Mundi, 2020). Factors that promote successful palm oil industries particularly in Indonesia and Malaysia include plantation areas, suitable climate and good management of research and development (Basiron and Weng, 2004).

Palm oil is produced, traded and consumed at large scale over the world, and supersedes production of other vegetable oils such as soybean oil, rapeseed oil and sunflower oil especially in food industries (Matthijs, 2007). According to Sambanthamurthi et al. (2000), its content of unsaturated and
A saturated fatty acids is well balanced with 39% oleic acid (monounsaturated), 11% linoleic acid (polyunsaturated), 44% palmitic acid, 5% stearic acid and 1% myristic acid, respectively, although not enabling to fulfill the recommended daily intake alone. Eighty percent of the market is for frying fast foods due to its stability for repeated cooking compared to most vegetable oils. The rest is as derivatives in food industries where strict regulations are imposed (Mba et al., 2015). Long time ago, palmitic acid content was perceived to have cardiovascular disease effect on body lipid profile prevalent to heart disease (“Joint WHO-FAO expert consultation on diet, nutrition, and the prevention of chronic diseases”, 2003). Further studies however found that palm oil has similar profile effect to monounsaturated oleic acid (Odia et al., 2015) and the study helped regain customer’s trust and market. Meanwhile, palm oil was found to contain toxic fatty acid monochloropropanediol esters (MCPDE) and fatty acid glycidyl esters (GE) (Bakhiya et al., 2011; Pudel et al., 2011; Craft et al., 2012; Ramli et al., 2015) although no evidence supports the claim (MPOB, 2014). The demand of many Western countries was influenced again by this concern.

General quality assurance of palm oil production to follow the standard food regulations begins at upstream processes. Food and Agriculture Organization (FAO) and World Health Organization (WHO) in codex committee on fats and oils, have standardized many key components (Nations and WHO, 2017). In particular, free fatty acid (FFA) from virgin oil or crude palm oil (CPO) for food purposes should not exceed 10 mg KOH/oil of acid value (approximately 5 wt%). FFA existence in the oil indicates that the oil hydrolysis reaction has occurred in the palm fruit in the presence of endogenous and microbial lipase or sterilizing steam, and by-products like diacylglycerol (DAG) and monoacylglycerol (MAG) are simultaneously formed. They are the raw materials for MCPDE and GE syntheses in the presence of chlorine in refinery via 3 synthesis routes as summarized in Figure 1.

Chlorine term used in most of MCPDE and GE papers generally refers to free radical chlorine and all kind of chlorine-contained chemicals, either organic or inorganic substances. To date, no limitation of chlorine content in CPO is imposed by the Codex committee in spite of chlorine mainly coming from CPO. Fertilizers (Afandi et al., 2016), pesticides (Muhamad et al., 2010), soil minerals and treated raw water are the potential sources of chlorine.

Many papers on palm oil have been discussing on the production in perspective of economic sustainability (Lim et al., 2015), processing, characterization and utilization in food industries (Mba et al., 2015). This review discusses findings from various studies and actions taken by industries and relevant authorities in implementing initiatives for improving CPO quality in mills for safe food use, particularly on the reduction of DAG, MAG and chlorine as the feedstock for MCPDE and GE formation. Not many reports were unfortunately published in high impact journals even though they are peer-reviewed and most of the publications in English are from Malaysia. As the impact of palm oil to lipid supply in many food industries is significant, this review perhaps deserve such a high-ranking publication.

2 Fruit harvest and milling process

Ripe palm fruit is characterized by a reddish orange colour and a bunch of matured palm fruits usually weighs around 10 to 40 kg. Each fruit contains a nut that is made up of kernel (endosperm) enclosed by the hard, woody shell (endocarp). This nut is surrounded by fibrous, oily pulp (mesocarp) and is covered by thin-layered skin (exocarp) as shown in Figure 2. Two weeks after anthesis (WAA), the fruit usually starts to develop and differentiate before the oil accumulates in the mesocarp between 16 WAA and 21 WAA (Oo et al., 1985). According to the researchers, the growth of the palm fruits can

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**Fig. 1.** Schematic diagram of the route of MCPDE and GE formation (Gao et al., 2019).
be classified into three stages, from the oil deposition until the fully oil occupied mesocarp. Upon the final stage, the fruit matures and the bright yellow mesocarp results from the high content of carotene in the oil (Rangkuti et al., 2018). The three stages of palm fruit growth are summarized in Table 1.

Fresh fruit bunch (FFBs) harvesting process is performed manually by the field workers during regular field visits using sickles attached to pole ends, and oil palm trees and ground are cleaned. The FFBs are then transported to mills for extraction within no more than 24 h to avoid oil loss due to the oil hydrolysis reaction.

Generally, palm oil mills involve five basic unit operations: FFB sterilization, FFB stripping, digestion, oil extraction and oil clarification. FFBs are initially pre-treated in a high-temperature sterilization chamber to deactivate the lipolytic enzymes and loose fruits (Subramaniam et al., 2010). Both temperature and residence time are closely controlled; the FFBs are steamed at 40 psig and 140 °C for 70 to 90 minutes according to Sivasothy et al. (2005). The use of high temperature causes the cell wall to rupture and subsequently increase the oil yield (Kasmin et al., 2016). However, over-sterilization may cause other reactions such as oxidation and poor bleachability of the final product which affects its quality (Junaidah et al., 2015).

The sterilized FFBs are then sent to a stripper, which is usually a rotary drum thresher, to separate oil palm fruitlets from stalks and bunches. The separated empty fruit bunches (EFBs) are sent back to plantations as fertilizer, or to boiler as energy process, some of these components are also captured following the pressing process is essential to retain the desirable quality of CPO. The liquid extract is now a mixture of oil, water and vegetable impurities such as cell debris and fibrous materials. Clarification following the pressing process is essential to remove suspended solids from CPO. A vibrating screen is usually used in between, to filter the extract, leaving behind debris. To enhance the process, the CPO is further clarified by gravity in a settling tank followed by a centrifugation step. The decanted CPO is then transferred to a vacuum dryer for moisture removal before it is stored in appropriate containers for export or sent off to the refinery. Table 2 summarizes the purposes of each unit operation in palm oil mills.

The performance of the extraction process, the oil extraction rate (OER), is determined from the mass ratio of final CPO product to fresh fruit bunch, FFBs, as shown in equation (1).

\[
\text{OER} = \frac{\text{Mass of extracted oil}}{\text{Mass of a fresh fruit bunch (FFBs)}} \quad (1)
\]

3 Issue with CPO quality

CPO is a complex mixture of chemicals, 95–99% of triacylglycerol (TAG), DAG, MAG, and FFA. The rest (1–5%), comprises carotenoids, tocopherols, tocotrienols, sterols, phosphatides, aliphatic alcohols and other non-acylglycerol components as shown in Figure 4 (Kumar and Krishna, 2014). Carotenoids, tocopherols and tocotrienols are important in stabilizing the CPO (Nagendran et al., 2000).

CPO normally contains 500 to 4000 ppm of carotenoids. 37% and 50% of them are α- and β-carotene, respectively, which are acceptably high as a vitamin A source (Nagendran et al., 2000): 15 times that of carrots and 300 times that of tomatoes, and as antioxidant and anti-carcinogenic agents, and against cardiovascular diseases (Odia et al., 2015; Santos et al., 2015). Due to light colour preference of the final product, the carotenoid content is reduced during the refinery process. Other two beneficial components are tocopherols and tocotrienols, which provide nutritional properties as vitamin E and similarly act as antioxidant. The presence of the tocopherols and tocotrienols also gives CPO the ability to withstand at high temperature, and thus make it suitable to be used as cooking oil (Okolo and Adejumo, 2014). However, during the refinery process, some of these components are also lost leaving the remaining 69% in palm oil, 76% in palm stearin and 72% in palm olein (Sambanthamurthi et al., 2000).
Physically, CPO has a semi-solid nature at room temperature and may be fractionated into two major fractions based on the acylglycerol crystallization properties (Kellens et al., 2007). At the operation temperature, some of the acylglycerols will solidify and separate from the remaining liquid portion forming two different fractions. The solid fraction with high melting point between 48–50°C is called palm stearin while the liquid faction with low melting point between 18–20°C is known as palm olein (Jacobsberg and Ho, 1976).

### Table 1. Growth of palm fruits (Oo et al., 1985).

<table>
<thead>
<tr>
<th>Stage</th>
<th>Parts of individual palm fruit</th>
<th>Estimated week after anthesis (WAA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First stage</td>
<td>Endosperm: Starts of oil deposition</td>
<td>– Fully formed</td>
</tr>
<tr>
<td></td>
<td>Endocarp: Firm</td>
<td>– Easily sliced</td>
</tr>
<tr>
<td></td>
<td>Mesocarp: Cream-colour</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Exocarp: Greenish-yellow colour</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12–13</td>
</tr>
<tr>
<td>Second stage</td>
<td>Endosperm: Starts of oil deposition</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Endocarp: Hard</td>
<td>– Greenish-yellow colour</td>
</tr>
<tr>
<td></td>
<td>Mesocarp: Deep brown colour</td>
<td>– Deep red at outer tip</td>
</tr>
<tr>
<td></td>
<td>Exocarp: Non-oily</td>
<td>– Orange towards the stalk</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16–17</td>
</tr>
<tr>
<td>Third stage</td>
<td>Endosperm: Bright yellow colour</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Endocarp: Bright waxy reddish orange</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mesocarp: Filled with oil</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Exocarp: Greenish-yellow colour</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20–21</td>
</tr>
</tbody>
</table>

### Table 2. Basic unit operations in palm oil mills.

<table>
<thead>
<tr>
<th>Unit operation</th>
<th>Purposes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFB sterilization</td>
<td>– To deactivate lipolytic enzyme activities.</td>
<td>(Kasmin et al., 2016; Owolarafe et al., 2008; Sivasothy et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>– To soften the fruit pulp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– To ease the cracking process by heating and partial dehydration of the nuts.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– To coagulate the protein in the oil-bearing cells: prevents formation of colloidal complexes and facilitates oil clarification.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– To hydrolyze the mucilaginous materials: facilitates oil clarification.</td>
<td></td>
</tr>
<tr>
<td>FFB stripping</td>
<td>– To separate mesocarp fibre and nut.</td>
<td>(Ebongue et al., 2006)</td>
</tr>
<tr>
<td>Digestion</td>
<td>– To destroy exocarp.</td>
<td>(Hosseini and Wahid, 2015; Owolarafe et al., 2008; Poku, 2002; Syahro et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>– To digest palm mesocarp into homogeneous mash.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– To enhance the oil cell breakdown process.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– To reduce the oil viscosity.</td>
<td></td>
</tr>
<tr>
<td>Oil extraction</td>
<td>– To extract oil by pressing process.</td>
<td>(Subramaniam et al., 2010)</td>
</tr>
<tr>
<td>Oil clarification</td>
<td>– To yield the pure oil.</td>
<td>(Subramaniam et al., 2010)</td>
</tr>
<tr>
<td></td>
<td>– To remove water and non-oily solid.</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 3. Percentage of total oil loss in different samples of waste (Zulkifli et al., 2017).](image1)

![Fig. 4. Composition of CPO (Kumar and Krishna, 2014; Bahadi et al., 2016; Japir et al., 2017).](image2)
Both palm stearin and palm olein are commonly found in daily food products such as shortenings and cooking oils, respectively (Kadandale et al., 2019). CPO is an important raw material for food industry, oleochemicals and biodiesel that will determine its required quality. The quality is highly dependent on the mill practices, storage and handling of CPO. Figure 5 shows the common parameters used in assessing the CPO quality.

3.1 Free fatty acid

Existence of FFA indicates the formation of MAG and DAG, the reactants for undesired MCPDE and GE formation in refineries, through any of three consecutive hydrolysis reactions of acylglycerols as shown in Figure 6. Hydrolysis speed of DAG and MAG was about 30 times higher than that of TAG hydrolysis in the presence of pancreatic lipase (Mattson and Beck, 1955) indicating that the latter is the limiting step. FFA presence will generate rancidity, and deteriorates palm oil for food consumption (Sambanthamurthi et al., 2000). It is usually assessed and termed as acid value in grading and determining the commercial pricing of CPO (Cadena et al., 2013). FFA should be maintained as low as possible in order to prolong the lifespan of the oil. FFA content is usually around 3–4% in CPO (Kumar and Krishna, 2014). The acceptable limit of FFA content for food application is 5% (Bahadi et al., 2016), and CPO with more than 5% FFA is suitable for other applications such as in the manufacture of biodiesel (Hayyan et al., 2013). Other components in CPO that can generate rancidity and deteriorates of the oil are trace metals, moisture and non-acylglycerol impurities (Nagendran et al., 2000).

FFA content is basically determined by using titration method where sodium hydroxide or potassium hydroxide and phenolphthalein are used as standard solution and indicator respectively (Bahadi et al., 2016; Japir et al., 2017; Ramli et al., 2017; Tan et al., 2017). FFA content may increase due to the enzymatic activities where the presence of endogenous and microbial lipases in the CPO induces the formation of FFA by hydrolysis reaction of the TAG. As a result, more FFA, DAG and MAG will be produced and eventually increases the FFA content of the CPO (Japir et al., 2017). FFA will reduce the cooking oil production in refineries while DAG and MAG are the key feedstock in forming MCPDE and GE in the presence of chlorine. Determination of FFA is important not just due to the loss of oil product but also decreasing the food safety (Gao et al., 2019). Previous studies had found that the lipase activities are highly related to the ripeness level, fruit bruising and post-harvest storage. Lower FFA level was found in palm oil fruits at 20 WAA compared to 21 WAA, which was attributed to different ripeness (Oo et al., 1985; Sambanthamurthi et al., 1991). It was reported in another study conducted by Tagoe et al. (2012) that high level of FFA was found in the palm oil extracted from the over-ripe fruit. This is in agreement with the research done by Morcillo et al. (2013) where the increase of FFA was observed when the harvest day was delayed. Detachment due to chopping or over-ripeness and harvested FFBs left for many days will also increase FFA (MPOB, 2015; Teng et al., 2015).
Table 3. Analysis of endogenous lipase activity.

<table>
<thead>
<tr>
<th>Type</th>
<th>Method of assaying lipase</th>
<th>Substrate</th>
<th>Temperature</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder obtained from maceration of mesocarp tissue with liquid nitrogen</td>
<td>Cold induction assay</td>
<td>Glycerol ([^{14}C]) trioleate</td>
<td>Optimum temperature: 45°C Active at 20–50°C</td>
<td>Optimum pH: 9–10 Not active below 7.0 and above 11.5</td>
<td>(Cadena et al., 2013)</td>
</tr>
<tr>
<td>Oleic acid released from emulsion</td>
<td>Chemical extraction</td>
<td>Olive oil</td>
<td>Maximum at 5°C</td>
<td>–</td>
<td>(Henderson and Osborne, 1991)</td>
</tr>
<tr>
<td>in vitro</td>
<td>Chemical extraction</td>
<td>Glycerol ([^{14}C]) trioleate</td>
<td>Maximum at 18°C</td>
<td>–</td>
<td>(Sambanthamurthi et al., 1995)</td>
</tr>
<tr>
<td>Powder obtained from maceration of mesocarp tissue with liquid nitrogen</td>
<td>Cold induction assay</td>
<td>Glycerol ([^{14}C]) trioleate</td>
<td>Maximum at 5°C</td>
<td>–</td>
<td>(Cadena et al., 2013)</td>
</tr>
<tr>
<td>in vivo</td>
<td>Cold induction assay</td>
<td>–</td>
<td>No FFA detected at room temperature or higher (45°C)</td>
<td>–</td>
<td>(Henderson and Osborne, 1991)</td>
</tr>
</tbody>
</table>

Besides, the over-ripe fruit is more susceptible to the bruising and microbial contamination due to the softening of the mesocarp.

Fruit bruising upon harvesting, transportation and moving from the lorry to the hopper promotes the lipase activity and consequently forms FFA (Krisdiarto and Sutiarso, 2016). Approximately 2.88% of the fruitlets in a freshly harvested bunch are bruised and subsequently FFA increases to 30.74% after crushing (Sivasothy and Halim, 2000). Hadi et al. (2009) reported that the bruise category has significant effect towards the development of FFA. The minor bruise and unbruised fruit showed no significant difference in the amount of FFA produced while high FFA was produced in both cases of moderate and major bruise. These results are supported by Ali et al. (2014) who found a significant difference of FFA in both major and minor bruised fruits after two-hour storage. For a bruised palm fruit, it is possible for FFA content to be as high as 8% to 10% in 40 minutes, while for the unbruised fruit the FFA content may increase only 0.2% in 4 days (Norris, 1979; Ekwenye, 2006).

The formation of FFA increases proportionally with the time hence, the length of storage of the FFBS prior to sterilization process also contributes to the high level of FFA content (Ali et al., 2014). Based on the research done by Kumaradevan et al. (2015), the FFA content had not attained the allowed limit of 5% of FFA when the FFBS were stored longer than 72 h after harvest. Meanwhile, it was reported in another study that all the FFBS did not meet the standard required, except for the fresh harvested bunches (Basyuni et al., 2017). A study was done by Hadi et al. (2009) to investigate the effect of time interval between stripping and oil extraction towards the formation of FFA. The delay period of 4 to 12 h however did not portray a significant effect in the FFA formation. According to Berger (2006), it is possible to produce CPO with FFA level below than 2.5% by quick harvest to reduce the over-ripe fruitlets. Besides that, the effect of bruise during harvesting is minimized by immediate sterilization using cages to reduce delay time (Berger, 2006).

3.1.1 Lipase activity

Endogenous lipase activities were assayed and studied under several conditions as summarized in Table 3. The activity is genotype-dependent (Sambanthamurthi et al., 2000; Cadena et al., 2013), E. guineensis showing higher lipase activity than E. oleifera. Previous study showed around 52.7%, 32.9% and < 0.6% FFA were recorded for E. guineensis, the hybrid of E. guineensis \( \times \) E. oleifera, and E. oleifera respectively (Cadena et al., 2013). According to Sambanthamurthi et al. (1991), maximum lipase activity in palm fruit was observed at 18°C for in vitro assay and at 5°C for in vivo assay, respectively. This statement was contended by who reported that the lipase in the palm fruit (in vivo) is sensitive to chilling inactivation at 8°C. The lipase activity was found to continuously decrease after cooling in the refrigerator. The study was later explained by Sambanthamurthi et al. (1995) that the reduction of lipase activity was due to the remarkable increase of FFA in the palm oil. Further study by Cadena et al. (2013) agreed that the lipase activity was strongly activated at low temperature of 5°C for in vivo assay.

Optimum pH of palm lipase activity located in the oil body fraction can be obtained at 7.5 (Sambanthamurthi et al., 2000). Based on the study conducted by Ebongue et al. (2006), the activity was not detected below pH 7.0 and above pH 11.5 of palm oil. While lipase activity is deactivated at acidic and strongly basic conditions, it is stated that lipase enzyme is only stable in a hydrophobic environment and will lose its activities in polar environment (Sambanthamurthi et al., 2000).

High possibilities of lipase activity are originated from bacteria and fungi (exogenous lipase). Under suitable growth conditions including carbon and nitrogen sources, temperature, pH and moisture content, the microbes undergo fermentation process and release lipase as one of the products (Muthumari et al., 2016). Factors that favour the multiplication of the microorganisms include contamination of water or soil in the plantation, improper storage of FFBS and delayed processing time (Tagoe et al., 2012). Besides, the over-ripe palm fruit is...
more susceptible to high lipase activity since the fruit is easily bruised and further contaminated by the microbes. The activity of exogenous lipase was studied by Tombs and Stubbs (1982) and higher FFA content was found at the bruised edge of the fruits compared to middle part. The researchers explained that contamination occurred as the microbes started to penetrate via the bruise. Tagoe et al. (2012) in his study stated that various species of microorganisms were identified on the palm fruits but most of them would be eliminated throughout the oil extraction process.

Other than enzymatic lipolysis, the reaction of hydrolysis in palm oil may also be caused by the autocatalysis due to the presence of water in the fruit, the second needed liquid phase. In order for autocatalytic hydrolysis to proceed, the water must be present in significant amount and the reaction rate will be depending on the temperature, moisture content and initial FFA concentration (Sambarthamurthi et al., 2000). It was reported that the moisture of palm fruits decreased as the post-harvest storage time increased which could probably explained due to autocatalysis reaction, and also enzymatic hydrolysis (Tagoe et al., 2012). This type of hydrolysis reaction really occurs in the sterilization where plenty of water in the form of steam is used to kill microbes and fungi (Junaidah et al., 2015). There is high possibility for the microbial contamination and autocatalytic hydrolysis to occur at moisture content above 0.2% (Albert and Astride, 2013).

### 3.2 Other quality assessment

Quality of CPO is also evaluated through other parameters such as peroxide value (PV), anisidine value (AV), iodine value (IV), moisture and impurities (M&I), deterioration of bleachable index (DOBI) and colour. Some of them are indirectly related to above discussed FFA, MAG and DAG formation.

PV is the parameter used to estimate the oil spoilage especially in cooking oils. PV, which is expressed as milli equivalent of peroxide per 1000 g of the material, is a determination of the oxidized products from the lipid peroxidation process where the unsaturated fatty acids, regardless of FFA or acetylgllycerols, undergo a chain reaction mechanism at favourable conditions such as the presence of oxygen, high temperature or moisture contents and produce peroxides. In the analysis, the oil will be dissolved in solution of acetic acid and chloroform, and left in saturated potassium iodide for further reaction. The free iodine is then titrated with sodium thiosulfate solution (Ekwenye, 2006; Ngassapa et al., 2012; Tan et al., 2017; Wahab et al., 2017). Ngassapa et al. (2012) who studied the stability of Tanzania traditionally processed oils and their blends, found that vegetable oils such as palm oil, sesame oil and sunflower oil showed poor stability upon heating at high temperature through the high PV. According to Merwe et al. (2003), PV however may not be a reliable indicator for the degree of oxidation of palm oil. Long-term storage of the oil gave a trend of decreasing PV, which can lead to a false conclusion (Augustin et al., 2015; Merwe et al., 2003). This can be explained due to the increase of FFA (Paradiso et al., 2010) and conversion of peroxides into the secondary oxidation products (Ariffin, 2001). These findings can be supported by Faridah et al. (2015) who studied palm oil quality used for frying fish. The researchers had repeatedly used the palm oil to fry for nine times at 180°C for 15 minutes. It was found that the PV had increased until its maximum on third frying and decreased afterwards. On the other hand, the extraction methods and storage practices could affect the oxidation of the CPO through the presence of metals (Akusu et al., 2000; Wahab et al., 2017). Besides of contamination by metal wear of the equipment, the natural level of metals in CPO was also reported in the range of 0.5 to 1.0 ppm for iron and 0.01 to 0.18 ppm for copper (Chong and Gapor, 1983).

Due to the unstable transitory products, the peroxides further oxidize to form aldehydes and ketones that are responsible for the rancid smell and test of the oil (Ariffin, 2001; Albert and Astride, 2013). These secondary oxidized products are measured as AV based on the absorbance of solution of oil and a solvent at 350 nm (Xu et al., 2014). Based on the research done by Yoshida et al. (1992), AV was significantly affected by the presence of FFA. The researchers had studied the AV of the oils and found that the FFA with shorter carboxylic chain had faster oxidation rate. According to Xu et al. (2014) who investigated on oxidative stability of edible oils under continuous frying conditions, palm oil showed a moderated change in AV compared to peanut oil and camellia oil. Metal, temperature, light and oxygen, may also induce the oxidation reaction besides polyunsaturated fatty acids in the oil (Xu et al., 2014). Instead, the oxidation products can be measured as total oxidation value (TOTOX) which includes both primary and secondary oxidation products. While a study conducted by Chew et al. (2018) includes the TOTOX value, others studies on MCPDE and GE have presented the PV and AV separately (Aniolowska and Kita, 2015; Wong et al., 2017).

IV is the number of grams of iodine consumed by 100 g of fats. The parameter is used to determine the unsaturated fatty acids or C=C double bonds in the oil by reacting with iodine compound where high IV indicates high unsaturated-fatty acid content in the oil. It is usually analysed by using Wijs method and further titrated with sodium thiosulfate (Ngassapa et al., 2012; Bahadi et al., 2016; Japir et al., 2017; Ramli et al., 2017). However, this analysis is not related to the elimination of MCPDE and GE as their formation is not affected by presence of double-bond carbon in the aliphatic chain of FFA (Tarmizi et al., 2019).

M&I is another important criterion in grading the CPO quality which has a critical limit at 0.25% based on the standard by Malaysian Palm Oil Board (MPOB) (Berger, 2006; Bahadi et al., 2016). The parameter is analysed by measuring the oil sample weights before and after drying in the oven. The difference in weight will be recorded after constant weight of the dried sample is achieved (Tagoe et al., 2012; Ramli et al., 2017). Water is known as a catalyst for many chemical degradation reactions especially hydrolysis reactions thus excessive moisture content will be harmful to the oil and fat products. High M&I reading will probably increase the process loss as the water will be converted to water vapour and removed from the refinery plant. According to Tagoe et al. (2012) who studied on factors influencing the CPO quality at the mills, M&I is one of the sources that favour contamination of microbes towards the CPO. According to the researchers, moisture content is positively correlated with water activity (aw) whereby the requirement of aw for growth of bacteria and
Table 4. Parameters used to identify the CPO quality.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Purpose</th>
<th>Correlation with good CPO quality</th>
<th>Allowable limit</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFA content</td>
<td>Determination of the FFA content. Yield will be reduced when FFA content is high.</td>
<td>Low</td>
<td>&lt; 5.0%</td>
<td>(Arifin, 2001; Halim and Ngn, 2001; Nations and WHO, 2017)</td>
</tr>
<tr>
<td>PV</td>
<td>Determination of the oxidized products from the lipid peroxidation process.</td>
<td>Low</td>
<td>&lt; 2.0 meq/kg</td>
<td>(Arifin, 2001; Halim and Ngn, 2001; Malaysian Standard, 2007)</td>
</tr>
<tr>
<td>AV</td>
<td>Determination of the secondary oxidized products from the lipid peroxidation process.</td>
<td>Low</td>
<td>&lt; 5.0</td>
<td>(Arifin, 2001; Malaysian Standard, 2007)</td>
</tr>
<tr>
<td>IV</td>
<td>Determination of the unsaturated fatty acids or C=C double bonds.</td>
<td>Low</td>
<td>50.1–54.9</td>
<td>(Ekwenye, 2006; Malaysian Standard, 2007; Ramli et al., 2017)</td>
</tr>
<tr>
<td>M&amp;I</td>
<td>Determination of the moisture and impurities.</td>
<td>Low</td>
<td>&lt; 0.25%</td>
<td>(Arifin, 2001; Bahadi et al., 2016; Halim and Ngn, 2001)</td>
</tr>
<tr>
<td>DOBI &amp; colour</td>
<td>Determination of the numerical ratio of the UV absorbance of carotene to the UV absorbance of oxidative products.</td>
<td>High</td>
<td>&gt; 2.3</td>
<td>(Arifin, 2001; Halim and Ngn, 2001; Malaysian Standard, 2007)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Determination of chlorine content. Chlorine will be involved in MCPDE and GE formation.</td>
<td>Low</td>
<td>&lt; 2 ppm</td>
<td>(Kadir, 2019)</td>
</tr>
</tbody>
</table>

fungi are 0.9 and 0.7, respectively. Tagoe et al. (2012) had further stated that the presence of M&I in CPO might be caused by the methods of processing. This is supported by Akusu et al. (2000) who studied on effect of extraction methods on the stability of CPO whereby the CPO extracted by applying digestion prior to extraction gave higher M&I content compared to that of without digestion. According to Basyuni et al. (2017) who investigated the effects of FFB storage on the physicochemical properties of palm oil, freshly harvested bunches indicated the lowest M&I and increased above the standard requirement after 7 days of storage. Other than damaged outer layer, the accumulation of both dirt and mould could be seen on the surface of the FFBs (Basyuni et al., 2017).

Another parameter used to identify the CPO quality is by a numerical ratio of the UV absorbance of carotene (446 nm) to the UV absorbance of oxidative products (269 nm) or so-called DOBI. Kasmin et al., 2016; Tan et al., 2017; Wahab et al., 2017. Although the carotene is highly beneficial for human health, it has to be removed due to the susceptibility to some chemical reactions at high temperatures and light yellowish colour preference of consumers. Arifin, 2001. The bleaching process will remove organic compounds such as carotenoids, xanthophylls, chlorophyll and their degradation products and impurities, trace metals and high molecular oxidative components from the oil thus improving the colour and taste (Okolo and Adejumo, 2014). According to Jusoh et al. (2013), DOBI was highly related to the temperature and time in which over-sterilization will cause high oxidation risk and poor DOBI of the CPO. Residence time in the sterilizer however showed more significant effect as compared to temperature Jumaidah et al., 2013. DOBI and carotene content can also be affected by the length of storage time. Based on the research done by Basyuni et al. (2017), after 28 days of harvesting, the oil extracted showed a decreasing trend of DOBI and carotene content. This can be supported by a study on the effect of ripeness level of the FFBs on the DOBI where DOBI value was observed to decrease as the FFBs ripen (Rangkuti et al., 2018). It was further explained due to higher carotene content in the over-ripe fruits compared to ripe and under-ripe fruits. DOBI value indicates the freshness of the fruit similar to AV.

Chlorine in CPO comes from several sources in the upstream process of palm oil production. Besides chloride fertilizer use in plantation Afandi et al., 2016 the content of the soil also contributes chloride content in oil palm tree and fruit Chung, 2018. A lot of raw water is used in the extraction process and in many palm oil mills it is treated by using chlorine gas and hypochlorites of sodium or potassium (Menon, 2017). Chlorinated water will be in contact with oil chlorination, and GE formation. Chlorine will be involved in MCPDE and GE formation.
In the research of oil productivity in oil palm germplasm type tenera by Krualee et al. (2013), there are positive correlations between oil production with the production of bunches, bunch weight, fruit to bunch ratio and pulp (mesocarp) to fruit ratio. Another study conducted by de Almeida Rios et al. (2018) showed similar results for the germplasm type dura. Meanwhile, in term of stability towards the bacterial and fungal deterioration, tenera is more stable compared to dura (Ekwenye, 2006).

During nursery, the plants are grown in polyethylene bags until 10 to 12 months under close supervision before being field-planted (Muhammad et al., 2010). Two objectives of nursery stage: to ensure the plants are getting sufficient nutrients and protection from the pests. In the plantation field, the spacing between each palm trees is crucial as it may contribute to Basal Stem Rot (BSR) disease, a disease that causes a destruction of basal tissue of the plant and affect palm oil production (Azahar et al., 2011).

Chemical treatment and fertilizers are important to ensure the health of the oil palm tree. Chlorine in the fruit is mostly from pesticides and herbicides such as Diuron (Muhammad et al., 2010), 2,4-D (Kuntom et al., 2007), Aldrin, Endrin, δ-BHC, 4-DDT, Methoxychlor and Endosulfan (Kuntom et al., 2007; Sharip et al., 2017). Reducing their use decreased the cost while the same yield of oil palm fruits remained for 2 years (Darras et al., 2019).

4.2 Harvesting stage

Raw material quality in palm oil processing depends on the ripeness standard of the fruits and feed passing to the digester. The ripeness of palm fruits is particularly related with the FFA content whereby as the fruits ripe, higher FFA will be produced (Oo et al., 1985; Sambanthamurthi et al., 1991; Tagoe et al., 2012; Morcillo et al., 2013). Meanwhile, minimizing dirt on the feed (FFBs) will reduce the probability of the metal wear in the upcoming processes and thus avoid the contamination by iron. Harvesting is thoroughly done by the plantation workers to ensure the appropriate ripeness level and minimal fruit bruising. Minimizing the bruising is one of the proposed improvements of the process of fruit picking and delivery (Menon, 2017) as was directly outlined in standard operating procedures (MPOB, 2015). This procedure is indirectly emphasized in sustainability standards such as Malaysian Sustainable Palm Oil (MSPO) and Roundtable Sustainable Palm Oil (RSPO) (Lim et al., 2015). It is a critical process as the ripeness level and fruit bruising may affect the final product quality through FFA content, DOBI value and colour. The workers are usually guided, well trained and knowledgeable regarding the ripeness standard as regulations are enforced to ensure ripe FFBs are harvested (Hassan and Mohammad, 2005; MPOB, 2007). Natural indicators commonly used to determine the appropriate time to harvest are colour appearance of fruits and number of loose fruits detached (Kassim et al., 2011). It is the roles of field managers to ensure the ripeness of FFBs and manage appropriate harvesting intervals so that only right bunches are picked. The FFBs are then transported to mills for extraction within not more than 24 h to avoid oil loss due to the hydrolysis reaction. Depending on the ripeness level of the oil palm fruits, the oil content is

4 Current Quality Control

As an important resource for human food industries, palm oil quality is controlled by government and palm oil private sectors by implementing systematic assurance systems that follow international standards such as Hazard Analysis and Critical Control Points (HACCP), ISO 9001 and Good Manufacturing Practices (GMP) (MPOB, 2007; Nazir et al., 2012). Codex international food standard was introduced by the FAO and WHO to provide guidelines, codes and practices in order to protect health of the community and to ensure the fair trade practices (Nations and WHO, 2017). Indonesian Sustainable Palm Oil (ISPO), Malaysian Sustainable Palm Oil (MSPO) and Roundtable Sustainable Palm Oil (RSPO) certifications are currently code of practice employed in most of palm oils in not only production of palm oil but also community and supply chain (Efeca, 2016; Rival et al., 2016).

Quality coordination division assures the oil product complies with the standards and regulations. Meanwhile, the plant manager is responsible to initiate and perform follow-up of the corrective action regarding quality issue. Overall, it is crucial to ensure that the oil produced conform to quality requirement particularly FFA and chlorine content controls.

4.1 Plantation stage

To obtain high quality palm oil product, the process is strictly supervised since the plantation stage. The very first step is to maintain the quality of seedlings by performing cross-pollination of selected parent palms. Generally, there are three different forms of palm fruits namely dura, pisifera and tenera as shown in Figure 7. Each one is differentiated by the physical appearance of mesocarp, endocarp and kernel. Table 5 compares the different characteristics among the three types of palm fruits. Although pisifera is shell-less and has the highest mesocarp to fruit ratio, there is low oil content in the pulp. This is because of the pisifera does not develop beyond the stage of anthesis (Sambanthamurthi et al., 2009).

Fig. 7. Different types of oil palm fruits (de Almeida Rios et al., 2018).
approximately 15–25% of its total weight (Sambanthamurthi et al., 2009; Sheil et al., 2009). Although detached fruits are considered as the indicator to the maturity of the FFBs, those fruits especially the bruised ones are usually not taken due to high FFA content (Hadi et al., 2009).

Several studies have introduced other methods but they seemed not practical and tedious. A microwave-based sensor was used to determine the stage of maturity of FFBs based on its moisture and oil content (Abbas et al., 2005; Khalid and Abbas, 1992) but the method was only applicable for the lab-scale works. Similarly, the RGB colour camera was studied to capture an image of the harvested FFBs where the intensity value of red (R), green (G) and blue (B) will differentiate the scale works. Similarly, the RGB colour camera was studied to capture an image of the harvested FFBs where the intensity value of red (R), green (G) and blue (B) will differentiate the FFBs into black, hard, ripe, over-ripe, empty and rotten (Ishak et al., 2008). The application faced some limitations in real plantation as the experiment was conducted under controlled environment in the lab (Ishak et al., 2000). Razali et al. (2009) and Ishak and Hudzari (2010) had developed a model that determines the FFB maturity by taking into considerations both FFB colour and moisture content. A maturity table was developed by them to manage and display the location of FFBs and the maturity stage. According to the researchers, application of this method to large-scale plantation requires an automated system data collection as data needs to be consistently recorded; time interval between harvesting and stabilizing is reduced as low as possible in order to minimize the lipase activity.

### 4.3 Milling stage

In palm oil mill processing, there are generally three important things to be considered: to minimize the degradation of oil quality, to keep the product losses at the lowest possible level and to maintain the production cost at the lowest possible level (Eng and Tat, 1985). These can be achieved systematically by having the control on the quality of the raw materials and of manufacturing.

As above said, three inducing factors of FFA formation in palm oil mill process are heat, moisture and catalyst. There are two unit operations involving the heating process: sterilizer and digester. The heating temperature and time are inevitably crucial for both unit operations as the FFA will increase alongside with those variables (Berger, 2010; Junaidah et al., 2015). During the sterilization, heat may not completely penetrate due to various sizes of FFBs and crammed arrangement in the chambers. However, sterilizing the FFBs at longer time or higher temperature will additionally cause slow non-catalytic hydrolysis reaction of oil since moisture is introduced throughout the process (Lau et al., 2006). Besides, the oil is also susceptible to the oxidation reactions and over-sterilization may lead to poor bleachability of the final product (Junaidah et al., 2015). MCPDE and GE contents are not high in CPO but if they are, this sterilization section will be suspected first, because here ionic chlorine (chloride) starts the contact with FFA, DAG and MAG at high temperature (Menon, 2017).

Control of manufacturing quality in palm oil mill can be divided into four categories: process control, process inspection, and machine maintenance (Eng and Tat, 1985; MPOB, 2007).

- **Process control:** Good quality palm oil product and minimal production losses determine the effectiveness of process control. These require knowledge, skills and intensive trainings on how to run machines properly.
- **Process inspection:** The conformity of the processing conditions and product quality will be regularly checked according to the standards. If the product quality is below standard, the overall process needs to be revised by the supervisor.
- **Inspection and test:** The inspection and test division will observe the efficacy of the ongoing process by doing the sampling, testing, and comparing with the standard specifications. Sample testing of palm oil quality should meet the food safety requirements, and these includes the FFA content, PV, AV, IV, M&I, DOBI and colour.
- **Machine maintenance:** Machine maintenance should be performed regularly to avoid the production loss, product contamination and hazardous situation.

Besides the formation of MAG and DAG indicated by the FFA content, chlorine is also the key reactant in the formation of MCPD and GE at refineries. Limitation of chlorine content, either aqueous or organic, has been imposed by Malaysia Government through a circular to all palm oil industries in Malaysia (Kadir, 2019). Chlorine in CPO is removed by second water washing using treated raw water in Malaysian palm oil mills (Yassin, 2018) and following the patent numbered EP 2 716 746 A1 (Yamamoto and Haneishi, 2014). Other possible methods of dechlorination include electrolysis and chemical derivatization with dechlorinating reagents as reported by other patent for waste cooking oil (唐应彪 et al., 2019) and dechlorination of aqueous chlorine by using an adsorbent (Spaparin et al., 2017).

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**Table 5.** Fruit form characteristics of *dura*, *tenera* and *pisifera* (Sambanthamurthi et al., 2009).

<table>
<thead>
<tr>
<th>Fruit form characteristic</th>
<th>Dura</th>
<th>Tenera</th>
<th>Pisifera*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell thickness (mm)</td>
<td>2–8</td>
<td>0.5–4</td>
<td>Shell-less</td>
</tr>
<tr>
<td>Fibre ring</td>
<td>Absent</td>
<td>Present</td>
<td>Absent</td>
</tr>
<tr>
<td>Mesocarp to fruit ratio (%)</td>
<td>35–55</td>
<td>60–96</td>
<td>95</td>
</tr>
<tr>
<td>Kernel to fruit ratio (%)</td>
<td>7–20</td>
<td>3–15</td>
<td></td>
</tr>
<tr>
<td>Oil to bunch (%)</td>
<td>16</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>

*Female sterile where bunches seldom develop to maturity.
4.4 Storage management

The final oil product requires proper handling to avoid increase of FFA at the storage tank and formation of radical polysaturated fat due to autoxidation and photosensitized oxidation with oxygen from air and rusted material (Almeida et al., 2019). Based on the recommended practices of storage and transport of edible oils and fats by MPOB, the suitable material of storage tank for palm oil is either aluminium or 316 stainless steel (Berger, 2010). The cleanliness of the storage tank is assured prior to the oil transfer to maintain the oil quality (MPOB, 2007).

5 Conclusion

As conclusion, the formation of toxic ester during the refinery is highly associated with the quality of CPO from the upstream process. FFA, the main parameter for quality verification indirectly becomes an indicator for the presence of MAG and DAG. Other feedstocks’ assessments include AV, M&I and chlorine content. Since chlorine is concerned for being a potential feedstock for MCPDE and GE, the sources should be further investigated and regulated. Current practices in controlling the feedstocks’ formation during the upstream process are matter of fruit handling, CPO mill processing and method of storing the final product.

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