

REVIEW

Mitigation of 3-MCPDE and GE in palm oil in Indonesia

Mitigasi kontaminan 3-MCPDE dan GE pada minyak sawit di Indonesia

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Abstrak

Di antara minyak nabati yang dikonsumsi, RBDPO (refined, bleached and deodorized palm oil) terbukti mengandung kontaminan 3-MCPDE dan GE yang lebih tinggi, di mana ke-2 jenis kontaminan ini diklasifikasikan berpotensi karsinogenik dan/atau genotoksik pada manusia. Kontaminan pada RBDPO ini terbentuk selama proses deodorisasi dengan suhu tinggi dan juga berkorelasi dengan kandungan klorida dan kualitas CPO sebagai bahan baku. Batas maksimum kandungan 3-MCPDE dan GE dalam minyak nabati telah ditetapkan sebesar 2500 dan 1000 $\mu\text{g kg}^{-1}$, serta 750 dan 500 $\mu\text{g kg}^{-1}$ bila digunakan untuk produksi makanan bayi dan makanan berbahan dasar sereal untuk bayi dan anak-anak. Mitigasi 3-MCPDE dan GE pada RBDPO cukup menantang bagi industri pemurnian (refinery) minyak sawit dalam menghasilkan minyak sawit berkualitas baik dari aspek sensori atau organoleptis, stabilitas, keamanan, dan nilai gizinya, khususnya di Indonesia. Telah terbukti bahwa modifikasi pada proses pemurnian konvensional dapat menurunkan kandungan 3-MCPDE dan GE. Diantaranya adalah melalui pencucian CPO dengan air untuk mengurangi kandungan klorida, netralisasi alkali untuk menghilangkan asam yang ada dalam minyak sebelum proses deodorisasi, menggunakan adsorben bleaching earth ber-pH netral, menambahkan antioksidan setelah bleaching untuk mengurangi pembentukan 3-MCPDE dan GE yang dimediasi oleh radikal bebas, menurunkan suhu deodorisasi dengan waktu yang lebih lama, dan bahkan proses bleaching ganda dan/atau deodorisasi ganda minyak sawit. Perlakuan post refining dengan menggunakan adsorben spesifik juga diterapkan untuk menghilangkan 3-MCPDE dan GE. Namun, industri pemurnian minyak sawit harus menerapkan kombinasi beberapa strategi mitigasi untuk mengurangi tingkat 3-MCPDE dan GE, termasuk menggunakan CPO berkualitas baik dengan kandungan FFA, klorida, dan komponen teroksidasi yang rendah.

[Kata kunci: minyak sawit, 3-MCPDE, GE, kontaminan, mitigasi]

Abstract

Among consumed-vegetable oils, RBDPO (refined, bleached and deodorized palm oil) is indicated containing higher level of 3-MCPDE and GE, which have been classified as potentially carcinogenic and/or genotoxic to human. Those contaminants in RBDPO are formed during deodorization process with high temperature and also correlate with chloride content and quality of CPO as raw material. The maximum limit for 3-MCPDE and GE content in vegetable oil has been set at 2500 and 1000 $\mu\text{g kg}^{-1}$, and as low as 750 and 500 $\mu\text{g kg}^{-1}$ when used for production of baby food and cereal-based foods for infants and young children. The mitigation of 3-MCPDE and GE in RBDPO is quite challenging for palm oil refineries in producing a good quality of palm oil in term of sensory, stability, safety, and nutritional value, especially in Indonesia. It has been proven that modification of conventional refining process can reduce the 3-MCPDE and GE content. They are including pre-treatment of CPO by water washing to reduce the chloride content, alkali neutralization to remove any acids present in the oil prior to deodorization, using neutral bleaching earth, adding antioxidants after bleaching to reduce free radical-mediated formation of 3-MCPDE and GE, lowering the deodorization temperature with a longer time, and even double bleaching and/or double deodorization of the palm oil. Post-refining treatment using specific adsorbents is also applied to remove the 3-MCPDE and GE. However, palm oil refineries have to apply combination of several mitigation strategies to adequately reduce the levels of 3-MCPDE and GE, including using good quality of CPO with low FFA, chloride, and oxidized components content.

[Key words: palm oil, 3-MCPDE, GE, contaminants, mitigation]

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Introduction

Recent issue of palm oil having a negative impact on health is regarding higher contaminants level of 3-MCPDE (3-monochloropropanediol ester) and GE (glycidyl fatty acid esters) compare to other vegetable oils. The 3-MCPDE and GE level in refined palm oil ranges between 2.16-15.2 and 0.32-6.3 mg kg⁻¹, respectively (Weißhaar & Perz, 2010). Both ester compounds are proven to be carcinogenic when they are completely hydrolysed into their free form in gastrointestinal tract in human body. The 3-MCPD has been identified as non-genotoxic threshold carcinogen that affects kidneys and male fertility, while glycidol is known as a genotoxic non-threshold carcinogen with various toxicity evidences found in animal studies (EFSA et al., 2018; EFSA, 2016).

European Commission (EC) established the Commission Regulation (EU) 2020/1322, which amended the regulation (EC) No. 1881/2006 regarding maximum levels of 3-MCPD, 3-MCPDE, and GE in September 2020. The maximum levels of 3-MCPDE and GE in refined oils and fats used as ingredients of food products are 2500 and 1000 µg kg⁻¹, respectively. Furthermore, the maximum limits of 3-MCPDE and GE contents are even smaller when the refined oils and fats used for infant and young children food, i.e. 750 and 500 µg kg⁻¹, respectively. As the maximum limits of 3-MCPDE and GE is very low, it pushes the researcher to get effective mitigation strategies to be implemented in palm oil industries. Previously Codex Alimentarius Commission (CAC) as a food safety and nutrition standard-setting body established by FAO (Food and Agriculture Organization) and WHO (World Health Organization) has published Code of Practise for the reduction of 3-MCPDE and GE in refined oils and food products made with refined oils - CXC 79-2019 (CAC, 2019). The guidance recommends three strategies for reducing 3-MCPDE and GE formation, in particular to palm oil, i.e. good agricultural practises (GAP), good manufacturing practices (GMP), and selection and uses of refined oils in food products made from these oils.

The 3-MCPDE is formed at temperatures starting 140°C and the GE rises exponentially at 230°C. Thus, the MCPDE and GE in palm oil mostly are formed during deodorization process which is carried out at high temperature (>240°C) and also during bleaching process especially when acid-activated clays were used. The reaction mechanism of MCPDE formation involves the

incorporation of chlorine in the glycerol backbone of diacylglycerol (DAG) and monoacylglycerol (MAG) (Cheng et al., 2017b), two components derived from triacylglycerol (TAG) because of hydrolysis reaction. DAG and MAG react with the chlorine via an acyloxonium ion and a nucleophilic substitution to form 2-, 3-MCPDE, and GE (Destailats et al., 2012). Šmidrkal et al. (2016) reported that 3-MCPDE formation from DAG was 2-5 times faster than MAG. Furthermore, the formation of GE has strong correlation with the DAG as well and increases exponentially from temperature of 230-240°C and at DAG level of more than 4% (Hrncirik & Duijn, 2011; Matthäus et al., 2011; Craft et al., 2012). Besides formed from DAG and MAG, GE can be also formed from 2-MCPDE and 3-MCPDE under certain temperature, pH, and time, which this conversion is reversible (Shimizu et al., 2012a; Cheng et al., 2017a).

Many approaches to mitigate the 3-MCPDE and GE level in refined palm oil have been studied, which are focused on (i) reducing the precursor of the esters in the raw material prior to processing, i.e. chlorine and DAG/MAG, (ii) modification of novel oil refining process to prevent 3-MCPDE and GE formation, and (iii) 3-MCPDE and GE removal in refined palm oil using suitable adsorbents (post refining). This paper aims to overview and provide up-to-date insights of the 3-MCPDE and GE mitigation strategies based on the literature and its implementation in palm oil industries in Indonesia.

Reducing precursor of 3-MCPDE and GE in palm fruits and crude palm oil (CPO)

One of the precursors of 3-MCPDE formation is chlorine, which the correlations between chlorine content in palm oil and 3-MCPDE level in its refined oil have established by many researchers (Matthäus et al., 2011, Chew & Saparin, 2021, Tivanello et al., 2021). In palm oil, chlorine-containing compounds could come from the plantation, i.e. fertilizers (NH₄Cl and KCl), herbicides (such as diuron, 2,4-D amine, fluroxypyr), and irrigation water including palm oil mill effluent (POME) applied in land application as fertilizer. The chlorine-containing compounds can be exposed to oil palm fruit through nutrient uptake or absorbed by the palm trees during cultivation (Hashim et al., 2007). But the risk of chlorine contamination is more from soil and solid impurities that are attached to FFB during harvesting and included in the next processes in palm oil mill.

The mitigation strategy in chlorine removal prior to oil extraction in palm oil mill is by washing off the oil palm fresh fruit bunches (FFB). The washing solution was not limited on pure water, but also alkaline water and mixture of water with solvent such as ethanol, acetone, and isopropanol. Using water washing in FFB before extraction, Matthäus and Pudel (2013) reported a reduction of 38% of 3-MCPDE in its refined palm oil. Washing palm fruits with water has been practised in Sime Darby Plantation Malaysia as well and it was reported that chlorine content in the CPO was as low as 0.5 ppm, which is 50% lower than unwashed CPO, and the 3-MCPDE content in its refined oil showed a reduction of 53% (Chew & Saparin, 2021).

As mentioned previously, the acylglycerol in form of DAG and MAG are able to form 3-MCPDE and GE at high temperature in deodorization step, thus making the acylglycerols as the esters precursors too. Partial acylglycerols, DAG and MAG, are more reactive than TAG in acting as acylglycerol precursor for 3-MCPDE and GE formation (Ermacorá & Hrnčirik, 2014). Therefore, the higher free fatty acid (FFA) content, which is positively correlated with the DAG and MAG content, may cause higher 3-MCPDE and GE content in the refined palm oil. FFA itself can act as active catalyst in hydrolysis reaction to accelerate the FFA and DAG formation. At below 10% FFA, hydrolysis reaction leads to DAG formation, then FFA 10-20% in oil leads some MAG formation (Siew, 2000). These findings are useful for palm oil refining industries to put concern on choosing CPO as an input or raw materials during the refining process.

Based on the best practises in palm oil refineries in Indonesia, FFA level in CPO should be less than 3.5% to get RBDPO with good or acceptable quality in term of organoleptic, oxidative, and colour stability. Furthermore, FFA level in CPO should be less than 3.0% to get RBDPO with low 3-MCPDE and GE. A study from IOPRI (Indonesian Oil Palm Research Institute) showed the range of FFA content in CPO processed in palm oil refineries in Indonesia was 1.26 – 7.00% with average 3.94% (Hasibuan, 2012). Our study showed FFA content in CPO was 2.6 – 7.7% with average level was 4.2% (unpublished data). Therefore, it is a big challenge for Indonesian palm oil industries to get CPO with FFA content less than 3%.

There are several factors affecting the FFA level in palm oil, i.e. harvesting time and method, ripeness index of the oil palm fruit bunches, time interval between harvest and sterilization of the fruits, and handling of CPO during storage and transportation. Over ripe fruit bunches during harvesting will

produce higher FFA content in the CPO. Bad handling of fruit bunches may damage the palm fruits, escalate the enzymatic hydrolysis reaction of the palm oil, and increase the FFA content as a result of enzymatic degradation process in the palm fruits. The bruising on palm fruits also has risk of oil contact with the inorganic chloride on the fruit's skin (Krisdiarto & Sutiarto, 2016). Therefore, it is required to separate the damaged and loose fruits from the good ones up to CPO production in palm oil mill. The mechanizations in oil palm harvesting and transportation in the plantation need to be corrected, developed, and improved to reduce the damage of palm fruits.

The efforts to get low FFA content in CPO should include to shorten time interval between harvest and sterilization of the fruits in the palm oil mill, which is influenced by distance and length of transportation time from plantation to palm oil mill. In Indonesia, improvement on transportation infrastructure and optimization of transportation route are important to reduce the 3-MCPDE precursors (FFA, DAG, and MAG) formation. Transportation route should be paid more attention because palm oil refineries in Indonesia is more in Java Island and CPO could come from other islands, especially Kalimantan and Sulawesi. Mostly the CPO is transported by barges and also road tankers to and from the port. CPO handling during transfer from storage tanks to road tankers and barges and vice versa may affect the increasing of FFA content because of hydrolysis reaction. In addition, water contamination in road tankers, barges, and ships should be avoided to maintain low moisture content of CPO. Fully understand that the high moisture content may accelerate the hydrolytic reaction. It was recommended to have moisture content less than 0.25% in CPO during storage and transportation to inhibit hydrolysis deterioration (Siew, 2000).

The other concern to minimize the 3-MCPDE formation in palm oil is to control chlorine content and pH of the water used in the sterilization process during oil extraction in the palm oil mill. It was proven that acidic condition would promote the 3-MCPDE formation. It was not only the pH of water used in the palm oil mill, the high FFA content also could affect the pH of the oil and resulted increasing of 3-MCPDE formation (Shimizu et al., 2012a). As the contaminants esters formation was dependently on high temperature in the mechanical extraction, several studies have developed enzymatic oil extraction process as an alternative method for low 3-MCPDE palm oil production, as it uses lower temperature (50°C) compare with the mechanical extraction (Silvamany & MdJahim, 2015).

It is recommended that the chloride content in CPO must be reduced to below 2.0 mg kg^{-1} to get maximum limit of 3-MCPDE (Matthäus & Pudel, 2013; Ibrahim & Menon, 2017; Silva et al., 2019; Shyam & Yen, 2020). By water washing of CPO, Oey et al. (2019) could get chloride level in CPO and 3-MCPDE level in refined palm oil less than 1 mg kg^{-1} . Furthermore, Shyam and Yen (2020) resulted 3-MCPDE level less than 1.25 mg kg^{-1} consistently in actual plant using water-washed CPO with pure or mildly acidified water. This water washing method might be an effective way of reducing the 3-MCPDE in palm oil, although it would increase the process complexity in palm oil mills or refineries and also wastewater handling. These methods also have higher risk on the refined palm oil quality if not handled carefully. It can increase FFA and peroxide value which may impact to the oil oxidative and colour stability, and also difficulty of water separation because of emulsification by phospholipids content in the CPO. Choosing the CPO water washing method must consider the condition of CPO initial quality, utilization of the refined palm oil, and also the cost incurred due to requirement of water phase separation facilities and oil losses.

Modification or novel oil refining process to prevent 3-MCPDE and GE formation

Palm oil refining process includes degumming, neutralization or de-acidification, bleaching and deodorization steps. Mostly palm oil refineries in Indonesia are using physical refining process only, without neutralization or de-acidification, and the FFA is removed during deodorization step with temperature $> 255^\circ\text{C}$. To reduce the 3-MCPDE and GE concentration, several possibilities can be applied during this refining steps. In chemical refining, the FFA content in the palm oil is removed through neutralization process prior to deodorization step. Pudel et al. (2011) and Šmidrkal et al. (2016) showed reduction of 3-MCPDE formation through neutralization of palm oil using alkaline carbonates or hydrogen carbonates. Replacing the current physical refining into chemical refining surely increase the production cost due to higher oil losses and also has a higher environmental impact because of the alkaline waste water.

Water degumming has been also studied and was able to reduce the 3-MCPDE and GE level more than existing dry degumming which is using concentrated phosphoric acid or citric acid. Water degumming is likely washing step to remove chlorine in the CPO, but the water amount is less. Ramli et al. (2011) reported that degumming with water resulted lower 3-MCPDE level compared with 0.02% phosphoric acid solution. The 3-MCPDE concentration in water degumming was

0.75 mg kg^{-1} compared to 2.1 mg kg^{-1} with 0.02% phosphoric acid solution. Zulkurnain et al. (2012) also reported a higher reduction of 3-MCPDE using water degumming with 1% water at 70°C for 20 min compared with acid degumming with 0.05% phosphoric acid. The 3-MCPDE level was reduced from 9.79 to 1.55 mg kg^{-1} or 84% reduction.

Although water degumming looks effective to lower the 3-MCPDE level, but the refined palm oil did not meet standard quality in term of oil colour, whereas the red colour was high, i.e. 4.0 – 5.9 Red on the RYBN colour scale (Zulkurnain et al., 2012). The usual standard colour quality for refined palm oil is 3.0 Red maximum. The colour problem is related to incomplete removal of phosphatides and metal ions during degumming process, which may impact in oil darkening at deodorization process and colour reversion during oil storage. Therefore, this water degumming cannot be implemented in palm oil refineries in Indonesia, as the oil quality should fulfil the quality and stability aspect as well.

Type of bleaching earth used in bleaching process plays role in the 3-MCPDE concentration in refined palm oil. Natural bleaching earth showed better 3-MCPDE reduction compare with acid-activated bleaching earth (Vispute & Dabhade, 2018). The natural bleaching earth resulted in an average 2.2 mg kg^{-1} , while the acid-activated bleaching earth resulted 2.8 mg kg^{-1} of 3-MCPDE in palm oil (Ramli et al., 2011; Blow et al., 2018). The acid-activated bleaching earth, especially with hydrochloric acid, may contain residual acids and act as chloride precursor of 3-MCPDE. Furthermore, the role of bleaching earth in 3-MCPDE reduction was more significant when applied in the pre-refined oils compared to CPO, where the 3-MCPDE concentration decrease from 6.06 mg kg^{-1} to 2.48 mg kg^{-1} (Franke et al., 2009).

GE is a temperature dependent and formed in palm oil during deodorization process, which is usually carried out at temperature $250\text{--}265^\circ\text{C}$, pressure 2-4 torr, and 0.5 to 3 hours processing time. In further studies, 3-MCPDE was not influenced by the deodorization temperature. Higher deodorization temperature resulted higher GE concentration, as shown in report from Craft et al. (2012). The GE content in both refined palm oil deodorized at 200°C and 220°C were 0.4 mg kg^{-1} and it increased into 1.7 mg kg^{-1} at 240°C deodorization temperature.

The application of mild deodorization conditions is a good in GE mitigation strategy, but it affects to the palm oil quality and stability in term of sensory (odour and taste) and also colour. Several studies on double-deodorization, which the palm oil was deodorized twice with different temperature and time, showed more promising result. Matthäus and Pudel (2013) reported that double deodorization at 200°C for 120 min followed by 250°C for 5 min

decrease the 3-MCPDE content from 2 mg kg⁻¹ to 0.7 mg kg⁻¹ and GE content from 2 mg kg⁻¹ to 1.3 mg kg⁻¹. Meanwhile, double deodorization at 200°C for 120 min followed by 270°C for 5 min decrease the 3-MCPDE content from 2 mg kg⁻¹ to 0.5 mg kg⁻¹ and GE content from 16 mg kg⁻¹ to 3.5 mg kg⁻¹.

On the other hand, study by Oey et al. (2020) showed that 3-MCPDE were formed prior to deodorization step and remained stable throughout the refining process. It gave an insight that GE mitigation need a different approach. Double refining process with a high-low deodorization temperature (265 and 220°C) resulted the higher GE reduction (87%) compare with double refining process with high-high temperature and double deodorization only with high-low temperature. The GE elimination actually was happened at the second degumming and bleaching step. Although the implementation of this double refining in palm oil refining industries was relatively easier to reduce the 3-MCPDE and GE content, but it definitely affects the throughput or plant capacity and the production cost at the end.

Zulkurnain et al. (2013) combined five refining parameters on the effort to minimize the 3-MCPDE and GE formation. Those parameters were water dosage, phosphoric acid dosage, degumming temperature, activated clay dosage, and deodorization temperature. They reported that the optimum degumming conditions was with 3.5% water dosage, 0.08% phosphoric acid, and 60°C degumming temperature. In the bleaching step, 0.3% of bleaching clay and deodorization temperature 260°C were used. By this way, it could reduce the 3-MCPDE concentration by 87.2%, from 2.95 to 0.37 mg kg⁻¹. Several effective methods to mitigate 3-MCPD and GE in palm oil is summarized in Table 1.

Optimum processing condition is also recommended by Hew et al. (2020) to get refined palm oil with 3-MCPDE and GE level less than 1 mg kg⁻¹. The process is with 0.08% of acid, 1.50% of water, and temperature of 67°C during pre-treatment (degumming and bleaching process); 251°C and 105 min of deodorization temperature and processing time. The CPO quality used in this research were with FFA content < 3.8%, peroxide value < 1 meq kg⁻¹, DOBI 2.8 – 3.0, and phosphorus content < 19 mg kg⁻¹. The formation of 3-MCPDE was mainly controlled by the pre-treatment and deodorization temperatures and the interaction between water and acid dosage, while the formation of GE was mainly influenced by the deodorization

temperature, deodorization duration, and the pre-treatment temperature.

Adding antioxidant as free radical scavengers in bleached palm oil prior to deodorization process also affected the 3-MCPDE and GE reduction. Several antioxidants have been tested, i.e. TBHQ (Cheng et al., 2017b), α -tocopherol, rosemary extract, lipophilic tea polyphenols, and L-ascorbyl palmitate (Zhang et al., 2016). Increasing amount of TBHQ addition resulted increasing reduction of GE. Cheng et al. (2017b) reported a reduction of GE level from 1.7 mg kg⁻¹ into 0.8 mg kg⁻¹ with 1.8 mg g⁻¹ TBHQ addition. Zhang et al. (2016) used 6% w/w of rosemary extract to reduced 3-MCPDE level from 2.11 into 0.13 mg kg⁻¹ and used 6% w/w lipophilic tea polyphenols extract to reduced 3-MCPDE level from 2.44 into 0.61 mg kg⁻¹. This approach might be easily implemented in existing refinery plants, but the cost should be considered because high amount of antioxidant usage, besides the presence of unwanted odour of the natural antioxidant and the risk of TBHQ residual in the oil, which is regulated quite strictly and even banned in several countries.

Removal of 3-MCPDE and GE using adsorbents

Another strategy to mitigate the 3-MCPDE and GE from palm oil is by using specific adsorbents that can be added during bleaching process together with the clay/bleaching earth or after complete refining (post refining). Many kinds of adsorbents have been studied such as magnesium silicate, zeolite, white clay, and activated carbon from different material. Study of Restiawaty et al. (2021) has proved that using 2% activated carbon treated with 2 N HCl could adsorb both 3-MCPDE and GE in palm oil with process temperature 35°C and 2 hours contact time. The activated carbon adsorbed GE much better than 3-MCPDE, which the reduction capability was 97% of GE (from 6.7 into 0.2 mg kg⁻¹) and 68% of 3-MCPDE (from 19.7 into 13 mg kg⁻¹), respectively.

Similar result on GE removal with activated carbon was also obtained from study of Cheng et al. (2017a), who used acid-washed oil palm wood-based activated carbon with concentration 30 mg/100 ml. They found 95% of GE reduction from 3.75 to 0.2 mg kg⁻¹. The activated carbon showed the best reduction of GE among alkaline cellulase, activated clay, and non-acid-washed activated carbon. On the other hand, Shimizu et al. (2012a) reported that using 1% acid-activated bleaching clay could remove 99% of GE in refined vegetable oils, including palm oil.

Table 1. Various effective methods to mitigate 3-MCPDE and GE in palm oil.
 Tabel 1. Beberapa metoda efektif untuk mitigasi 3-MCPDE dan GE pada minyak sawit.

Methods Metode	Reduction Pengurangan				References Referensi
	3-MCPDE		GE		
	%	ppm	%	ppm	
1. Degumming					
– Water degumming (2% w/w); 80-85°C; 15 min	64	2.1 → 0.75	ND		Ramli et al. (2012)
– Water degumming (1% w/w); 70°C; 20 min	84	9.79 → 1.55	ND		Zulkurnain et al. (2012)
– Water degumming (5% w/w)	80	1.0 → 0.2	ND		Zulkurnain et al. (2013)
– Water degumming (1% w/w, 90°C, 10 min) after acid degumming	78	3.22 → 0.68	53%	0.68 → 0.32	Hew et al. (2020)
2. Neutralization					
– Neutralization with 1 mmol kg ⁻¹ NaHCO ₃	81	5.9 → 1.1	84	7.0 → 1.1 (3-MCPDE and related compounds)	Freudenstein et al. (2013)
– Neutralization with 5 mmol kg ⁻¹ NaHCO ₄	53	5.9 → 2.8	69	7.0 → 2.2 (3-MCPDE and related compounds)	Freudenstein et al. (2013)
– Neutralization with 45% KOH	45	ND	ND		Matthäus & Pudel (2013)
3. Bleaching					
– Pre-refined palm oil; 1% Tonsil Optimum 214FF	59	6.06 → 2.48	ND		Franke et al. (2009)
– 1% Tonsil 4191FF; 60°C	45	5.5 → 3.0 (incl. related compounds)	ND		Pudel et al. (2011)
– 1% Magnesol R60, 95°C vacuum, 30 min	67	1.55 → 0.51	ND		Zulkurnain et al. (2012)
4. Deodorization					
– (290°C; 4 hrs) vs (290°C; 2 hrs)	100	5 → 0	83	48 → 8	Pudel et al. (2011)
– (290°C; 6 hrs) vs (290°C; 2 hrs)	80	5 → 1	94	49 → 3	Pudel et al. (2011)
– (Stage 1 - 200°C, 2 hrs; Stage 2 - 250°C, 5 min) vs (250°C, 1.5 hrs)	65	2 → 0.7	35	2 → 1.3	Matthäus & Pudel (2013)
– (Stage 1 - 200°C, 2 hrs; Stage 2 - 270°C, 5 min) vs (270°C, 1.5 hrs)	75	2 → 0.5	78	16 → 3.5	Matthäus & Pudel (2013)
5. Other Processes					
– Short-path distillation vs regular process	90	3 → 0.3	98	64 → < 0.1	Pudel et al. (2016)
– Double refining with high-low deodorization temperature (265°C and 220°C) vs single refining	-	Relatively no changes	87	4.0 → 0.5	Oey et al. (2020)

Zulkurnain et al. (2013) has tested acid-activated clay and magnesium silicate as bleaching agent and suggested to use a mixture of both adsorbents to get a relatively low level of 3-MCPDE and with acceptable refined palm oil quality. Magnesium silicate was acted as chloride adsorbent, the major precursor of 3-MCPDE formation. Their study also showed that water degumming, bleaching with acid-activated clay, and followed by using magnesium

silicate in poor quality CPO resulted the lowest 3-MCPDE (from 9.79 mg kg⁻¹ to 1.55 mg kg⁻¹), but it could not meet the standard quality of palm oil in term of colour and oxidative stability. As per above explanation, it can be described that performance and adsorption capacities of adsorbents are very important factors in the removal of 3-MCPDE and GE.

Mitigation strategies for low 3-MCPDE and GE palm oil in Indonesia

Palm oil uses in Indonesia is more than 40% for food application as shown in Figure 1 (GAPKI, 2023). So far, Indonesian government has not set any regulation yet on 3-MCPDE and GE content in vegetable oils, including palm oil. To improve quality of human resources in Indonesia, food safety in term of 3-MCPDE and GE content should be put more concern and its maximum limit need to be set in Indonesian standard. Moreover, the palm oil industries need to comply to standards set by international authorities and food multinational companies, since more than 50% of Indonesian palm oil product goes for export and mostly used for food application (GAPKI, 2023).

Based on the data of palm oil usage in Indonesia, it is proposed to do a segregation of CPO for food and non-food application. The segregation should be carried out starting from the initial stage of production, i.e. FFB harvesting time and techniques and also its postharvest handling and transportation. In fact, it is not easy to influence the agricultural conditions and practises in the oil palm plantation in Indonesia, since it relates to so many stakeholders, including more than 2.6 million smallholders or farmers in Indonesia. The preventive actions might cause high cost in the plantation, whereas not all palm oil used for food products.

Several approaches need to be applied in the whole chain of palm oil production to get RBDPO with low content of 3-MCPDE and GE. The first strategy aims to reduce the precursor of chloride and DAG level. Water washing of FFB could be considered to be applied in palm oil mills if the CPO is known to be processed further and used in food application. Therefore, this approach is good to be implemented at integrated palm oil industries who can assure good quality FFB to get CPO with low FFA and high DOBI (deterioration of bleachability index). Water washing can be costly if applied in a stand-alone palm oil mill without integrated refineries, as chlorine removal has no benefit at all for CPO used in non-food application. Control the water quality used in the palm oil mill to avoid chlorine contamination is also important.

To get CPO with low FFA and good oxidative properties (DOBI and peroxide value), palm fruits segregation of good and damaged/loose fruits in the plantation and separate extraction process in the palm oil mills, storage segregation of good and bad quality of CPO in palm oil mills and refineries are very important to note. The segregation can be reflected in comparison of quality standard of CPO in Indonesia (SNI/ Standar Nasional Indonesia) and proposed standard for production of low 3-MCPDE and GE CPO based on researches' result and current condition in refineries in Indonesia, especially average of CPO quality in Indonesia, shown in Table 2.

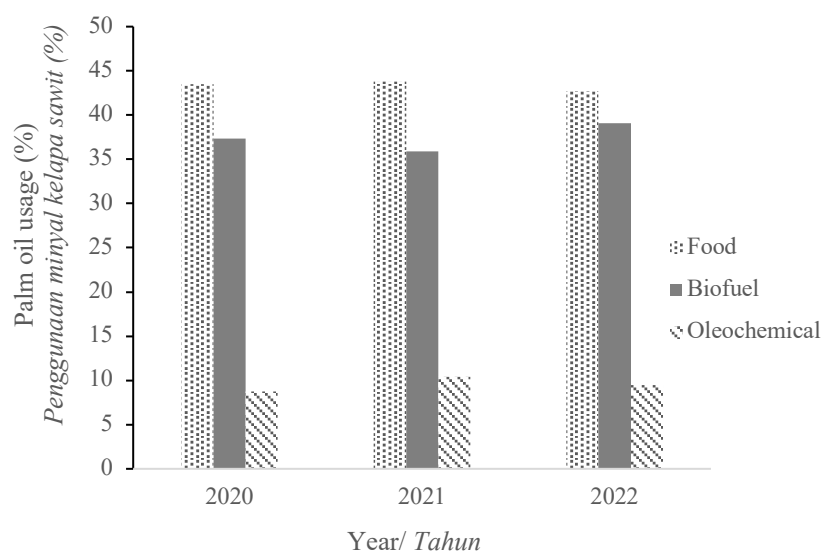


Figure 1. Palm oil usage in Indonesia 2020-2022

Gambar 1. Penggunaan minyak kelapa sawit di Indonesia 2020-2022

Table 2. Comparison of CPO standard quality and proposed new standard for low 3-MCPDE and GE content.
 Tabel 2. Perbandingan mutu standar CPO and usulan standar baru untuk 3-MCPDE dan GE rendah

Parameters <i>Parameter</i>	Indonesian Standard SNI 2091:2021 <i>Indonesia standar SNI 2091:2021</i>		Malaysian Standard <i>Standar Malaysia</i>		Proposed as Indonesian Standard for Low 3- MCPDE and GE content
	Regular	Premium	Standard Quality (STD Grade)	Super Quality (SQ Grade)	<i>Usulan standar Indonesia untuk 3-MCPD dan GE rendah</i>
Free fatty acids (as C16:0)	5.0% max	3.0% max	5.0% max	3.5% max	3.0% max
Moisture and impurities	0.5% max	0.25% max	0.25% max	0.25% max	0.25% max
Iodine value	50 -55		-	-	50 -55
Colour	Orange-red		-	-	Orange-red
DOBI	2.0 min	2.5 min	2.3 min	2.5 min	2.5 min
Peroxide value	-	-	2.0 meq kg ⁻¹ max	1.0 meq kg ⁻¹ max	2.0 meq kg ⁻¹ max
Anisidine value	-	-	4.0 max	5.0 max	4.0 max
Phosphorus(P)	-	-	-	-	10 ppm max
Chlorine (Cl)	-	-	2 ppm max	2 ppm max	2 ppm max

The important thing to get good quality CPO is to not mix the residual palm oil extracted from the palm fiber and/or palm oil recovered from sludge in palm oil mills, which many palm oil mills do in Indonesia to get higher oil extraction yield. In the practise, it could be easier to segregate the CPO based on its quality along with the palm fruits segregation based on its certification sustainable status, i.e. RSPO (roundtable sustainable palm oil) and or ISPO (Indonesian sustainable palm oil). Mostly certified sustainable palm oil (CSPO) in Indonesia has better quality in term of FFA level, DOBI, iron and phosphorus content, and hence it is more suitable for food application. Using CSPO as throughput in the refineries does not relate to 3-MCPDE and GE reduction only, but it improves the overall quality of CPO as it has good benefits on the hydrolytic and oxidative stabilities of the CPO and its derivative products.

Degumming and bleaching process are the most critical refining stage in 3-MCPDE formation. Water degumming or washing with 1-5% water usage and palm oil bleaching with neutral clay, which is discussed in Zulkurnain et al. (2013), can be implemented in Indonesia to reduce the 3-MCPDE and GE content in refined, bleached, deodorized palm oil (RBDPO). This method should be carried out carefully to achieve good

overall quality of CPO, i.e. low 3-MCPDE and GE and also good colour and oxidative stability. The neutral clay used in the bleaching process should be an acid-activated and washed until neutral pH to provide a higher surface area to adsorb phospholipids, metallic impurities, and oxidized components but without affect much on 3-MCPDE formation. The other promising method is to implement water degumming with 1% water after conventional acid degumming (Hew et al., 2020). These two methods can be implemented in refineries with high quality CPO only. Another approach of mitigation of 3-MCPDE and GE is required if the CPO quality is not good. In addition, these two methods need process of modification and additional plant facilities to add water and also to separate it properly.

Neutralization of CPO before goes to further conventional refining process can reduce the 3-MCPDE and GE content besides removing FFAs by converting them into soap. Currently in conventional refining process of palm oil in Indonesia, the alkaline neutralization process is not implemented when physical refining is applied, but it is proven that combination of neutralization and conventional physical refining process can produce RBDPO with low 3-MCPDE and GE.

As described previously, high temperature in deodorization process (255-265°C) is a culprit of GE formation in palm oil, whereas 3-MCPDE content does not increase significantly (Hrncirik & van Duijn, 2011; Oey et al., 2020). However, deodorization with lower temperature is not sufficient to remove FFA and unwanted taste, and cannot meet the standard quality. Therefore, it is proposed to use one of the two methods in deodorization process of palm oil in Indonesia, i.e. (i) dual deodorization with lower temperature and longer deodorization time (200°C, 120 min) then with higher temperature and shorter time (250°C, 5 min) as discussed in Matthäus & Pudiel (2014), and (ii) double refining with high-low deodorization temperature (260°C and 220°C), as discussed in Oey et al. (2020). Several vegetable oil refinery plant manufacturers have improved their plant design by adding another stripping column with high temperature and low pressure (260°C and 1 mbar) in the deodorization section for dual deodorization, especially to remove GE.

Using specific adsorbent to remove 3-MCPD and GE palm oil is recommended when refineries have to process low grade CPO. Several commercial adsorbents are ready in market, like Magnesol R60. In practise with existing refinery facilities, the adsorption method is conducted as post

refining process, which palm oil refinery do double refining without acid degumming and the refined oil goes through the deodorization section with low temperature and high throughput at the second step of refining. The implementation of this method will reduce the plant capacity up to half and increase cost production. The palm oil refineries need to invest production facilities of post refining to keep the plant capacity, by adding main facilities of tank reactor and leaf filtration system.

Based on the above explanation, it can be described that the mitigation step the 3-MCPDE and GE in palm oil should be implemented with an integrated approach in the whole chain of palm oil production. Since there are two main market requirement of 3-MCPD level in palm oil, i.e. 2.5 ppm and 1.0 ppm maximum, the mitigation step should be different for each. So far, almost all requirement for GE level is 1.0 ppm max. It seems very difficult to get palm oil as ingredient of baby food and cereal-based foods for infants and young children in Indonesia, i.e. with 3-MCPD content 0.75 ppm max and GE 0.5 ppm max. Supposed that it can be produced with a super quality of FFB with very carefully handling in the plantation to get a premium grade of CPO. The proposed mitigation strategies for low 3-MCPD and GE palm oil production shown in Table 3.

Table 3. Proposed mitigation strategies for low 3-MCPDE and GE palm oil production in Indonesia

Tabel 3. Usulan strategi mitigasi untuk produksi minyak sawit rendah 3-MCPDE dan GE di Indonesia

Requirement/ Persyaratan		
3-MCPDE < 2.5 ppm	3-MCPDE < 1.0 ppm	GE < 1.0 ppm
1. Good CPO (FFA 3.5% max)	1. Very good CPO (FFA 3.0% max)	1. Good CPO (FFA 3.5% max)
– Optimum harvesting index and interval	– Optimum harvesting index and interval	– Optimum harvesting index and interval
– Good handling of FFB	– Good handling of FFB	– Good handling of FFB
– Transportation time from plantation to palm oil mill	– Transportation time from plantation to palm oil mill	– Transportation time from plantation to palm oil mill
– Separate recovered palm oil from fiber and sludge	– Separate recovered palm oil from fiber and sludge	– Separate recovered palm oil from fiber and sludge
– Water or mild acidic washing of FFB	– Water or mild acidic washing of FFB	
2. Acid and water degumming of CPO	2. Acid and water degumming of CPO	2. Double refining with dual deodorization temperature (high - low)
3. Chemical refining (with neutralization)	3. Chemical refining (with neutralization)	3. Dual deodorization temperature (high - low)
4. Double bleaching/refining	4. Double bleaching/refining	
5. Post refining with specific adsorbents	5. Post refining with specific adsorbents	

Conclusion

The best way to prevent the 3-MCPDE and GE formation is to control the precursors in the raw material starting from the palm fruit bunch quality to get CPO with low FFA (3.0% maximum), high DOBI (2.5 minimum), and low chlorine content (2 mg kg⁻¹ maximum). Implementation best agricultural practises in oil palm plantation to get good quality of palm fruits and low chlorine content, followed by immediate process in palm oil mill can minimize the 3-MCPDE and GE formation. As more than 40% of total area in Indonesia is owned by small holder farmers, it is certainly a big challenge for Indonesia to implement best agricultural practises in the plantation to produce palm fruits with good and consistent quality.

Segregation strategy is required from the initial stage, starting from palm fruits segregation of good and damaged/loose fruits in the plantation, and segregation of good and bad quality of CPO in palm oil mills and refineries. The important thing is to not mix the residual palm oil extracted from the palm fiber and/or palm oil recovered from sludge in palm oil mills, which is implemented in many palm oil mills in Indonesia to get higher oil extraction yield. In the practise, it could be easier to segregate the CPO based on its quality along with the palm fruits segregation based on its certification sustainable status.

Water-washing to remove the chlorine precursors in FFB; chemical refining by using neutralization process; control the phosphoric acid dosage and temperature during degumming process; select the appropriate bleaching earth and dosage; double refining with two-step deodorization temperature profile (265°C and 220°C), and post refining the refined palm oil using specific adsorbents, like magnesium silicate, activated zeolite and acid-activated carbon, are the tools of 3-MCPDE and GE mitigation in palm oil.

It can be concluded that no single mitigation strategy can be implemented in producing refined palm oil with required standard levels of 3-MCPDE and GE. Combining multiple mitigation strategy needs to be studied in each palm oil refinery based on the CPO quality, not only to meet the standard 3-MCPDE and GE requirement but also the acceptable oil quality and stability. All mitigation efforts will have an impact on additional costs which must be calculated based on the willingness to pay of RBDPO buyers in the market with premium costs ranging from USD 100-150 per ton.

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