The Possible Mitigation Procedures for the Reduction of the Formation of Chloropropanol Esters and Related Compounds

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INTRODUCTION

Fatty acids esters of chloropropanols are food-processed contaminants formed as a result of high temperature reactions. They have been found in a wide variety of food products (Weißhaar, 2011). In many of these foods, the free form of the ester is present as well. While the free form is a known carcinogen, the toxicological significance of the esters is still being evaluated. In 2006, Zelinkova *et al*. (2006) first reported high levels of 3-Monochloropropane-1,2-diol esters (3-MCPD esters) in some edible oils. Since then, many research publications and presentations in conferences have referred to the higher levels noted in refined oils, particularly palm oil (Weißhaar and Perz, 2010; Kuhlmann, 2011).

So, what is possibly in palm oil which, under high temperature processing results in the formation of 3-MCPD esters and glycidyl esters? The picture is increasingly becoming clearer as many researchers have worked on this topic. The formation of 3-MCPD esters occurs between lipids (triacylglycerols, diacylglycerols, monoacyglycerols) and chlorides at high processing temperature of 200°C and above. As crude palm oil is extracted at low temperatures (<100°C), these compounds are not detected. The refining of crude palm oil involves a physical process, where the crude oil is first degummed, bleached and deodorised at a high temperature of 260°C. The less common alkali refining process uses a lower deodorisation temperature of 240°C. We now know that even at 220°C, some formation of 3-MCPD esters and glycidyl esters already occurs.

The formation of 3-MCPD esters requires the presence of chlorides. Hrncirik and Duijn (2011) showed that the chloride content in palm oil varies from 3-10 mg kg^{-1}, while studies by Nagy *et al.* (2011) have shown the presence of organochloro- compounds in crude palm oil. In the work by Destaillats *et al.* (2012), it was shown that the triacylglycerol (TAG) species are the more reactive species involved in the formation of 3-MCPD esters with the organo-chlorines. On the other hand, diacylglycerol (DAG) has a more prominent role in the formation of glycidyl esters. As palm oil is known to have a higher concentration of DAG, it would therefore appear that the pieces of puzzle are now in place to form a clearer picture. However, there are still pieces that do not seem to fit; as were found samples that had reasonably high DAG levels, and yet had low and even undetectable glycidyl esters, when subjected to high temperature.

Many possible options have been put forth for the reduction of these contaminants. These range from upstream approach (dealing with the crude oil), modification of refining and downstream approach (cleaning up the refined oil). This paper reviews the practical aspects of some of these mitigation ap-

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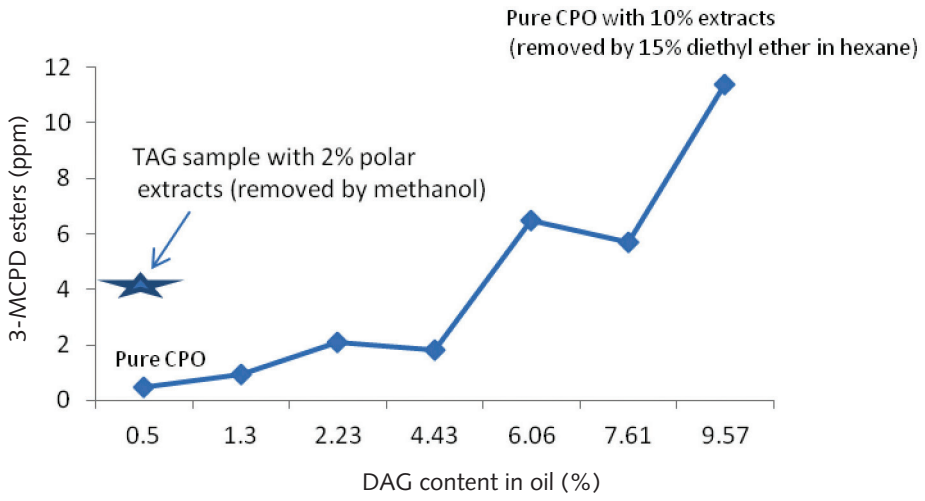
proaches, with a view to offering possible solutions to the issue.

EXAMINING CRUDE PALM OIL (CPO) QUALITY

Several researchers (Matthäus *et al*., 2011; Rahn and Yaylayan, 2011) have suggested that DAG is one of the possible components reactive enough to form MCPD and glycidyl esters. In spite of good correlation figures shown of the relationship when DAG was added to oils (Matthäus *et al*., 2011), in practice the trend for the correlation between the DAG content of CPO and its tendency to form these esters is not so clear cut. Hrncirik and Ermacora (2010) discussed the possibility of other factors being involved, and that the DAG content was not the limiting factor; an extraction of polar compounds in CPO by column chromatography followed by an addition of these compounds to another clean CPO sample revealed results shown in *Figure 1*. The addition of polar extracts of crude palm oil obtained by eluting a column of oil with 15% diethyl ether in hexane, showed increasing formation of 3-MCPD esters.

Although these extracts contain high amounts of DAG, it cannot be concluded that DAG is the component affecting the 3-MCPD esters formation, as there may be other polar components in the extracts as well, such as chlorides. In addition, a purified oil from the column (TAG) when added with a 2% polar extract which was removed from column chromatography of palm oil using only methanol, also showed higher 3-MCPD esters when heated. As the pure TAG and the methanol eluted polar extracts contain no DAG, it can be concluded that DAG is not necessarily the lipid component involved in the formation. It confirms Hrncirik's work, who concludes that DAG is not the limiting factor impacting the formation, as many other polar compounds are present in the extracts as well. Furthermore, some oils with high DAG contents have not shown very high MCPD esters.

Another factor in the equation is obviously the chloride contents in the oils. Chlorides are ubiquitous in nature, and are found in water, acids, bleaching clays, *etc*. and in the oil as well. Nagy *et al*. 2011 and Craft *et al*. (2012a) described the type of chlorides present in palm oil. According to them, inorganic compounds of ferric and ferrous chlorides, magnesium and calcium chlorides exist in the oil. Not surprisingly, iron compounds have long been known to be present in crude oils. Another source of the chlorides apparently comes from organic forms. Their presence is not surprising, given that plants need chlorides for their growth, and chlorides are present in soil, water and fertilisers. The total chlorides in CPO averaged at about 16.5 ppm, with a range of 8-29 ppm for 11 samples. *Table 1* shows the disappearance of chlorides from the oil in the mill extraction process. It is perhaps possible that efficient removal of chlorides from the oil can be further fine-tuned in the mills. Further centrifugation in the laboratory could actually reduce chloride content from 6.5 to 1 ppm. Among chemicals used in processing, bleaching earths



Note: Purified oil obtained by column chromatography; 1st extract – TAG oil, 2nd extract – polar extract containing DAG, 3rd extract – polar extracts obtained with methanol.

Figure 1. 3-MCPD esters formation in purified palm oil with addition of its polar components obtained via column chromatography.

TABLE 1. REMOVAL OF CHLORIDES (PPM) IN CRUDE PALM OIL PRODUCTION

Sample	Mill 1	Mill 2
CPO before dilution	588	1088
CPO after dilution	677	16
CPO after purifier	17	6.5

contain the most chlorides (51-152 ppm), while citric acid and phosphoric acids contain much lower contents (1-2 ppm). So far, no correlation has been observed between chlorides in bleaching earths and formation of 3-MCPD esters, and it is assumed that the chloride present in the oil is the more critical chloride to watch out for.

UPSTREAM APPROACHES

Sime Darby Malaysia Berhad filed a patent WO 2011/002275 A1, whereby fresh fruit bunches (FFB) are harvested to produce an oil of free fatty acids (FFA) less than 1.5 wt.% and DAG less than 5.5 wt.%, and the crude oil is fractionated prior to refining. The main claims are in the harvesting and collection of fruits for immediate extraction such that oil quality is excellent, as defined by FFA and other parameters. Fruit processing, otherwise follows the norm for palm oil extraction. In this process, loose fruits are not acceptable as they contribute to higher FFA and DAG levels. The process would incur high cost due to the harvesting of slightly under-ripe fruits and the rejection of loose fruits, resulting in high oil losses. For large corporations, these loose fruits can be channeled to other mills for the production of CPO to be utilised for biodiesel production, *etc.* It is not clear how fractionation can assist in reducing chloropropanols, except in partitioning the precursors into liquid and solid fractions, and therefore being less available in each fraction for the formation of 3-MCPD esters during refining.

In the paper by Craft *et al.* (2012b), they described several strategies for mitigation of MCPD diesters, such as by application of glycerol and ethanol to oil during deodorisation, ethanol-water (1:1) washing of CPO prior to deodorisation, and also water washing of palm fruit pulp (mesocarp). Both glycerol and ethanol together with ethanol: water washing method resulted in a lowering of about 25%-35% in the MCPD formation, while the water washing of fruit pulp was found to be the most effective, with 95% reduction. The high cost of both ethanol and water wash, and glycerol and ethanol would deter refiners from trying these two procedures. Water washing of the pulp appears to be the better option as seen from the significant reduction.

However, considering the voluminous amount of oil palm pulp in any mill, water washing of the pulp does not appear practical. Besides, the emulsification properties of phospholipids, and other components present would cause difficulties in separation of water from oil. The better option here is to utilise water washing at the stage in palm oil mill, before separator and before drier. This allows the water to remove chloride precursors as well as separate easily with centrifuges and then dried. In this way, there is minimal additional cost. Data on water washing of CPO carried out in this research is tabulated in *Table 2*.

MODIFICATION IN THE REFINING PROCESS

An obvious consideration is the lowering of deodorisation temperature. What is the present state of technology for a lower deodorisation temperature process which would yet be able to produce low colours, FFA and odourless oil? Some options are available for dual temperature operations, (low-high, high-low) which may help to reduce deodorisation time at the higher temperature range. In addition, stronger vacuum systems may be useful if a high temperature is used for the operation. Lower deodorisation temperature will therefore prevent the formation of 3-MCPD esters, particularly if other precautions are also taken in degumming and bleaching processes.

WO/2010/063450 provides a method for reducing the 3-MCPD content in refined oils by degumming with either water or acid and bleaching earth added. In addition, water can be added to the acid at the degumming stage, followed by bleaching with

TABLE 2. WATER WASHING EFFECT ON CRUDE PALM OIL

Type of sample	3-MCPD esters level (ppm)	3-MCPD esters level after heat test (ppm)
CPO 1	0.263 (± 0.177)	5.061 (± 0.475)
After washing 1	< LOD	0.6915 (± 0.026)
After washing 2	< LOD	0.646 (± 0.028)
CPO 2	< LOD	3.007 (± 0.035)
After washing 1	< LOD	0.6065 (± 0.067)
After washing 2	< LOD	0.537 (± 0.027)

Note: LOD= 0.25 ppm.

suitable earths. The inventors showed that without adding in the degumming agent and bleaching earth, 3-MCPD formation is high (5.50 µg kg^{-1}), and that phosphoric acid degumming without bleaching earths, in contrast to water degumming resulted in even higher formation (11.80 µg kg^{-1} *vs.* 6.15 µg kg^{-1}). These findings have been corroborated by Ramli *et al's* (2011) study. The difference lies in the type of bleaching clays, whereby WO/2010/063450 recommends a certain brand of earth.

Work by Ramli *et al.* (2011) examines other aspects of refining which contribute to increasing levels of 3-MCPD esters and have found that high acidity from degumming acids and acid activated clays enhances the formation of 3-MCPD esters during deodorisation. From this study, it is recommended that for good quality crude palm oils, a lower dose of degumming agent and natural bleaching earths could help provide a refined oil with lower 3-MCPD esters. However, with poorer oil quality, more degumming agent and highly acid activated earths are generally required. This might work against producing oils with low 3-MCPD esters as acidic conditions tend to enhance formation. Thus, the recommendations are best applied to generally better quality oils. If acidity is retained in the oil after bleaching, higher 3-MCPD esters will be formed during deodorization. It may be helpful to neutralise the acidity by adding calcium carbonate to the bleaching process or to the degummed oil. Another aspect of the study uses water as the degumming agent in place of acid. This reduces the formation by about 60% especially when combined with low pH earths. However, it is noted that only with excellent crude oil quality is this process feasible, as the water degumming procedure is not sufficient for oils having high iron and phosphorus contents. Thus, refined, bleached and deodorised palm oil (RBDPO) may not be able to achieve the required specifications under such circumstances. On the other hand, if water degumming is combined with some Trisyl silica, improvements in removal of metallic impurities such as copper and iron are better.

Another two patents filed in 2011, were by Nestec S.A. described processes of modifying current refining practices. In the WO/2011/009841 application, an ion exchange resin or a carboxymethyl cellulose is contacted with the oil. In the description, at least three adsorbents are required, *viz a viz* 0.5% Trisyl silica, 2% bleaching earth, and varying amounts of ion exchange resin or carboxymethyl cellulose. In pack bed form, contacting time of 1-5 hr had been given as an example, while in batch process, dosage of between 1%-20% has been recommended. Another embodiment of the process also involves the use of an inert gas such as nitrogen in the stripping step before or during deodorisation. Similarly, a co-patent application WO/2011/009843 described the use of inert gas as a stripping agent either before or during the deodorisation step. How and why this works is not very clear, presumably, the inert gas prevents the direct contact of the chloro-compound with the oil. The use of three types of adsorbents would be costly and deter refiners from adopting the process. In

addition, ion exchange resins have strong amine odour, which may be imparted to the oil, and would need further deodorisation. Furthermore, high oil loss would be incurred, depending on amount of adsorbents used.

DOWNSTREAM APPROACHES

Downstream approaches take the form of either adsorbents or possibly enzymes. The use of adsorbents was described by Strijowski *et al.* (2011) and other several patent applications, while the use of enzymes were described by Kasai *et al.* (2006) and Bornscheuer and Hesseler (2010). Enzymatic approaches require several different enzymes for final conversion of the monochloropropanol fatty acid ester to glycerol. While effective in the laboratory, the high cost of enzymes, and the possible modification in composition of the oil substrates, as well as high oil losses, make such approaches non-viable on an industrial scale.

Patent Application WO201104 0539 on the method for reducing chloropropanols and formative substances thereof, glycidol fatty acid esters, in glyceride oils, uses silica gel and/or a basic activated carbon with the decolorised and deodorised oil in a solvent medium. The solvent would have to be removed, in a solvent distillation process. The reduction of glycidol esters occurs through the contact of the deodorised oil with an acid.

WO2011/005081A1 also describes a similar type of process for removing unwanted propanol components from unused triglyceride oil, by contacting refined oils with a silicate adsorbent. The silicate is preferably of neutral to basic type, of which magnesium silicate is highlighted as one of the preferred silicate. The dosage of the silicate is described to be between 0.3%-10%, and preferably at less than 5% of the oil. Examples given use about 2% silica. Contact time range between 5 and 200 min, preferably within 60 min. According to the inventors, at least 50% reduction of 3-MCPD esters can be achieved, leaving the oil with less than 50 μg kg^{-1}.

Another example of the use of silica is also given by Archer Daniels Midland Company (WO 2011/069028 A1). In this application, gylcidyl esters reduction is the main focus of the inventors. A wide range of possible procedures were described, ranging from using silica, enzyme, low temperature deodorisation, deodorisation with either ethanol, carbon dioxide or nitrogen sparge, contacting the refined oil with an acid, and re-bleaching. Generally, some or all of the steps are similar to the ones reported above. Among the methods given, contacting with Magnesol R60™ and re-bleaching are the most effective ways of removing or reducing glycidol esters from refined oils. However, interestingly enough, the inventors gave two contrasting examples of the effect of using Magnesol R60™. In one case, treating refined soyabean oil spiked with glycidol esters of 13.6 ppm with Magnesol R60™ was able to reduce the levels down to less than 0.1 ppm. However, if refined and deodorised palm oil is treated with the adsorbents and then re-deodorised, there is increase in glycidyl esters instead. If adsorbents impart an odour to the oil, this process may not be very feasible, without re-deodorisation. The other steps such as chemical interesterification and enzyme treatment will change oil composition and properties and can only be used if such results are desired. Contact with an acid needs the removal of traces of acid. Ethanol, carbon dioxide or nitrogen sparging are expensive steps to consider, as is the use of adsorbents.

CONCLUSION

Mitigation steps for the reduction of 3-MCPD esters and glycidyl esters can involve costly procedures, which, oil refiners or food product manufacturers can ill adopt. Approaches that are more practical are necessary in the search for ways to prevent or reduce the formation of 3-MCPD esters. Past research has shown that most processes used thus far, involve costly procedures requiring high doses of adsorbents and longer reaction time consequently resulting in lower throughputs, and oil losses. The more practical steps appear to be upstream approaches, removing precursors in the oil during the extraction process. A simple solution is discussed in the light of various options available. The best option currently appears to be the removal of precursors through a thorough water wash at the mill, or/and with modifications of degumming combined with the use of non-acidic type earths. Removal of precursors such as chlorides can be improved at the mills. Acidic earths may be used, provided the residue acids in the earths have been well removed. Lowering the temperature during deodorisation may be considered, if other quality specifications are

maintained. Finally, for premium oils and sensitive products for infants, adsorbents may provide the answer.

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