3-MCPD Ester in Palm Oil Production Chain: Sime Darby's Experience

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ABSTRACT

3-MCPD is a processing contaminant that occurs in food in free (diol) as well as in an esterified (with fatty acids) form. Potential safety issues in relation to this compound was first raised in 2016, and since then the urgency to limit the formation of 3-MCPD ester in the edible oil industry especially palm oil became the main priority due to the contaminant toxicity related to food safety. It is known that 3-MCPD ester formation is a multivariate problem influenced by many factors such as heat, chloride ions, acylglycerols content and acidic processing chemicals. Therefore, designing efficient mitigation strategy requires more than one modification in the entire palm oil supply chain process.

INTRODUCTION

3-monochloropropane-1,2-diol (3-MCPD) is known as a processing contaminant especially in food containing acid-hydrolysed vegetable protein (acid-HVP), such as soy and oyster sauce which occurs in food in its free (diol) form. 3-MCPD has also been found in unprocessed and processed food as well as in various food ingredients. The presence of 3-MCPD in food was first described by Velisek *et al.,* in 1979. The presence of 3-MCPD has been detected in treated foodstuffs such as malt products (Divinová *et al.,* 2007), roasted coffee (Doležal *et al.,* 2005), breadcrumbs (Hamlet and Sadd, 2004) and french fries (Svejkovská *et al.,* 2004).

Along with free 3-MCPD, Zelinkova *et al.,* (2016) reported the presence of 3-MCPD ester in refined, bleached, and deodorised vegetable oils in 2006. Ramli *et al.,* (2011) reported that 3-MCPD ester were detected in the range of <300 (LOQ) to 2462 in majority refined oils. High variations of 3-MCPD ester levels are found between different vegetable oils in which soybean, rapeseed, coconut, kernel and virgin olive oil were found to have the lowest esters level <1.0 mg kg^{-1} (*Table 1*). Palm oil, especially palm olein contained the highest 3-MCPD ester at more than 2.5 mg kg^{-1}. Due to high level of this contaminant in palm oil, the urgency to bring down the level of 3-MCPD ester is required. Thus, this paper summarises the factors that affect the formation of 3-MCPD ester, overview of palm oil milling and refining processing effect on 3-MCPD ester formation and discussion on mitigation strategies to lower the level of this contaminant.

CHLORIDE

It is known that chlorides or other chlorinated compounds are the main precursor for the formation of 3-MCPD ester. Source of chlorine in palm oil might originate from fertilisers (KCl, NH_4Cl), water, flocculants that used in water treatment or pesticides (Nagy *et al.,* 2011). Due to this, chlorine might have accumulated in palm fruits during oil palm maturation process. In addition, additional chlorine might come from leaves, soil and debris that were in contact with the fresh fruit bunch (FFB) during harvesting and transportation. Other possible origin

TABLE 1. 3-MCPD ESTER IN REFINED OILS AND FATS

Level	Concentration, mg kg^{-1}	Types of vegetable oils and fats
Low	0.2-1.0	rapeseed, soyabean, coconut, kernel sunflower oil, virgin olive oil
Medium	1.01-2.5	safflower, groundnut, corn, pomace olive
High	>2.5	palm oil, palm olein

of chloride processing material or chemical used during milling and refining.

Study was carried out on the correlation between total chloride (TC) in crude palm oil (CPO) with 3-MCPD ester concentration in refined bleached deodorised palm oil (RBDPO). Significant ($p<0.05$) and positive correlation

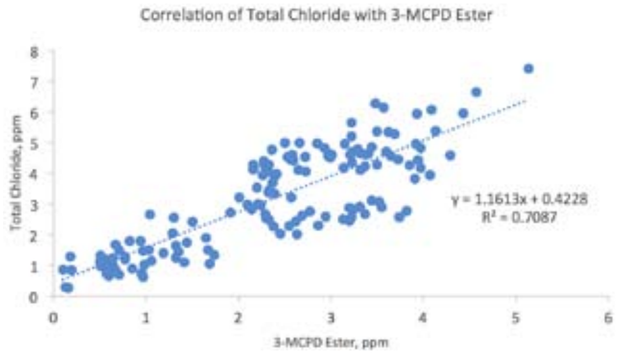

Figure 2. Regression of 3-MCPD esters in RBDPO relative to total chloride content in CPO (n = 145).

between both parameters with r=0.7 were observed which indicates that when TC concentration in CPO is high, 3-MCPD ester in RBD palm oil will be high (*Figure 2*).

Aside from chlorinated compounds, there are other factors responsible for formation of 3-MCPD ester such as FFA which contributes to low pH oil, processing chemicals and high temperature during deodorisation process.

Free Fatty Acids (FFA) and Acylglycerol

TAG hydrolysed to FFA, DAG and monoacylglycerols (MAG). Hrncirik (2011) studied the effect of FFA and DAG on the formation of 3-MCPD ester and concluded that DAG and FFA may play a role in 3-MCPD ester formation even though the results showed poor correlation between the two factors. A study conducted by Ermacora and Hrnncirik (2014), concluded that partial glycerides (FFA, MAG and DAG) are not the critical factors that contribute to the final concentrations of 3-MCPD ester. Conversely, the current study showed FFA has weak but significant ($p<0.001$) correlation towards 3-MCPD ester formation due to low pH oil contributed by hydrogen ion which act as catalyst for 3-MCPD ester formation *(Figure 3)*.

Processing Chemicals

Other possible factors that contribute to the formation of 3-MCPD ester are dosage and type of degumming acid and bleaching earth. Additional 3-MCPD ester can be formed under acidic conditions. In a study carried out by Ramli *et al.,* (2011) it was reported that, phosphoric acid with significance amount of chloride used in the degumming process may increase the formation of 3-MCPD ester. Apart from that, bleaching earth with high acidity also resulted in high formation of 3-MCPD ester. Bleaching earth is activated by either sulfuric acid or hydrochloric acid, providing a larger surface area for adsorption. This acidic earth has the ability to donate proton and cause the protonation of the organic compound.

Additionally, a study carried out to determine TC content in acidic bleaching earth showed that the TC level of beaching earth varies between 11-700 ppm.

PALM OIL MILLING PROCESS

To mitigate this issue, it is important to understand the effect of milling process on the introduction of 3-MCPD ester precursor inside CPO. Therefore, a study to investigate the introduction of TC in crude oil extraction process during the sterilisation, dilution and in CPO was

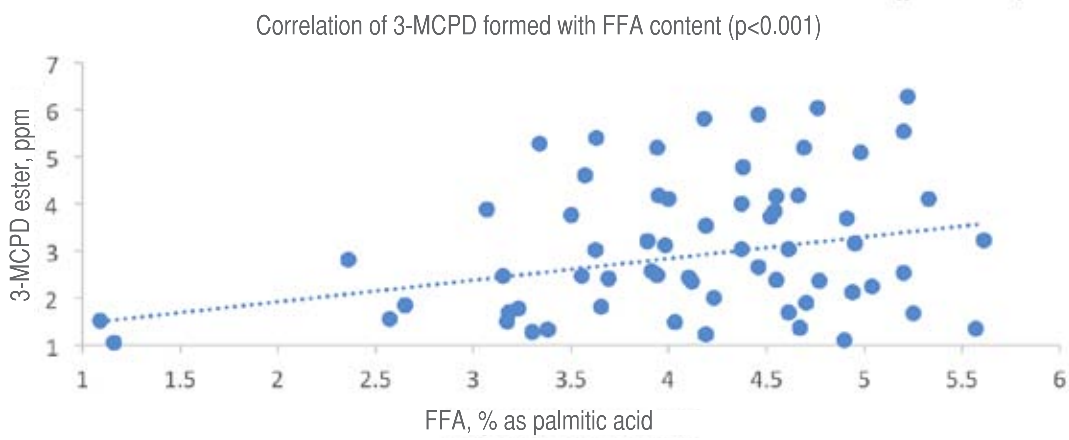

Figure 3. Regression of crude palm oil (CPO) free fatty acid (FFA) with 3-MCPD ester in RBDPO.

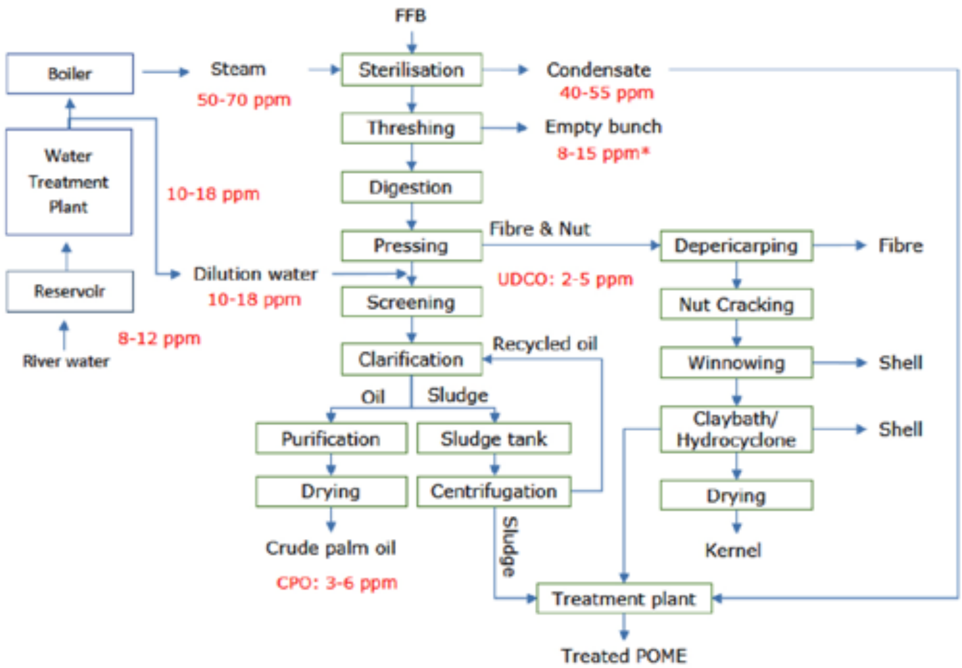

Figure 4. Investigation of total chloride (TC) in processing materials during palm oil milling process.

conducted. From the study, it was found that high TC level was detected in steam at 50-70 ppm (n=12) SCO (n=24), dilution water (n=24) and EFB liquor (n=24) as shown in *Figure 4*.

VEGETABLE OIL REFINING

The study on 3-MCPD ester proved that refining process especially deodorisation gave significant impact to its formation. Therefore, to achieve effective reduction of 3-MCPD ester, modification on refining process is required. In general, refining is a purification process to remove or reduce unwanted compounds such as FFA, oxidative products, phospholipids, impurities and undesirable odour, flavour and colour. There are two types of refining processes - chemical refining and physical refining (*Figure 5*). Deodorisation is the last step of the chemical refining, whereas steam distillation is the final physical refining process whereby the oil temperature can increase above 240°C and undesired side reactions formed some unwanted substances. The major difference between the two routes is how the FFA are removed. For physical refining, most of the FFA are removed in the deodorising unit by using vacuum steam distillation principle. Physical refining requires high-temperature deodorisation and the oil must be carefully degummed and bleached before entering the deodorising unit. In contrast, majority of FFA in chemical refining is removed during alkali neutralisation step. This resulted in production of soap stocks, thus making the next step, washing, prior to bleaching process relevant. Since most of the FFA are removed during the neutralisation process in chemical refining, the deodorisation process can be carried out at lower temperature of max 240°C.

Study by Sime Darby Research (SDR) on the differences of 3-MCPD ester level from both chemical and refining process found that lower level of 3-MCPD ester was observed in neutralised bleached deodorised palm oil (NBDPO) produced from chemical refining than in RBDPO as shown in *Table 2*. This may be due to several factors such as alkaline pH introduced by Sodium hydroxide (NaOH) that used in neutralisation process, precursors removal during water washing process and lower deodorisation temperature.

TABLE 2. 3-MCPD ESTER IN CHEMICAL AND PHYSICAL REFINING OIL

Sample	FFA, (%)	Total Chloride, (ppm)	3-MCPD Ester, (ppm)
CPO	4.15	3.81	
RBDPO	0.04		3.47
NBDPO	0.03		1.12

MITIGATION OF REDUCING 3-MCPD ESTER IN PALM OILS

It is known that it would be better to remove the reactive chlorine species at earlier process rather than from the

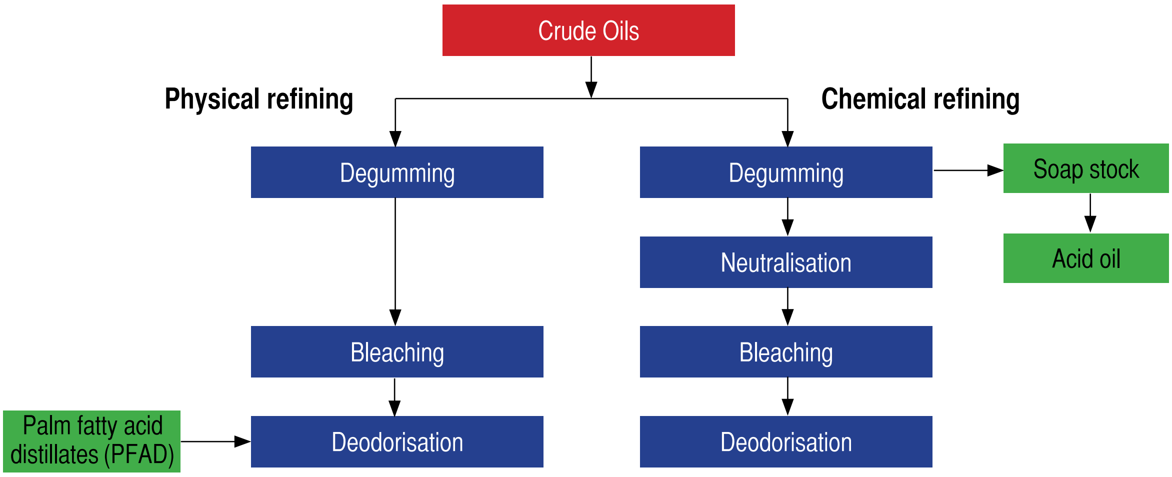

Figure 5. Chemical and physical refining process.

CPO as it may convert to more polar compounds during processing. Therefore, cleaning and water washing of fresh fruit bunch prior to sterilisation is one of the option. Trial on FFB showed that this process is able to reduce TC in CPO which subsequently reduce the concentration of 3-MCPD ester in RBDPO. This technology is patented by Sime Darby Plantation in 2018 with publication No. WO/2019/027315.

The formation of 3-MCPD ester requires a chlorine source that easily dissociate to create the required chloride ions. Therefore, there is a need to include the process to reduce the chloride concentration to avoid 3-MCPD ester formation during refining. Nagy *et al.,* (2011) in his study observed that the chlorinated compounds in plant material are polar in nature which effectively can be removed using liquid-liquid extraction with a polar solvent solution. Considering these findings, lab trials were conducted by SDR on water washing in CPO. Laboratory experiments showed that the concentration of TC in washed CPO (1.2 ± 0.02 ppm) are lower than unwashed CPO (2.4 ± 0.05 ppm). The 3-MCPD ester in RBDPO obtained from washed CPO was 1.11 ppm, as compared to 2.4 ppm in the RBDPO obtained from unwashed CPO which showed a reduction of 53% of 3-MCPD ester.

Other than water washing, dechlorination of CPO as pre-treatment process before refining is one of the possible mitigation strategy to be considered. This pre-treatment process used declorination agent which was selected from sodium metabisulfite, sodium bisulfite, sodium thiosulfate, sulfur dioxide, sodium ascorbate, hydrogen peroxide, sodium nitrite, sodium sulphite and calcium thiosulfate which was mixed with heated CPO before filtration to produce dechlorinated CPO which contain <2 ppm TC. This process is patented by Sime Darby Plantation in 2017 with publication no. WO2018182396A1.

Other significant mitigation strategy is the prevention of 3-MCPD ester formation during refining processing. Ramli *et al.,* (2011) suggested water degumming as an alternative treatment in oil refining in where it can act as washing process. During this step, chlorine-containing polar precursors of the 3-MCPD ester can be removed from the oil. The researchers also suggested the use of natural clay due to its neutral pH. However natural clay usually has lower surface area that might affect the refined oil quality. Zulkurnain *et al.,* (2012) proposed the use of magnesium silicate as bleaching clay which can give the greatest reduction of 3-MCPD ester compared to activated and natural clay, especially with water degumming. Magnesium silicate has larger surface area and active basic site that is responsible for adsorption or degradation of 3-MCPD ester.

Deodorisation process is a critical factor for the formation of 3-MCPD ester, which is temperature dependent. The deodorisation temperature plays a big role possible influence on the formation of 3-MCPD ester. The high temperature may cause reactions of chlorides with acylglycerols in oils in which 3-MCPD ester generated at temperature as low as 180°C (Seefelder *et al.,* 2008).

Oil refining is a combination of degumming, bleaching and deodorisation processes. A combined mitigation strategy may be promising for limiting the final concentrations of 3-MCPD ester in refined oil. The possible mitigation through the supply chain is illustrated in *Figure 6*.

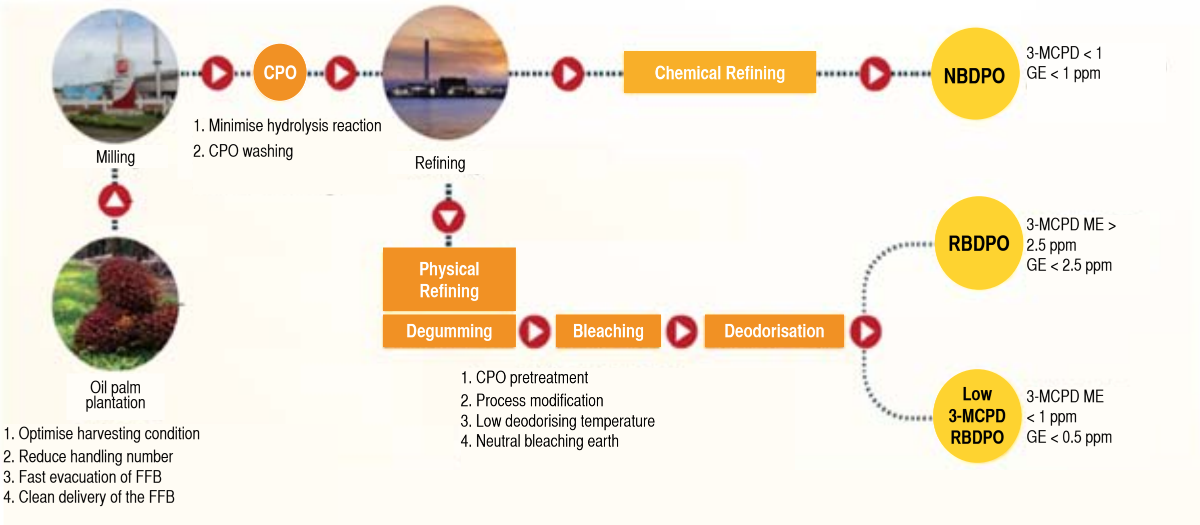

Figure 6. Possible mitigation for 3-MCPD ester issue in palm oil supply chain.

CONCLUSION

There are numerous studies and efforts in the industry to eliminate or prevent the formation of 3-MCPD. These include careful selection of raw materials and modification of the refining conditions. Although chlorine substances have become the limiting factor of the formation, the generation of 3-MCPD ester is also affected by refining conditions. Changes in refining process are crucial to mitigate the 3-MCPD ester formation. However, since oil refining is a combination process of degumming, bleaching and deodorisation, several possible mitigation strategies need to be applied which requires a combined mitigation strategy that may be promising for limiting the final concentrations of 3-MCPD ester in refined oil.

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