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Effects of Degumming and Bleaching on 3-MCPD Esters Formation During Physical Refining

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Abstract Crude palm oil (CPO) was physically refined in a 200-kg batch pilot refining plant. A study of the possible role of degumming and bleaching steps in the refining process for a possible critical role in the formation of 3-chloropropane-1,2-diol (3-MCPD) esters was evaluated. For the degumming step, different percentages of phosphoric acid (0.02–0.1%) as well as water degumming (2.0%) were carried out. Six different types of bleaching clays, mainly natural and acid activated clays were used for bleaching process at a fixed dose of 1.0%. Deodorization of the bleached oils was performed at 260 °C for 90 min. Analyses showed that 3-MCPD esters were not detected in the CPO. Phosphoric acid degumming (0.1%) in combination with acid activated clays produced the highest levels (3.89 ppm) of 3-MCPD esters in the refined (RBD) oil. The esters were at the lowest levels (0.25 ppm) when the oil was water degummed and bleached with natural bleaching clays. However, the refined oil qualities were slightly compromised. Good correlation of 0.9759 and 0.9351 was obtained when concentration of the esters was plotted against acidity of the bleaching earths for the respective acid and water degumming processes. The findings revealed the contribution of acidic conditions on the higher formation of 3-MCPD esters. In order to lower the esters formation, it is important to reduce acid dosage based on the crude oil qualities or to find alternatives to acid degumming process. Neutralization of the acidity prior to deodorization was effective in reducing the formation of 3-MCPD esters.

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Introduction

Crude oils are refined in order to remove undesirable substances before consumption. During refining, minor components including oxidation products, free fatty acids (FFA), phospholipids, pigments, trace metals and other impurities are removed. There are two methods commonly applied to refine oils and fats, namely chemical (alkali) and physical refining. In alkali refining, sodium hydroxide was used to neutralize the degummed oil before bleaching and deodorization. Most of the FFA are removed during neutralization. Oil losses of up to 30% are expected when alkali refining is used [1]. The process is also expensive, time consuming, energy intensive and contaminates the environment due to the effluent. Alkali refining is usually applied to soft oils (unsaturated) which contain high amount of phosphatides. These oils include soybean, sunflower, cottonseed, peanut and rapeseed oil. Physical refining is a more environmental friendly method and operates at a lower cost. Steam is used to remove the FFA

during deodorization. Reduced amount of chemicals are applied and the oil losses are significantly lower as compared to chemical refining [2].

Beside removal of unwanted substances, oil refining also removes part of valuable components such as tocols, carotenoids, oryzanol and phytosterols [3, 4]. Side reactions mainly isomerization of unsaturated fatty acid occurs during refining especially at the deodorization step as it involves high temperatures. As a result, *trans* fatty acids may form as well, especially in soft oils. Intra-molecular rearrangements of fatty acids are also reported in oils subjected to drastic refining conditions [1].

Recently, refining processes have been linked to the formation of 3-chloropropane-1,2-diol (3-MCPD) esters [5, 6]. The presence of bound 3-MCPD in oils and fats and its relation to the refining processes were first reported by Zelinková et al. [7] in late 2006. They found free the 3-MCPD content in oils ranging from <3 (LOD) to 24 μg/kg, while, higher 3-MCPD esters were detected in the range of <300 (LOQ) to 2,462 μg/kg in the majority of refined oils, including refined olive oils. High variations of 3-MCPD ester levels have been reported between oils, and appeared higher in refined palm oils [8, 9].

Franke et al. [10] conducted a chemical refining of palm and rapeseed oils to study the influence of refining process on the formation of 3-MCPD esters. The studies showed that in the post-refining of a pre-refined palm oil, 3-MCPD esters content decreased from 6.1 to 2.5 mg/kg after the bleaching step, but increased to 4.6 mg/kg after deodorization. Meanwhile, chemical refining of CPO showed an elevated amount of 3-MCPD esters only after deodorization (4.4 mg/kg). Levels of 3-MCPD esters increased after deodorization of crude rapeseed oil, and was significantly lower (1.0 mg/kg) than that of palm oil.

Several claims were made on the critical effects of deodorization step in the formation of the 3-MCPD esters [10–12]. High deodorization temperatures were found to facilitate the esters formation. Study by Hrncirik and van Duijn [6] indicated that 3-MCPD esters and the related compounds (glycidyl esters) are formed during deodorization, but that it is independent of bleaching versus neutralization/bleaching and deodorization conditions, and that oil types play a more critical role in determining the tendency to form such contaminants. Indeed, it seems that some oils have higher tendency to form 3-MCPD esters and glycidyl esters. The reason for this is yet to be fully understood, although some have alluded to the possible presence of precursor or catalyst, which may activate the reaction [13].

In palm oil refining, high deodorization temperature is utilized, as it takes out the FFA as well as colored components and volatile compound. As most researchers have studied the deodorization conditions (temperature and

time) as the main critical factor, we decided to examine other possible conditions in refining which may also enhance the formation of 3-MCPD esters during the deodorization step.

Hence, both degumming and bleaching steps are looked into. A 200-kg batch pilot refining plant was used for the study as it provides the most realistic information, and could represent the actual conditions of commercial plants and their practices.

Materials and Methods

Materials

Crude palm oil (CPO) was purchased from a local mill in Banting, Selangor, Malaysia. Different types of bleaching earths (natural and acid activated) were obtained from the following manufacturers; Taiko Bleaching Earth Sdn. Bhd., Parit Buntar, Perak, Malaysia; Wantotik Clay Products Sdn. Bhd., Kota Kinabalu, Sabah, Malaysia; Hudson Phosphate Additives Sdn. Bhd., Petaling Jaya, Selangor, Malaysia and Oil Dri Corporation, USA. Phosphoric acid (85% concentration) used for the degumming process was purchased from Merck, Darmstadt, Germany and all reagents used for analyses were of analytical grade.

Pilot Plant Refining

Pilot plant refining of palm oil was conducted at the High Oleic Pilot Plant, MPOB Head Office. The 200-kg per batch pilot plant comprises a degumming tank, bleacher, filter press and a deodorizer. Prior to each refining trial, the CPO was heated to 60 °C in an oven to totally melt the oil before its being transferred into the degumming tank. For the degumming process, 2.0% of distilled water (water degumming) or in the case of acid degumming experiments, 0.02–0.1% of phosphoric acid was added to the oil at temperatures of 80–85 °C. The retention time was 15 min. The degummed oil was then transferred into a bleacher and bleached with 1.0% bleaching clay for 30 min at 105–110 °C under vacuum (50 mbar). After filtration with a filter press, the bleached oil was deodorized under vacuum (3–5 mbar) at 260 °C for 90 min. The CPO, bleached oil (BPO) and refined, bleached and deodorized oil (RBD PO) samples were collected for analyses.

3-MCPD Esters Analysis

The analysis of the 3-MCPD esters was carried out in accordance to the Federal German Institute for Risk Assessment (BfR) Method 008—determination of 3-MCPD fatty acid esters in edible oils and solid fats by

GC–MS [14]. The internal standard used was deuterated 3-MCPD and the qualifier ions selected were m/z 150 and m/z 201, whereas for the derivatized 3-MCPD, the ions were m/z 147 and m/z 196. Quantification was based on the ratio of m/z 147–m/z 150. It should be noted that the method only analyzed for 3-MCPD esters but not the related compounds (glycidyl esters). All reagents used for the analyses were of analytical grade and purchased from Merck, Darmstadt, Germany. Analysis was carried out in duplicate.

Analysis of Oil Quality

Free Fatty Acid (FFA)

Free fatty acid (FFA) content was determined by titration according to AOCS Official Method Ca 5a-40 [15].

Deterioration of Bleachability Index (DOBI)

Deterioration of bleachability index (DOBI) was analyzed according to Malaysian Palm Oil Board (MPOB) Test Method p2.9:2004 [16]. Crude palm oil was measured in a UV visible spectrophotometer, Lambda 35, Perkin Elmer (Connecticut, USA) using a 10-mm cell. The solvent was iso-octane (Merck, Darmstadt, Germany). The oil sample of 0.1 g was weighed into a 25-mL volumetric flask and the solvent was added. Measurement at 269 and 446 nm was taken. The DOBI was reported as the ratio of absorbance at 446–269 nm.

Color

The color of the refined oil was measured by a Lovibond Tintometer Model F (Wilts, England). The melted oil sample was poured into a 5¼″ cell and the color was measured as described by ACOS Official Method Cc 13e-92 [15].

Trace Metals (Cu, Fe and P)

The oil sample (0.5 g) was weighed in a microwave vessel. 6 mL of nitric acid (65% concentration, super pure grade, Merck Darmstadt, Germany) and 2 mL of hydrogen peroxide (30% concentration, super pure grade, Merck Darmstadt, Germany) were then added. The mixture was digested in an Ethos Mod microwave digester (Milestone, Connecticut, USA) for 1 h and 40 min. After it is cooled, the sample was transferred into a 15-mL sample tube and de-ionized water (resistivity 18.2 mΩ cm) was added.

The trace metals analysis was performed by means of an inductively coupled plasma mass spectrometer (ICP-MS), Elan DRC II, Perkin Elmer (Connecticut, USA). The instrument was first calibrated with an internal standard

Table 1 ICP-MS operating conditions

Perkin Elmer Elan DRC II	
Spray chamber	Cyclonic
Nebulizer	Meinhard®
RF power (W)	1550
Ar (99.997% purity) nebulizer gas flow (L/min)	0.6–0.9
Measures	
Scan mode	Peak hopping
Replicate time (s)	1
Dwell time (ms)	200
Sweeps/reading	10
Integration time (ms)	2,000
Replicates	3
Isotopes	^{63}Cu, ^{56}Fe, ^{31}P

with a linearity of 0.999. The ICP-MS operating conditions are shown in Table 1.

Acidity of Bleaching Clays

The bleaching earth sample of 2 g was weighed into a 250-mL beaker and 100 mL of distilled water was added. The mixture was stirred for 1 min until the clay is well dispersed. The pH of the slurry was measured with a pH meter (Mettler Toledo 320, Shanghai, China).

Statistical Analysis

Statistical analysis was carried out by Microsoft Office Excel 2003. Average of duplicate analysis with standard deviation (±SD) was reported.

Results and Discussion

Degumming is a preliminary step in the refining process where, the gums, often in colloidal forms, are conditioned by either water or acid to enable the precipitation from the oil. In soft oils, gums are quite substantial (several percent) and are removed by both water and acid degumming, while in palm oil the gums being much lower, are removed by dry degumming process. Dry degumming consists of mainly use of phosphoric acid, followed by bleaching step. The gums are therefore removed at the filtration step, together with the spent earths. No water is added, unlike degumming of soft oils. Because of limited amount of phospholipids, they are also not recovered.

The amount of phosphoric acid used depends on the oil quality and varies from 0.05 to 0.15%. It must be noted that too much phosphoric acid may cause darkening of the oil, thus a balance is usually required, where, the dosage of
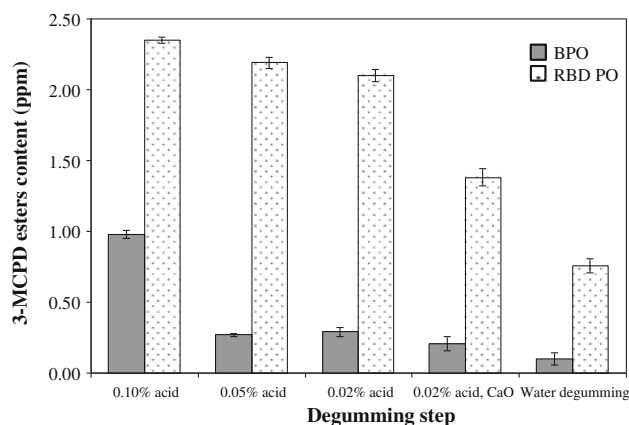
Fig. 1 Effect of degumming process on the formation of 3-MCPD esters in the bleached (BPO) and refined oils (RBD PO)

bleaching clay may have to be increased to enable efficient removal of the excess phosphoric acid. Some refiners practice neutralization of the phosphoric acid with calcium oxide or calcium carbonate prior to bleaching. In this study, the CPO was obtained fresh from production at a local mill, and quality reflected the mainstream of CPO used by refineries. The DOBI was 2.60, while FFA was 3.70%.

Effect of phosphoric acid as degumming agent on the formation of 3-MCPD esters is illustrated in Fig. 1. There is significant reduction of 3-MCPD esters in bleached oil when lower dosage of phosphoric acid is used for degumming. However, deodorization effect is more significant than bleaching, as seen in the relatively higher 3-MCPD esters.

In the study, natural bleaching earth was used for the bleaching. The 3-MCPD esters level in refined oil was much lower when the degummed oil was neutralized with 0.2% calcium oxide (CaO). The CaO in powder form was added after the degumming step and the neutral oil was washed with hot water. Neutralization eliminates the acidic conditions by forming soapstock. In addition, other components were also removed when the neutralized oil is washed by water to eliminate the soapstock. Dijkstra [17] reported that the soapstock contains soaps, phosphatides, sodium phosphate in solution and precipitated earth phosphates. Indeed, other impurities are removable in this manner, and more often than not, neutralized oils are generally more stable than physically refined oils. As such, the lower esters formation in the neutralized oil may also be due to precursors being removed after neutralization, or that the acidic conditions have been neutralized prior to deodorization.

Further reduction of the esters was also observed when water was used for degumming (Fig. 1). In this case, the 3-MCPD esters were significantly lower for both bleached and RBD oil, indicating that acidity of the phosphoric acid had an effect on their formation. The chloride content of

phosphoric acid is found to be low (2 ppm max.), thus the increased formation is not a result of any high chloride content in the phosphoric acid.

Table 2 shows the properties of the earths used in the experiments. These earths were chosen as they represent some of the types used by refineries. The neutral earths have a pH closer to 7. The effect of bleaching earths (natural type vs. acid) upon the formation of 3-MCPD esters was also monitored. Plots of the 3-MCPD esters content in the refined oil versus acidity of bleaching earth for standard (Fig. 2) and water degumming (Fig. 3) processes illustrated good correlations with coefficients of 0.9759 and 0.9351, respectively. Bleaching earth with higher acidity (lower pH values) resulted in a higher formation of 3-MCPD esters, irrespective of type of degumming whether it was acid or water. Most of the higher acidity earths have been activated with acid. Bleaching clays are acid activated by either sulfuric acid or hydrochloric acid to increase their surface (150–350 m^2/g) and thus providing a larger surface area for adsorption. On the other hand, natural clays usually have a lower surface area (40–160 m^2/g) but may have sufficient pore volume and pore size for adequate adsorption [18, 19]. The high acidity

Table 2 Properties of bleaching earths

Bleaching earth	pH	Moisture content (%)	Type	Remarks
A1	5.8	14.8	Bentonite	Acid activated[a]
A2	5.8	14.0	Bentonite	Acid activated[a]
A3	5.3	14.0	Bentonite	Acid activated[a]
N1	6.6	14.0	Bentonite	Natural
N2	7.7	8.0	Attapulgite	Natural
N3	6.6	15.5	Bentonite	Natural

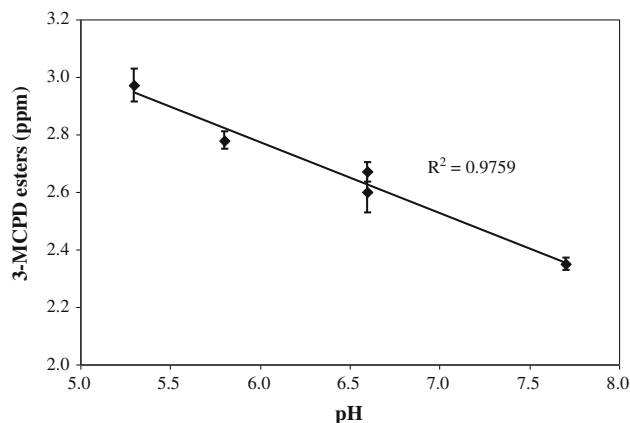[a] Acid activation by sulfuric acid

Fig. 2 Correlation between acidity of bleaching clays with 3-MCPD esters content in refined oil for standard process (0.1% H_3PO_4 for degumming)
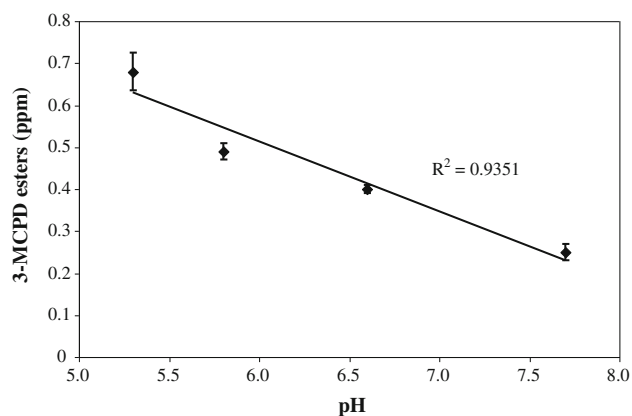
Fig. 3 Correlation between acidity of bleaching clays with 3-MCPD esters content in refined oil for water degumming (2.0% H_2O)

Table 3 Levels of 3-MCPD esters in refined oil for standard and water degumming processes

Process	3-MCPD esters content (ppm)			
	Max	Min	Average	$\pm$SD
Standard				
Acid activated ($n = 7$)	3.89	2.18	2.82	0.57
Natural ($n = 7$)	2.67	1.60	2.21	0.37
Water degumming				
Acid activated ($n = 3$)	1.50	0.49	0.91	0.52
Natural ($n = 6$)	0.76	0.25	0.49	0.22

(low pH) of acid activated clays may be the inherent acid sites of clays or due to residual mineral acid retained on the earth after washing. Good washing procedures generally are effective in removing residual mineral acid. Table 3 which tabulates the levels of 3-MCPD esters in oils refined with natural and acid activated clays for both water and acid degumming processes supports the correlation. The higher formation of the esters in acid activated clays may be due to its acidity. The ability of acidic clays to donate protons can cause protonation of organic compounds, and catalyze many organic reactions [20]. In this case, it may appear that there is protonation of the acylglycerols, and in the presence of chloride, result in the 3-MCPD esters.

There are four proposed mechanisms involving S_N2 nucleophilic attack of chloride ions on acylglycerols, either by nature of the substrate or the leaving group [21]. Two of the proposed mechanisms involved direct nucleophilic attack by the chloride ion at the glycerol carbon atoms carrying either an ester group or a protonated hydroxyl group. The other two proposals postulated the formation of an intermediate acyl oxonium or an epoxide before nucleophilic attack by the chloride ions. Our study showing the effect of acidity on the formation supports the direct nucleophilic substitution mechanism, which is considered as a plausible mechanism [22–24].

As water degumming and use of natural clay are possible options for processing CPO with lower 3-MCPD esters, an attempt was made to check this out by processing and analyzing the oil quality. The quality of the crude and refined oils is presented in Table 4. It shows that only the standard process could produce a refined oil quality acceptable according to trading specifications of Palm Oil Refiners Association of Malaysia (PORAM) [25]. PORAM specifications for refined oil are 3.0R for color and 0.1% max for FFA among others. The standard process gives an acceptable color of 2.1R, while, water and no degumming processes gave RBD oils of 3.5R and 4.7R, respectively. Water degumming affects the refined oil quality due to insufficient removal of iron and phosphorus compounds. Although the levels are just slightly higher than the RBD oil from the standard process, nevertheless, the color of RBD oil is adversely affected. Omitting the degumming step retained considerably high amount of phosphorus and resulted in the darker color of the refined oil. Phosphatides which are not properly removed in the early stages of physical refining darken during deodorization and leads to the darkening of the oil and off-flavor problems [1]. As such, only good or average quality oils could be water degummed because of their lower phosphatide content. Furthermore, the high residual iron in the un-degummed oil correlates with poor oil keepability [26]. In order to balance other quality characteristics with low 3-MCPD esters in RBD oils, there is a need to reconsider the degumming step, and the use of highly acidic activated earths. Not carrying out degumming is not a possibility, but was

Table 4 Quality analyses of crude (CPO) and refined palm oil (RBD PO)

Oil sample	FFA (%)	DOBI	Color	P	Fe	Cu
Crude palm oil (CPO)	3.7 max	2.60	–	14.9	4.0	0.08
RBD PO						
Standard process	0.04	–	2.1R	4.4	0.7	0.06
Water degumming	0.02	–	3.5R	5.0	0.9	0.06
No degumming	0.02	–	4.7R	13.0	4.5	0.07

considered in the experiment to show the effect of acidity on the formation of the 3-MCPD esters.

Conclusions

The formation of the 3-MCPD esters is found to be affected not only by high temperatures, but also by acidity during the refining process. While changes in high temperatures and retention time during deodorization may be possible mitigation steps to consider, the dosage of degumming acid and its removal prior to bleaching and deodorization steps, could be further looked into as other avenues of reducing the problem. In addition, reducing levels of non-hydratable phospholipids in CPO through early sterilization of fruit bunches upon harvesting would result in ease of gum removal during refining, and requiring less phosphoric acid.

Natural bleaching clays and acid activated clays with more neutral pH should be considered as options to reduce the formation of 3-MCPD esters. For low quality oils, neutralization could be performed to obtain acceptable quality oils with low 3-MCPD esters content. In order to reduce the 3-MCPD esters formation comprehensively, the routine practice of harvesting in plantations, and early arrival of fresh fruit bunches for the sterilization process in the oil mill must also be emphasized. Production of high quality CPO with less gum helps in managing the refining process more efficiently. However, little is known about the "catalyst" in CPO which seems to cause a higher formation of the esters, and research should be focused on its identification and removal for better control of 3-MCPD esters and other heat-derived contaminants.

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