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PRINCIPAL FORMATION AND MITIGATION STRATEGIES FOR 3-MCPDE IN PALM OIL PROCESSING

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Abstract

Palm oil is the most produced and consumed vegetable oil worldwide. Recently, the palm oil industry has received attention from food safety authorities due to the presence of 3-monochloro-1, 2-propanediol esters (3-MCPDE) in the refined oil. The European Food Safety Authority (EFSA) proposed to limit the presence of 3-MCPDE by 2.5 ppm in palm oil from year 2021 onwards. Various studies showed that the 3-MCPDE is a process contaminant induced by heat during the refining stage, in the presence of its precursors, such as diacylglycerol (DAG) and chlorine in palm oil. Research works have been conducted to mitigate 3-MCPDE formation. This paper provides an overview of the 3-MCPDE formation, mitigation initiatives and industrial practices in addressing the 3-MCPDE issue.

1. Introduction

The global production of edible oil reached 209 million tonnes in 2020 with the production of approximately 75 million tonnes of palm oil¹. Palm oil is the most consumed vegetable oil; its production volume is expected to rise owing to population growth and expanding economy of the developing countries. Palm oil is mainly used for food, while a small fraction as biofuel and oleochemicals. The oil palm (*Elaeis guineensis*) fruits are harvested, and the oil extracted from its mesocarp is known as crude palm oil (CPO)². The CPO can then be refined for food applications. The refined palm oil can be fractionated into two main fractions known as palm olein and palm stearin. Their application in food production differs due to the differences in physical and chemical properties^{3,4}. Palm olein is mainly used for

frying and cooking, whereas palm stearin is used for shortening and margarine productions^{3,5}. Due to the extensive food applications, food safety and security of palm oil are vital to the industry.

Keywords

palm oil, 3-MCPDE, chlorine, diacylglycerol, food safety

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Table 1: General composition of CPO

Composition	Value
Triacylglycerol (TAG)	88 – 95 %
Diacylglycerol (DAG)	3 – 7 %
Monoacylglycerol (MAG)	< 1 %
Free fatty acid (FFA)	1 – 5 %
Moisture	0.1 – 0.2%
Solid Impurities	0.01 – 0.03%
Tocopherols and tocotrienols	500 – 1100 ppm
Carotenoids	400 – 800 ppm
Phytosterols	300 – 600 ppm
Squalene	200 – 500 ppm
Phospholipids	3 – 140 ppm
Metals (Copper and Iron)	1 – 10 ppm
Lipid oxidation products	Traces

Table 2: Quality requirement for crude palm oil in PORAM specification ^{7,8}

Characteristics	Value
Free fatty acid (as palmitic), % max	5.0
Moisture and impurities, % max	0.25
Degree of Bleachability Index, min	2.3
*Chlorine, ppm max	2.0

**Additional quality requirement for CPO by January 2020*

In terms of composition, CPO is mainly made up of triacylglycerol (TAG), diacylglycerol (DAG), monoacylglycerol (MAG), free fatty acids (FFA), and other minor compounds (see

Table 1). As palm oil is mostly used for food applications, the quality of CPO produced must meet a few quality parameters. PORAM specification is the most used quality standard for palm oil trading between millers and

refiners in Malaysia (see Table 2). In short, PORAM specifications cover three main quality parameters of the CPO^{6,7}:

- i. hydrolytic stability (through the level of FFA content)
- ii. contaminant content (through the amount of moisture and solid impurities)
- iii. oxidative stability (through the deterioration of bleachability index (DOBI))

Lately, the quality of the produced palm oil has received attention from the food safety authorities due to the presence of process contaminant such as 3-monochloro-1, 2-propanediol esters (3-MCPDE) in the edible oil. In 2016, the European Food Safety Authority (EFSA) issued an extensive report about the health consequences of this process contaminant, which is a potential human carcinogen^{9,10}. Studies found that refined palm oil contains the highest amount of 3-MCPDE^{11,12,13}. EFSA proposed to set a Tolerable Daily Intake (TDI) limit of 0.8 µg/kg body weight for 3-MCPDE⁹. Meanwhile, The Joint FAO/WHO Expert Committee on Food Additives (JECFA) proposed Provisional Maximum Tolerable Daily Intake (PMTDI) of 4 µg/kg body weight for 3-MCPDE, either single or in combination with the glycidyl esters¹⁴. Therefore, EFSA has proposed to limit the presence of 3-MCPDEs in palm oil to 2.5 ppm and below from 2021 onwards¹⁵. Various studies showed that CPO with high levels of FFA, DAG and traces of chlorine promote the formation of 3-MCPDE during the refining stage^{16,17,18}. In response to these research works; Malaysian authorities have recently proposed the limit of chlorine content in CPO to be below 2 ppm (see Table 1). On the other hand, the limit of 3-MCPDE in refined palm oil should be kept below 2.5 ppm by year 2021 and 1.25 ppm by year 2022⁸.

In the following section, factors that cause the formation of 3-MCPDE will be discussed. This is followed by the section that discusses initiatives taken to mitigate this process contaminant through the minimisation of 3-MCPDE's precursors, with the manipulation of refining process conditions.

2. Formation and factors affecting chlorine precursors for 3-MCPDE in palm oils

The formation of 3-MCPDE in edible oils (including palm oils) occurs during the deodorisation process. This is mainly due to the high-temperature treatment of oils in the presence of chlorine^{19,20}. Destailats et al.¹³ demonstrated that thermally treated (235 °C) triolein oils model showed increased formation of 3-MCPDE with the addition of chlorine (such as organochlorine pesticide and FeCl₂). Mechanism of 3-MCPDE formation supported the involvement of oils as TAG, DAG and MAG with chlorine through SN2 nucleophilic substitution and free radical reaction^{12,21}. Various studies have shown that higher DAG and MAG in model oil increased formation after thermal treatment simulating deodorisation condition^{22,23}. Model oil studies conducted with only TAG or without partial acylglycerol also showed the formation of 3-MCPDE. This supports the involvement of TAG as acylglycerol precursor for 3-MCPDE formation along with DAG and MAG^{13,24}. However, it has been reported that partial acylglycerols are more reactive than TAG in acting as acylglycerol precursor for 3-MCPDE formation, while DAG is regarded as the most reactive precursor (among the acylglycerols)^{22,24}. As CPO has an abundance of acylglycerol (>99%), 3-MCPDE formation in palm oils is hence limited by the chlorine content^{24,25}. The latter affects the formation of 3-MCPDE in palm oil during the refining stage. Study shows that the total chlorine content in CPO has a direct correlation with 3-MCPDE in refined palm oil with R² > 0.73, as shown in Figure 1¹⁸. Nagy et al.²⁶ discovered that there are more than 200 monochlorinated organic compounds along with some chlorinated inorganic compounds such as FeCl₂, FeCl₃, MgCl₂ and CaCl₂ in CPO. Organochlorine compounds had also been identified as lipid constituents produced naturally and showed potential to liberate chlorine during deodorisation to form 3-MCPDE^{18,26}. The fact that organochlorine compounds function as chlorine precursors for 3-MCPDE was further confirmed. A model by Tiong et al.¹⁸ showed that an addition of enriched organochlorine compound mixture yielded higher 3-MCPDE formation after thermal treatment.

Figure 1: Regression of 3-MCPDE in refined bleached deodorised palm oils relative to the total chlorine content in CPO¹⁸

It was reported that organochlorine compounds were biosynthesised in oil palm fruits. These compounds were then extracted together with CPO from the mesocarp during processing in the mill^{18,26}. During palm oil production, organochlorine compounds are observed to partition and enriched in certain oil fractions such as those from steriliser condensate (SC) and empty fruits bunch (EFB) (Figure 2). Typically, the extracted crude oil (known as undiluted crude oil) from the press

machine contains a high amount of impurities. Hence, hot water (known as dilution water) is introduced to facilitate the oil clarification process. In some mills, SC and EFB liquor are used instead of hot water. Studies show that the combined use of SC and EFB liquor as dilution water exhibited the highest amount of the chlorine content in the CPO (see Figure 3²⁷). It is also worth mentioning that dilution water plays a role in reducing the chlorine content in water.

Figure 2: Sphingolipid organochlorine content in various oil products

Figure 3: Total Chlorine in CPO and 3-MCPDE content in its refined oil for various types of dilution water commonly used in the oil mill²⁷

Apart from the acylglycerol and chlorine precursor, other notable factors that affect 3-MCPDE formation include the content of minor oil constituents and the refining conditions. The oil pH would affect the formation of 3-MCPDE as acidic condition would promote and activate acylglycerol for chloride nucleophile attack to form 3-MCPDE¹². Reduction of oil pH by addition of disodium carbonate and sodium bicarbonate can reduce the formation of 3-MCPDE from 7 ppm to less than 3 ppm in the model oil study. Although FFA does not act as a direct precursor for 3-MCPDE formation, but it affects the pH value of the oils. Addition of 10 % lauric acid to oils reduces the pH of oils to yield a definite but small increase of 3-MCPDE formation²².

The existence of chlorine during refining was possibly originated from the addition of materials or chemicals. Bleaching clay and water had been reported to contain 60 - 152 ppm of total chlorine content²⁸. Chlorine in the bleaching clay was contributed by acid activation using HCl. Hence, manufacturers are providing bleaching clay with low chlorine content through acid activation using non-chloride acid. Bleaching earth, either natural or acid-activated that does not contain chlorine would assist in reduction of 3-MCPDE formation. Besides, the acid used for CPO degumming may also contain a trace level of chlorine. However, the chlorine content in acid used for degumming is negligible because its content is lesser than 20% of the total chlorine in CPO (range in 8-29 ppm)²⁸. Furthermore, the amount of acid used for degumming is relatively small. CPOs were refined through a

physical approach that does not have direct contact with water except chemical refined oil. Therefore, cross-contamination of chlorine from water is not a major concern. However, CPO that is exposed to water such as during water degumming had been reported to be beneficial in reducing 3-MCPDE formation^{29,30}. Therefore, the understanding of precursor and factors that affect 3-MCPDE formation are important for the oil palm industry to devise effective mitigation strategy, and intervention to ensure 3-MCPDE in palm oil products for food consumption would not expose consumers to higher than PMTDI set by food safety and health regulatory bodies.

3. Mitigation Strategies

External factors such as soil, irrigation, and pest control have different impacts on the chloride content of the oil palm trees. Other factors such as harvesting techniques, handling, and transport are also potential sources for chloride contamination in fresh fruit bunches (FFB) and CPO. During harvesting and evacuation, some solid impurities that are attached to FFB are processed together to produce CPO. These solid impurities consist of predominantly fibrous materials and soil and are the source of chlorine. Consequently, chlorine is then carried over to CPO during processing. Since the potential source of chlorine contamination is known, reduction in these sources helps to reduce the chloride concentration in CPO, and subsequently helps to mitigate 3-MCPDE. Although the most significant reduction effort is the mitigation done in the precursor from oil, the reduction of chlorine sources at the feedstock is expected

to further reduce contamination. Therefore, cleaning palm fruits (with water) before extraction is the first crucial step to minimise the carryover of chlorine sources. The results indicate a significant reduction of chlorine content in CPO produced from washed palm fruits, which subsequently lowers the 3-MCPDE of the refined oil. The palm fruit bunch and fruit cleaning systems developed by Sime Darby Plantation in 2018 were reported to produce CPO with chlorine content as low as 0.5 ppm^{31,32}.

Besides, the SC and EFB oils contain high chlorine content. The mixing of these oils in CPO during dilution (water) will eventually increase its chlorine content²⁷. To mitigate these issues, segregation of these two streams from primary CPO production (as non-CPO recovery oils) has been proposed. In short, the system recovers the SC and EFB oils with the sludge separator in separate processing line for non-food application. With the implementation of this system, approximately 30% reduction of chlorine and 3-MCPDE were recorded for CPO and its refined oil respectively. It is worth noting that this system also improves the overall quality of the CPO, particularly on the contaminants, hydrolytic and oxidative stabilities of CPO³³.

In the earlier discussion, the formation of 3-MCPDE requires a chlorine source that could easily dissociate to create the required chloride ions. Therefore, there is a need to include a process that decreases the chlorine concentration to avoid 3-MCPDE formation during the refining process. Destailats et al.¹³ reported that the chlorinated compounds in the plant material are polar in nature. Hence, it can be removed effectively from the plant material using liquid-liquid extraction with a

polar solvent solution. Given this positive finding, verification trials were conducted by Sime Darby Plantation with water washing and the result showed that the concentration of total chlorine in washed CPO is 50% lower than unwashed CPO (unpublished). Meanwhile, the 3-MCPDE in RBDPO obtained from the washed CPO had showed a reduction of 53% as compared to unwashed oil (see Table 3).

Another potential mitigation approach that is worth consideration is dechlorination of CPO prior to refining process. This pre-treatment process uses sodium metabisulfite (SMBS) as the dechlorination agent. SMBS is mixed with heated CPO followed by filtration to remove spent SMBS. As a result, the dechlorinated CPO has chlorine content which is lower than 2 ppm³⁴. Both water washing and dechlorination agents are found to be effective in reducing water-soluble inorganic chlorinated compound of CPO. However, the remaining challenge is to remove oil-soluble chlorinated compounds.

While most mitigation efforts focused on chlorine reduction, there is no emphasis on other factors that contribute to 3-MCPDE formation. Therefore, the authors suggested that the mitigation efforts to be extended to FFA, DAG and MAG reduction. This mitigation could be performed by improving harvesting and processing techniques to reduce hydrolysis reaction that produces FFA, DAG and MAG in CPO. The reduction of these compounds could eventually lessen the 3-MCPDE formation during refining. This mitigation strategy has been recently reviewed by Chew et al. (2021)³⁵.

Table 3: Effect of CPO Washing on Chlorine content and 3-MCPDE on its refined oil. Results represent the means $\pm$ standard deviation of the mean value (n = 3).

Refinery feed	Sample	chlorine, ppm	3-MCPD Ester, ppm
A	Control	5.17 $\pm$ 0.57	4.34 $\pm$ 0.13
	Washed	2.58 $\pm$ 0.39	2.03 $\pm$ 0.11
B	Control	3.55 $\pm$ 0.24	2.60 $\pm$ 0.09
	Washed	1.78 $\pm$ 0.12	1.26 $\pm$ 0.15

Another important mitigation strategy is the prevention of 3-MCPDE formation at refining stage. Some researchers have suggested the use of water degumming as an alternative washing process in oil refining^{36,37,38}. At this stage, chlorine-containing polar precursors of the 3-MCPDE can be removed from the oil. However, water degumming is less effective in reducing phosphatides, iron and colour as compared to the standard acid degumming procedure of CPO.

Interestingly, higher amount of water usage (1 - 5%) during water degumming could further remove the impurities and achieve the red colour specification of below 3.0³⁸. Besides, natural clays would be suggested as an alternative medium to acid activated bleaching clay due to its neutral pH that does not promote formation of 3-MCPDE. Nevertheless, natural clays usually have a lower surface area that might affect refined oil quality, as the adsorptive capacity of sorbent minerals depend on their surface area, particle size distribution, porosity, and surface acidity. Furthermore, research works on the use of magnesium silicate as bleaching clay was proposed, which shows significant reduction of 3-MCPDE compared to activated and natural clay, especially with water degumming³⁷.

Deodorisation process is the critical factor for the formation of 3-MCPDE. Note that this is a temperature-dependent process. High

temperature deodorisation may cause the reactions of chlorides in oils with acylglycerols. A study was carried out and it proved that the formation of 3-MCPDE is directly correlated to deodorisation temperature. In the study, CPO (with 4.2% FFA content and 4.75 ppm chlorine) was exerted between deodorisation temperatures of 230°C and 260°C for 90 minutes. Expectedly, the highest amounts of 3-MCPDE were observed in the samples that were deodorised at 260°C (see Figure 4).

The various possible mitigation options to mitigate the 3-MCPDE issue throughout the palm oil supply chain is summarised in Figure 5. The initiative should start from the upstream where the oil palm estate can improve the quality of palm fruits by reducing its sources of chlorine. The production of high-quality CPO with low DAG and chloride content through mill process improvement can be performed as subsequent mitigation. Lastly, the reduction of 3-MCPDE formation can be achieved through the improvement of refining conditions. With all combined efforts, the 3-MCPDE issue in palm oil industry can be addressed.

4. Conclusion

Palm oil processing starts from oil palm plantation where the palm fruits are harvested. The harvested fruits delivered to mills for oil extraction before it is refined into edible palm oil. Studies show that the presence of the

Figure 4: Effect of deodorisation temperature on the 3-MCPDE formation. Results represent the mean values and error bars indicate the standard deviation of the mean (n = 3).

Figure 5: Proposed mitigation strategies for 3-MCPDE issue in the palm oil supply chain.

3-MCPDE precursors such as DAG and chlorine content in the CPO promotes the 3-MCPDE formation during the refining stage (due to heat induction). Integration of mitigation strategies across the 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 the 3-MCPDE, particularly the chlorine sources and DAG formation. The approach is followed by the improvement of refinery process condition focusing on minimising the 3-MCPDE formation. Through the extensive research on 3-MCPDE, the principle formation, its factors, and precursors have been discovered. These findings lead to various possible mitigation strategies, and by combining all these efforts, the process contaminant issue can be addressed.

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