3-MCPDE in Palm Oil Processing: Formation Factors, Transference to Food and Mitigation Approaches

Chien Lye Chew, Amirul Al Hafiz Abdul Hamid, Hemavathi Silvamany, and Soon Huat Tiong

Abstract Palm oil is the world most produced and consumed vegetable oil. Food safety officials have recently focused their attention on vegetable oil, including palm oil, due to the presence of 3-monochloro-1, 2-propanediol and related esters (3-MCPDE). The European Food Safety Authority (EFSA) proposed to limit the 3-MCPDE in palm oil to 2.5 ppm by year 2021. This heat-induced process contaminant is formed during the refining process through its precursors, such as chlorinated compound and diacylglycerol in vegetable oil. The consumption of foods containing 3-MCPDE that exceed the tolerable daily intake limit may cause health complications. Therefore, many research works have been conducted to mitigate 3-MCPDE formation during palm oil processing. This chapter discusses the 3-MCPDE's formation factors, occurrences during food processing, mitigation initiatives and industrial practices in addressing the 3-MCPDE issue. It is hoped that the chapter could provide an insight into 3-MCPDE formation factors and their mitigation strategies.

The original version of the chapter was revised: There is a minor error on page 336 where the text in the bracket has been missed inadvertently ("and 3-MCPDE content by 50% (). The studies…") and this has been corrected to "and 3-MCPDE content by 50% (Chew et al., 2021). The studies…". The correction to the book is available at https://doi.org/10.1007/978-981-19-4847-3_15

C. L. Chew (✉) · A. A. H. Abdul Hamid · H. Silvamany
Sime Darby Plantation Research, R&D Centre—Carey Island, Lot 2664 Jalan Pulau Carey, 42960 Pulau Carey, Selangor, Malaysia
e-mail: chienlyechew@gmail.com

A. A. H. Abdul Hamid
e-mail: amirul.alhafiz.hamid@simedarbyplantation.com

H. Silvamany
e-mail: hemavathi.s@simedarbyplantation.com

C. L. Chew
Monash-Industry Palm Oil Education and Research Platform (MIPO), Monash University Malaysia, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor, Malaysia

S. H. Tiong
Sime Darby Plantation Technology Centre, UPM-MTDC Technology Centre III, 1st Floor, Block B, Lebuh Silikon, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia
e-mail: tiong.s.h33@gmail.com

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Abbreviations

3-MCPDE	3-Monochloro-1, 2-propanediol ester
CPO	Crude palm oil
DAG	Diacylglycerol
DCO	Diluted crude oil
EFB	Empty fruit bunch
EFSA	European food safety authority
FFA	Free fatty acid
FFB	Fresh fruit bunch
MAG	Monoacylglycerol
PORAM	Palm oil refiners association of Malaysia
SC	Sterilizer condensate
SFB	Sterilized fruit bunches
TAG	Triacylglycerol
TC	Total chlorine (combination of organic and inorganic chlorine)
TDI	Tolerable daily intake

1 Introduction

Palm oil is one of the world's most consumed vegetable oils, predominantly for food applications. Palm oil demand is expected to increase due to world population and economic growths, particularly in developing countries. In year 2020, the global edible oil production reached 208 million tons, with approximately 73 million tons of palm oil (USDA, 2020). The versatility of palm oil physicochemical properties enables the oil to be separated into two distinct fractions known as *palm olein* and *stearin*, depending on the food applications. Palm olein is primarily used for frying and domestic cooking, while palm stearin is used mainly to produce shortening and margarine. Therefore, the food safety and quality of the palm oil produced are essential to the industry.

The crude palm oil (CPO) comprises of triacylglycerol (TAG), diacylglycerol (DAG), monoacylglycerol (MAG), free fatty acids (FFA), and other minor components (e.g., micronutrients, oxidation products and metals) (Table 1) (Chew & Saparin, 2021). These components determine the overall quality of palm oil. Since CPO is primarily used for food, its quality criteria must be met. Typically, the millers and refiners use the specification set by Palm Oil Refiners Association of Malaysia

(PORAM) as the quality standard for palm oil trading (Table 2). The PORAM specifications cover three CPO's major quality parameters, which are (i) FFA (to measure oil hydrolytic stability), (ii) moisture and impurities (to measure solid impurities and moisture content) and (iii) degree of bleachability index (to measure the easiness of CPO to be refined) (Chong, 2012; PORAM, 2000).

Lately, the food safety authorities intensified their attention on the quality of vegetable oil, especially the process contaminant known as 3-monochloro-1, 2-propanediol esters (3-MCPDE). Studies showed that refined palm oil contained a considerable amount of 3-MCPDE (Destaillats et al., 2012; Rahn & Yaylayan, 2011). The Joint Food and Agriculture Organization and World Health Organization Expert Committee on Food Additives (JECFA) recommended a Provisional Maximum Tolerable Daily Intake of 4 µg/kg body weight for 3-MCPDE, either on its own or in combination with glycidyl esters, (JECFA, 2017). Subsequently, the European Food SafetyFood safety Authority (EFSA) has recommended that the limit of 3-MCPDE in palm oil to be kept at 2.5 ppm or below, starting in year 2021 (Union, 2020). Moreover, in year 2017, the EFSA published a comprehensive study on the benchmark dose approach in risk assessment of 3-MCPDE as a known human

Table 1 General composition of CPO

Composition	Value
Triacylglycerol (TAG) (%)	91.5 ± 3.5
Diacylglycerol (DAG) (%)	5.0 ± 2.0
Monoacylglycerol (MAG) (%)	0.5 ± 0.2
Free fatty acid (FFA) (%)	3.0 ± 2.0
Moisture (%)	0.15 ± 0.05
Solid Impurities (%)	0.02 ± 0.01
Tocopherols and tocotrienols (ppm)	800 ± 300
Carotenoids (ppm)	600 ± 200
Phytosterols (ppm)	450 ± 150
Squalene (ppm)	350 ± 150
Phospholipids (ppm)	71.5 ± 68.5
Metals (Copper and Iron) (ppm)	5.5 ± 4.5
Lipid oxidation products (ppm)	Traces

Table 2 Quality requirement for crude palm oil in PORAM specification (MPOB, 2019; PORAM, 2000)

Characteristics	Value
Free fatty acid (as palmitic) (% max)	5.0
Moisture and impurities (% max)	0.25
Degree of bleachability index (min)	2.3
[a]Total chlorine (ppm max)	2.0

[a] Additional proposed quality requirement for CPO

carcinogen and established its Tolerable Daily Intake (TDI) at 2 μg/kg of body weight (EFSA, 2018).

Several studies have shown that CPO with a high amount of FFA, DAG, chlorinated compounds (i.e., organochlorine and inorganic chlorine) during the refining process promotes the formation of 3-MCPDE (Craft et al., 2012; Šmidrkal et al., 2016). Presently, the overall chlorinated compounds in CPO are measured using a total chlorine analyzer, according to ASTM D4929-04 Method B (ASTM, 2010) and termed as 'total chlorine' (TC). Recently, Malaysian authorities proposed to limit the TC content in CPO by 2 ppm (Table 2). Meanwhile, the limit for 3-MCPDE in refined palm oil was proposed to be below 2.5 ppm and 1.25 ppm by years 2021 and 2022, respectively (MPOB, 2019). In this chapter, the factors contributing to the 3-MCPDE formation was first investigated. Subsequently, the influence of the 3-MCPDE during food processing was reviewed. This is then followed by recent initiatives to mitigate this process contaminant. This work provides industry insights into steps to reduce the content of 3-MCPDE (in ppm) to meet the allowable limits.

2 Factors Influencing 3-MCPDE Formation

The 3-MCPDE is formed in edible oils, including palm oil, during their refining process at the deodorizer. This is mainly due to the high-temperature process and the presence of chloride ions. A study shows that 3-MCPDE was formed and detected in refined oil but not in CPO (Ramli et al., 2011). Subsequently, Destaillats et al. (2012) found that thermal treatment (235 °C) of triolein oils in the presence of chlorinated compounds (i.e., organochlorine pesticides and $FeCl_2$) increased the formation of 3-MCPDE. The formation of 3-MCPDE had been proposed to proceed through both S_N2 nucleophilic substitution and free radical reaction initiated from acylglycerol such as TAG and TAG to for acyloxonium intermediate under high temperature condition, as shown in Fig. 1 (Rahn & Yaylayan, 2011; Zhang et al., 2013). Studies showed that high DAG and MAG in model oil increased 3-MCPDE formation after thermal treatment imitating the deodorization conditions (Freudenstein et al., 2013; Shimizu et al., 2012). The formation of 3-MCPDE was also observed in model oils with pure TAG, without partial acylglycerols (i.e., DAG and MAG). Therefore, TAG appears to be also the precursor for 3-MCPDE formation (Destaillats et al., 2012; Ermacora & Hrncirik, 2014). However, partial acylglycerols (i.e., DAG and MAG) were more reactive than TAG to form 3-MCPDE, with DAG being the most reactive precursor due to higher concentration compared to MAG (Freudenstein et al., 2013; Shimizu et al., 2012).

Since CPO contains a high percentage of acylglycerols (>95%), the 3-MCPDE formation in palm oil is constrained by the concentration of chlorinated compounds (Che Man et al., 1999; Ermacora & Hrncirik, 2014). Studies by Tiong et al. (2018); Lakshmanan and Yung (2021) showed that TC in CPO directly relates 3-MCPDE formed in refined palm oil with the r^2 of 0.73 and 0.91, respectively. Meanwhile, Nagy et al. (2011) found over 200 monochlorinated organic compounds and chlorinated

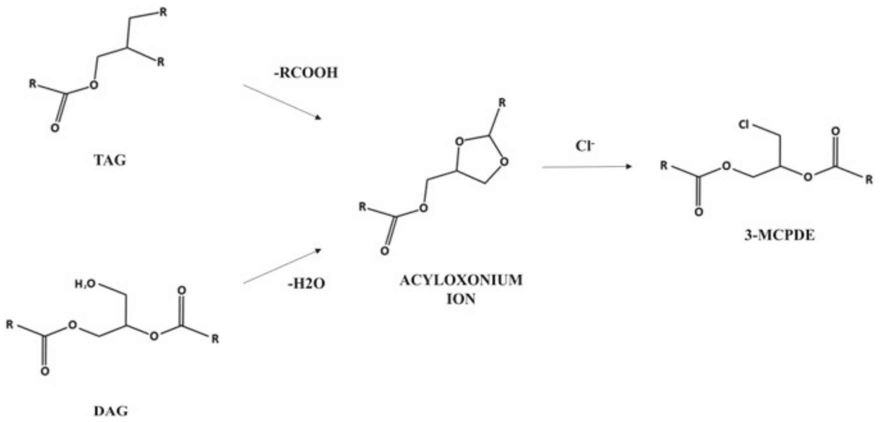

Fig. 1 Proposed formation mechanism of 3-MCPDE from DAG and TAG through acyloxonium ion

inorganic compounds (i.e., $FeCl_2$, $FeCl_3$, $MgCl_2$, and $CaCl_2$) in CPO. Organochlorine compounds, natural occurring lipid substances, could liberate chlorides during deodorization (Chew & Saparin, 2021). These free chlorides then react with acylglycerols to form 3-MCPDE (Nagy et al., 2011; Tiong et al., 2018). The organochlorine compounds as the precursor for 3-MCPDE were further verified by a model showing that oil enriched with organochlorine compounds under thermal treatment resulted in a higher 3-MCPDE formation (Tiong et al., 2018).

Organochlorine compounds are believed to be biosynthesized in all plant tissue not only in oil palm fruits (Tiong et al., 2018). Typically, the ripe palm fruits are harvested and delivered to oil mills for the oil extraction process. In the mill, the harvested palm fruits known as fresh fruit bunches (FFB) are subjected to a series of processing units (Chew et al., 2021b). First, the FFB is subjected to a heat treatment (known as sterilization process) with saturated steam (140 °C) to deactivate the lipase enzyme and loosen the palm fruits from its bunch (see Fig. 2). Then, the sterilized FFB undergoes a mechanical stripping process to separate the oil containing palm fruits from its bunch, producing empty fruit bunch (EFB) as by-products. In the pressing stage, the detached palm fruits are subjected to mechanical pressure to extract their pressed liquor, a mixture of oil, water and fine fibrous material from the palm mesocarp. Therefore, some organochlorine compounds could be extracted with the press liquor during pressing (Nagy et al., 2011; Tiong et al., 2018). The press liquor (containing <50% w/w oil) is then added with hot water (30% w/w) to facilitate the clarification process using a settling tank. This clarification process helps to enhance the separation of the oil from impurities (i.e., water and solid) to obtain the oil purity at 95% (w/w) and above. Subsequently, the recovered oil from the clarifier is delivered to a high-speed centrifuge and followed by vacuum drying to produce a final CPO with moisture and solid impurities of 0.25% (w/w) and below. Notably, the sterilization process causes some oil from the palm fruits to leech out, resulting in a small fraction of oil in the sterilizer condensate (SC) and EFB.

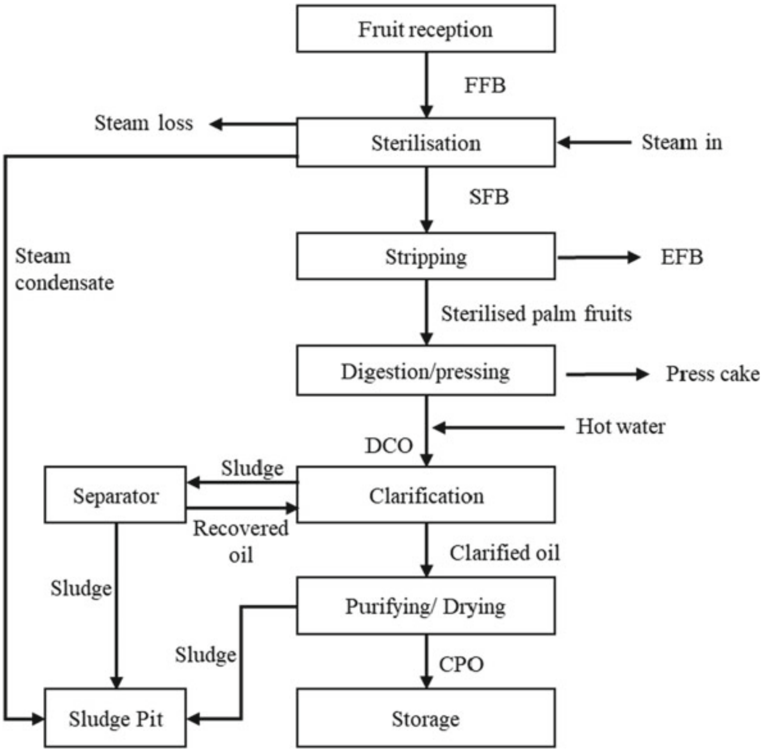

Fig. 2 Block diagram for palm oil mill processing

Therefore, some mills tend to recover SC and EFB oils to the CPO for maximizing their production.

A study was conducted to investigate the effect of each processing unit on the concentration of organochlorine compounds (Chew & Saparin, 2021). Samples for each process stream (i.e., EFB, SC, press liquor, clarifier, and CPO) were collected. Before analysis, the oil from each sample was mechanically extracted and purified to a similar purity with CPO. Interestingly, the organochlorine compounds are partitioned and concentrated in some oils' fractions during palm oil mill processing, particularly in EFB and SC oils (Fig. 3). This finding suggested that oil recovered from waste streams, mainly SC and EFB back into main CPO stream could increase the overall content of organochlorine in the CPO. Consequently, the 3-MCPDE in refined palm oil could be affected. Since the SC is predominant water (>98% w/w), it is used in some mills to replace hot water as dilution water and mixed into press liquor as an indirect method to recover the oil from SC (see Fig. 4). In recent years, many mills also tend to recover oils from EFB, where EFB press is used to extract EFB liquor containing water and some amount of oil (<20% w/w). As the volume of the EFB liquor is relatively low compared to SC (<15% v/v), it is then mixed with SC and used as dilution water in some mills. A separate study by Chew et al. (2018) investigated the

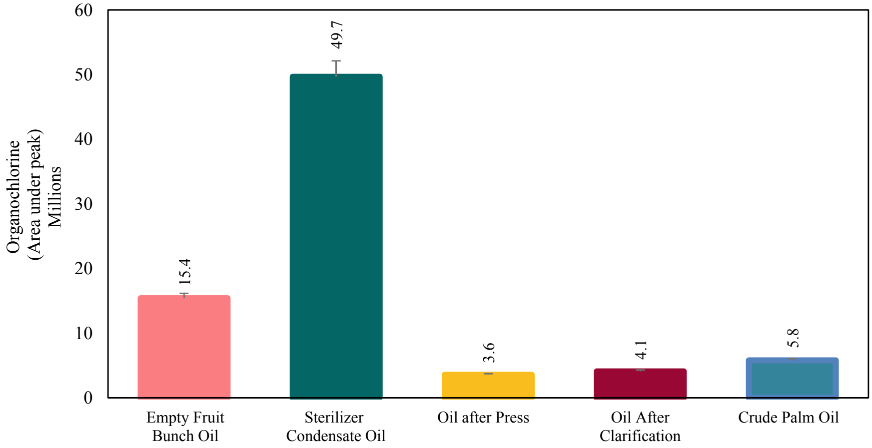

Fig. 3 Organochlorine content in various oil streams at palm oil mill

effect of dilution water on the amount of TC content in the oil. This study showed that the types of dilution medium used could affect the TC and 3-MCPDE in the CPO and its refined oil, where dilution medium using SC and EFB liquor mixture resulted in the highest TC level in the CPO (Fig. 5). This finding reaffirms the earlier postulation that mixing a chlorine-rich stream into a CPO processing line could increase its TC content and subsequently surge the 3-MCPDE content in its refined oil. Therefore, reducing 3-MCPDE's precursors, i.e., TC, is essential to mitigate this process contaminant.

Aside from the acylglycerols and chlorinated compounds as precursors, the composition of minor constituents in CPO and refining process conditions could also influence the 3-MCPDE formation. The acidity of CPO could encourage and trigger acylglycerols for chloride nucleophile attack to form 3-MCPDE (Rahn & Yaylayan, 2011). In a study by Freudenstein et al. (2013), increasing the alkalinity with disodium carbonate and sodium bicarbonate reduced the formation of 3-MCPDE from 7 ppm to less than 3 ppm. Contrarily, an addition of 10% lauric acid reduced the oil acidity and resulted in a higher 3-MCPDE formation. Although FFA is not a direct precursor for the formation of 3-MCPDE, it does influence the acidity of the oils that affect the 3-MCPDE formation (Zulkurnain et al., 2012).

During the refining process, chlorinated compounds could enter the CPO depending on the material and chemical used. Typically, the chloride in bleaching clay and water ranged from 50 to 150 ppm. The acid activation process using hydrochloric acid (HCl) in bleaching clay could introduce chloride into the oil. Therefore, bleaching clay manufacturers are now offering bleaching clay that is activated with non-chloride acid. Although another acid, such as sulfuric acid (H_2SO_4), contains no chloride ions, their higher acidity could also promote 3-MCPDE formation (Ramli et al., 2011). Therefore, natural bleaching earth that does not contain chloride and neutral pH is preferred to reduce 3-MCPDE formation. Furthermore,

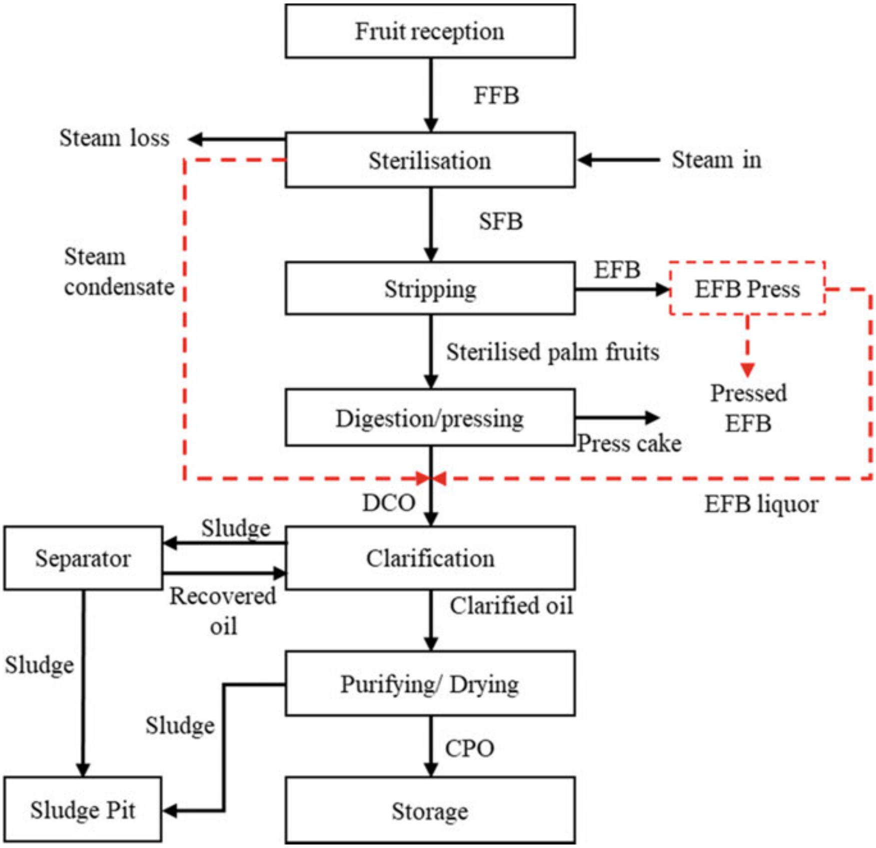

Fig. 4 Block diagram for palm oil mill processing with sterilizer condensate and EFB liquor as dilution medium

chloride is also detected in the acid used in the degumming process. Nevertheless, the amount of acid (<0.1% w/w to CPO) used for degumming is relatively low and negligible. Interestingly, CPO exposed to water, such as water degumming, shows a reduction of 3-MCPDE (Matthäus et al., 2011; Pudel et al., 2011; Ramli et al., 2011). As such, the oil palm industry must consider the precursors and factors that influence 3-MCPDE formation to effectively mitigate this issue and ensure the food prepared with oil does not exceed the allowable limit.

3 Transference of 3-MCPDE to Food

3-MCPDE is found in various household products, including foods that contain edible oils and fats. Additionally, domestic cooking methods such as frying, baking,

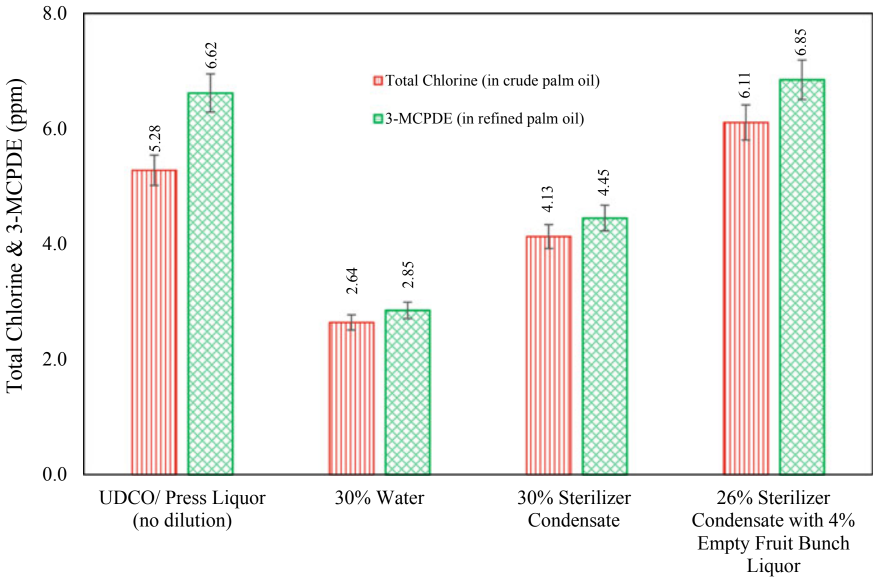

Fig. 5 Total chlorine in CPO and 3-MCPDE content in its refined oil for various types of dilution water—in the oil mill (Chew et al., 2018)

roasting, microwaving, and grilling have also increased 3-MCPDE levels in foods (Crews et al., 2001). Recent studies showed that the oil absorbed into food increases with the increase of the frying cycle (Lumanlan et al., 2019; Touffet et al., 2020). These studies further showed that the increase in oil absorption was due to prolonged heat treatment that degraded the oil. Under thermal treatment, the oil decomposed to produce total polar compounds that increase oil viscosity. In contrast, the 3-MCPDE content in refined oil during the deep-frying showed a decreasing trend over frying cycles (Chew et al., 2021c; Wong et al., 2019) (Fig. 6a). Therefore, a study by Chew et al. (2021c) showed that 3-MCPDEs absorbed into the food are averaged at 0.18 ± 0.04 ppm over 30 frying cycles (Fig. 6b). In another study, foods prepared with palm oil containing 1.64 ppm of 3-MCPDE resulted in 0.12–0.25 ppm of this contaminant in the fried foods (Arisseto et al., 2017). This study further reinforced the suggestion of Chew et al. (2021c) that 3-MCPDE in food was carried over from frying oil. However, the decomposition and formation of 3-MCPDE in the foods are influenced by the oil used (type, quality), cooking condition (frying temperatures, duration, cycles) and composition of food (salt and moisture content) (Dingel & Matissek, 2015; Wong et al., 2017; Zhou et al., 2014). Therefore, the risk of human exposure to 3-MCPDE in food products prepared with cooking oil containing 3-MCPDE is less of concern due to degradation of 3-MCPDE at high temperature cooking condition (i.e. during frying) compared to direct consumption of cooking oil.

In short, factors influencing oil absorption into food affect the 3-MCPDE concentration. Although the repeatedly use of oil shows a reduction in 3-MCPDE content,

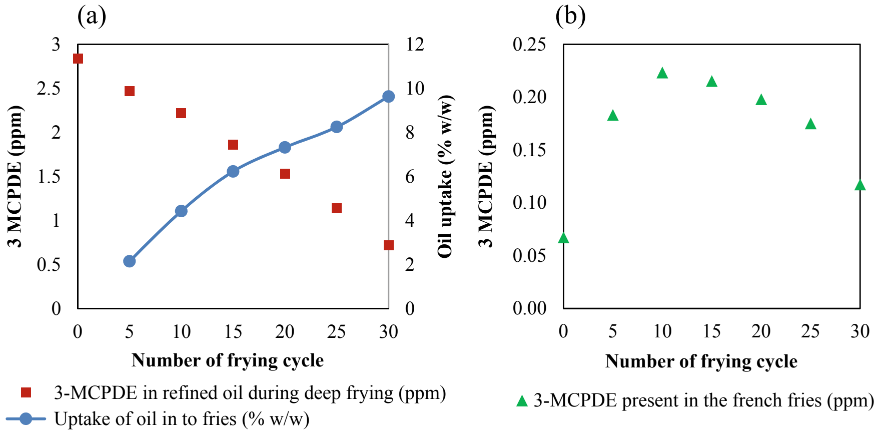

Fig. 6 3-MCPDE content in **a** refined oil and **b** in French fries during deep-frying (Chew et al., 2021c)

the prolonged exposure of frying oil to heat could deteriorate the oil quality. As a result, the nutritional value of the food is reduced. By taking Chew et al. (2021c) ‘s study with the average 0.18 ppm of 3-MCPDE in the fries, the maximum TDI for an average human body mass of 62 kg is equivalent to the consumption of 0.69 kg fries daily (EFSA, 2018; Walpole et al., 2012). However, it is essential to note that the 3-MCPDE is also detected in various heated foods. Therefore, minimizing the 3-MCPDE in foods is vital by reducing this contaminant in edible oil and ensure the overall consumed food is within the recommended limit of 3-MCPDE.

In recent studies, adding the antioxidants in the frying medium were suggested to reduce the 3-MCPDE formation during cooking (i.e., frying and baking) (Goh et al., 2020; Wong et al., 2019). Although the 3-MCPDE were reduced over the frying cycle (Chew et al., 2021c), the addition of antioxidants could further reduce the 3-MCPDE in the oil and food (Wong et al., 2019). This finding is in agreement with Huang et al. (2021), where frying oil added with tert-butylhydroquinone (TBHQ) resulted in a lower 3-MCPDE. It is well established that antioxidants could slow lipid oxidation and improve oil stability by scavenging the free radicals that oxidize the oil, especially the polyunsaturated fatty acid. Similarly, the antioxidants could minimize 3-MCPDE’s precursors such as chloride and cyclic acyloxonium radicals (Zhang et al., 2016). Therefore, the addition of antioxidants in frying oil could slow down the formation of 3-MCPDE during frying and improve the overall oil quality.

4 Mitigation Strategies

4.1 *Precursors Reduction in CPO*

One possible mitigation is to identify and to reduce the 3-MCPDE's precursor, i.e., chlorine sources in CPO. The chlorinated compounds of the oil palm fruits at the plantation are affected by various external factors such as soil, irrigation, and pest control (Destaillats et al., 2012). Some factors that may cause chlorinated compounds contamination in FFB and CPO are harvesting and transportation. During harvesting and evacuation, some solid impurities are attached to FFB and processed together to produce CPO. These solid impurities consist of predominantly fibrous materials and soil that contain chlorinated compounds. Consequently, some of the chlorinated compounds are then carried over to CPO during processing. These compounds could be leached out into press liquor during the pressing stage (see Fig. 2). Therefore, the reduction of chlorine source at the feedstock (FFB) is expected to minimize the process contaminant in CPO. The FFB washing with water before oil extraction is perhaps an essential step in reducing the accumulation of chlorine sources during milling processing. A study showed that the FFB cleaning system produced CPO with a TC content as low as 0.5 ppm (Syed Hilmi et al., 2018). Results showed that TC in CPO produced from washed FFB was significantly lower compared to conventionally produced CPO. As a result, the 3-MCPDE of the refined oil was reduced considerably.

Besides, the milling process could also influence the TC in CPO. In the effort to maximize the oil recovery during the milling process, some mills tend to recover oil from SC and EFB by using these streams as dilution water (Fig. 5). These poor-quality oils were then blended with CPO during the palm oil processing and enriched the TC (Chew et al., 2021b). Therefore, the oils recovered from waste streams is suggested to be segregated from the main CPO processing line. The oil mills could use a sludge separator to recover SC and EFB oils in a separate processing line for non-food applications. Through these methods, the TC and 3-MCPDE contents could be reduced by 30% in CPO and refined oil, respectively (Rahmat et al., 2019). In addition, this method improved the CPO's overall quality with higher hydrolytic and oxidative stabilities.

The formation of 3-MCPDE requires chloride ions that can be easily detached from chlorine sources. Therefore, a method that reduces TC concentration in CPO is crucial to prevent the formation of 3-MCPDE during the refining process. According to Destaillats et al. (2012), most of the chlorinated compounds in plant material are naturally polar. Therefore, liquid-liquid extraction using a polar solvent solution through water washing of CPO could effectively strip out the chlorinated compounds in CPO. Studies showed that reducing the 3-MCPDE in refined oil between 20 and 84% could be achieved by washing the CPO using water (Chew et al., 2021d; Matthäus & Pudel, 2013; Matthäus et al., 2011; Zulkurnain et al., 2012). In response to this positive finding, verification trials are performed in both laboratory and demonstration-plant with the capacity of 1 L and 20 t/hr, respectively.

At the laboratory scale, the reduction of TC and 3-MCPDE was only up to 50% and 51%, respectively. Meanwhile, the demonstration plant with 20 t/hr capacity showed a higher reduction of TC and 3-MCPDE with an average of 80% and 78%, respectively. The demonstration plant exhibited a better TC reduction, owing to the high-speed mixing system that increases the surface contact between the oil and water. However, CPO washing uses clean water and generates more wastewater. In the light of sustainability, the author has recently developed an alternative CPO washing system using aerobic liquor, treated water from a palm oil mill (Chew et al., 2021d). This sustainable and straightforward method was reported to reduce the TC and 3-MCPDE content by 50% (Chew et al., 2021). The studies on CPO washing are summarized in Table 3.

Another possible mitigation strategy for TC reduction is dechlorination of CPO using sodium metabisulfite (Spaparin et al., 2018). The sodium metabisulfite was first mixed with heated CPO. Then the spent sodium metabisulfite is filtered out to avoid the presence of the dechlorination agent in the oil. As a result, the dechlorinated CPO contained a TC content below 2 ppm and subsequently reduced the 3-MCPDE in its refined oil. Overall, reduction of TC in CPO is effective using dechlorination agents. However, the high cost of the sodium metabisulfite and oil loss of this method remains a challenge for commercial applications. Therefore, the economic viability of the mitigation methods is an essential factor to be considered for commercialization.

Apart from chlorine source reduction, the authors suggest improving the overall CPO quality as one of the mitigation actions. In short, the focus should be given to minimize the hydrolysis of oil during processing. Consequently, other factors contributing to the 3-MCPDE formation, such as FFA (pH), DAG, and MAG, could be minimized. Ebongue et al. (2006) and Tagoe et al. (2012) suggested that the FFB should be immediately treated with heat after harvesting to deactivate its lipolytic hydrolysis that forms the FFA. Besides, the segregation of poor-quality fruits is essential to improve the quality of CPO produced. For instance, detached palm fruits collected from estates are highly oxidized and hydrolyzed and could deteriorate the overall CPO quality (). Based on the authors' experience, the FFA of oil extracted from detached palm fruits is between 4 and 18%, depending on the quality of the detached fruits. In addition, the oil recovered from the waste stream should be segregated from the CPO production line. These segregation processes (i.e., detached fruits and oil from the waste stream) enable the production of CPO with low contaminants and FFA. It is worth highlighting that Sime Darby Plantation has commercially implemented this multilevel segregation technique to produce high-quality CPO (Chew, 2021). Through this method, CPO with exceptionally low FFA known as Premium Quality oil and Superior Quality oil with the FFA below 1.2% and 1.5% are produced. These oils contain lower TC as compared to conventionally produced CPO (Table 4). Furthermore, the 3-MCPDE content in its refined oils are low, i.e., an average of 1.25 ppm and 1.97 ppm, respectively. These unique CPOs are used for speciality fat products (i.e., infant formula, frying oil, and red palm olein). This finding showed that high-quality CPO with low FFA could reduce the 3-MCPDE formation during the refining process. Nevertheless, the 3-MCPDE in these oils could be further reduced with refining process modification.

Table 3 Effect of CPO washing on TC and 3-MCPDE on its refined oil. Results represent the means ± standard deviation of the mean value ($n = 3$)

Methods	Capacity (size)	TC (ppm)	3-MCPDE (ppm), (%)	References
Washing with water	^{a}NA	^{a}NA	20	Matthäus et al. (2011);
	^{a}NA	^{a}NA	38	Matthäus and Pudel (2013);
	^{a}NA	^{a}NA	84	Zulkurnain et al. (2012)
Washing with distilled water	Laboratory (1 L)	50.04 ± 0.88%	51.26 ± 1.56	–
	Demo-plant (20 t/hr)	80.13 ± 0.63%	78.40 ± 1.75	
Washing with aerobic liquor	Laboratory (1 L)	50.22 ± 0.36%	50.61 ± 1.42	Chew et al., 2021d; Chew, Kong & Chan, 2021e

^{a}NA indicates that the data is not available in the published work

Table 4 The level of TC and 3-MCPDE level in CPO and its refined oil, respectively

Type of CPO	CPO ($n = 60$)		RPO ($n = 60$)
	FFA (%)	TC (ppm)	3-MCPDE (ppm)
Normal	<5.0	4.06 ± 1.96	3.03 ± 0.87
Premium quality	<1.5	2.11 ± 0.61	1.97 ± 0.92
Superior quality	<1.2	1.77 ± 0.25	1.25 ± 0.6

4.2 Refining Process Modification

Besides precursor mitigation, modification of process conditions in the refinery could also address the 3-MCPDE formation issue. Water degumming has been proposed as an alternative to acid degumming in oil refining by some researchers (Ramli et al., 2011; Zulkurnain et al., 2012, 2013). Like the CPO washing technique, the chlorinated compounds that are polar can be extracted from the oil during this process. Compared to the conventional acid degumming technique of CPO, water degumming is less efficient in removing phosphatides, iron, and pigment, due to low concentration of these compounds in CPO compared to unrefined soft oils. These compounds cause color fixation issues during deodorization (Ramli et al., 2011). Surprisingly, using more water (up to 5%) during water degumming could remove impurities and achieves a red color specification of less than 3.0 (Zulkurnain et al., 2013).

In the bleaching step, the use of natural clay instead of acid-activated bleaching clay is recommended. Since natural clay is neutral in pH, it does not promote the formation of 3-MCPDE. However, natural clays typically have a lower surface area, which may affect the refined oil quality. The efficiency of bleaching clays in absorbing impurities is dependent on its absorptive capability, which in turn rely on the surface area. A study showed that a combination of water degumming and magnesium silicate as a bleaching clay resulted in the highest reduction of 3-MCPDE (Zulkurnain et al., 2012).

In the refining process, 3-MCPDE is formed almost exclusively during deodorization at high temperatures. A study by Matthäus et al. (2011) showed that the formation of 3-MCPDE is directly correlated to the temperature of deodorization. In this study, CPO containing 4.2% FFA and 4.75 ppm TC was subjected to deodorization temperature between 230 and 260 °C for 90 min. As anticipated, the highest levels of 3-MCPDE are found in oil samples that were deodorized at 260 °C. This finding is in good agreement with the low 3-MCPDE content in red palm olein. Typically, the production of the red palm olein undergoes mild refining with low deodorization temperature (<180 °C) and resulted in a very low amount of 3-MCPDE (Mayamol et al., 2007). Therefore, the deodorization temperature is recommended to be as low as possible to reduce the 3-MCPDE formation without compromising other quality parameters.

Chemical refining could also help to reduce 3-MCPDE formation. The review by Oey et al. (2019) showed that neutralization processes could result in 3-MCDPE reduction between 31 and 81% with different alkali solutions and concentrations. Similar to CPO washing, neutralization could reduce the TC content in the CPO, resulting in a low 3-MCPDE formation. Apart from lowering the 3-MCPDE precursor, the neutralization process reduces the acidity of the CPO before deodorization. During neutralization, most FFAs and excess acids (from the degumming process) are removed to produce neutral oil that is less susceptible to 3-MCPDE formation (Freudenstein et al., 2013). Furthermore, the neutralization process could enable mild deodorization and lead to refined oil production with low 3-MCPDE content. A recent study by Hori et al. (2021) showed that a combination of neutralization and steam sparging could reduce 80% of 3-MCPDE formation. Nevertheless, chemical refining resulted in high oil losses that could increase the production cost.

Another possible mitigation strategy is the adoption of frying applications in the refining process. A study showed that prolonged frying could reduce 3-MCPDE formation (Chew et al., 2021c). Therefore, prolonged heating during deodorization could help to decompose 3-MCPDE in the oil. However, it was worth noting that this method could result in the degradation of oil quality. Hence, an in-depth study of this method should be investigated. A prolonged deodorization time with a lower deodorization temperature could perhaps reduce 3-MCPDE without compromising the oil quality. Alternatively, the introduction of antioxidants during deodorization could minimize oil oxidation and slow down 3-MCPDE formation. A study showed that the addition of TBHQ (66 ppm) and alpha-tocopherol (172 ppm) into oil under heat (230 °C) for 30 min resulted in 44% and 22% of reduction of 3-MCPDE (Li et al., 2015). Typically, palm oil is rich in antioxidants, and most of these compounds are removed during refining (deodorization). As such, there is a possibility to explore the application of these abundantly available antioxidants in palm oil for 3-MCPDE mitigation. For instance, process modifications to retain these compounds in the oil or adding back the antioxidants into the oil could be a new strategy for 3-MCPDE mitigation.

It is well noted that not all mitigation strategies, especially the laboratory and pilot scales, could be successfully implemented commercially. Various aspects such as feasibility, cost, sustainability, scalability, and implementation risk should be considered for commercialization. The overall potential mitigation strategies for 3-MCPDE mitigation in the palm oil supply chain are summarized in Fig. 7. The mitigation should begin from upstream, in which the oil palm plantation estate could improve the quality of palm fruits in order to reduce the amount of solid impurities with chlorine sources. Subsequently, the mill could improve its processes to produce high-quality CPO with low DAG and TC contents. Finally, the reduction of 3-MCPDE formation can be made by improving the refining process conditions. With the integration of these mitigation strategies, the 3-MCPDE issue in the palm oil industry could be resolved. Additionally, high-quality oil products with exceptionally low 3-MCDPE (<0.35 ppm) could also be produced for speciality fat products such as infant formula.

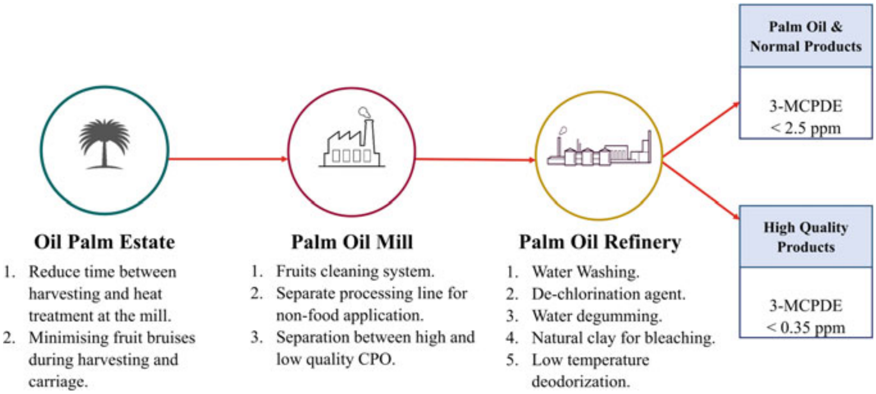

Fig. 7 Proposed mitigation strategies for 3-MCPDE throughout the palm oil supply chain

5 Conclusion

According to studies, DAG and chlorinated compounds in CPO promote the 3-MCPDE formation during the thermal treatment in the refining stage. Although the 3-MCPDE is formed during refining, chlorinated compounds are detected in palm fruits and CPO in the estate and oil mill. Therefore, an integrated mitigation strategy across palm oil processing could be a promising approach to address the 3-MCPDE issue. The mitigation strategy is proposed to start in estates and mills by addressing the precursors of 3-MCPDE. This approach is followed by the improvement of refinery process conditions focusing on minimizing 3-MCPDE formation. These findings lead to various possible mitigation strategies. By incorporating precursors reduction and process modification techniques, the overall content of 3-MCPDE in the palm oil could be reduced. This will help to produce food that complies with 3-MCPDE's dietary limit set by the authorities.

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