The Impact of Various Bleaching Techniques on the Mitigation of MCPDs and the Reduction of GEs

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ABSTRACT

A review of the impact of bleaching processes on the mitigation of 3- monochloropropane-1,2-diol fatty esters (3-MCPDs) and the reduction of glycidyl esters (GEs) in palm oil will be the topic of discussion. Our research has shown that the variables in the bleaching process (including standard bleaching and deodorization, finished oil post bleaching and soft deodorization) have a significant impact on the formation of MCPDs and/or remediation of GEs. Additionally, the effect of various additives employed in the bleaching process on MCPDs and GEs will be discussed.

INTRODUCTION

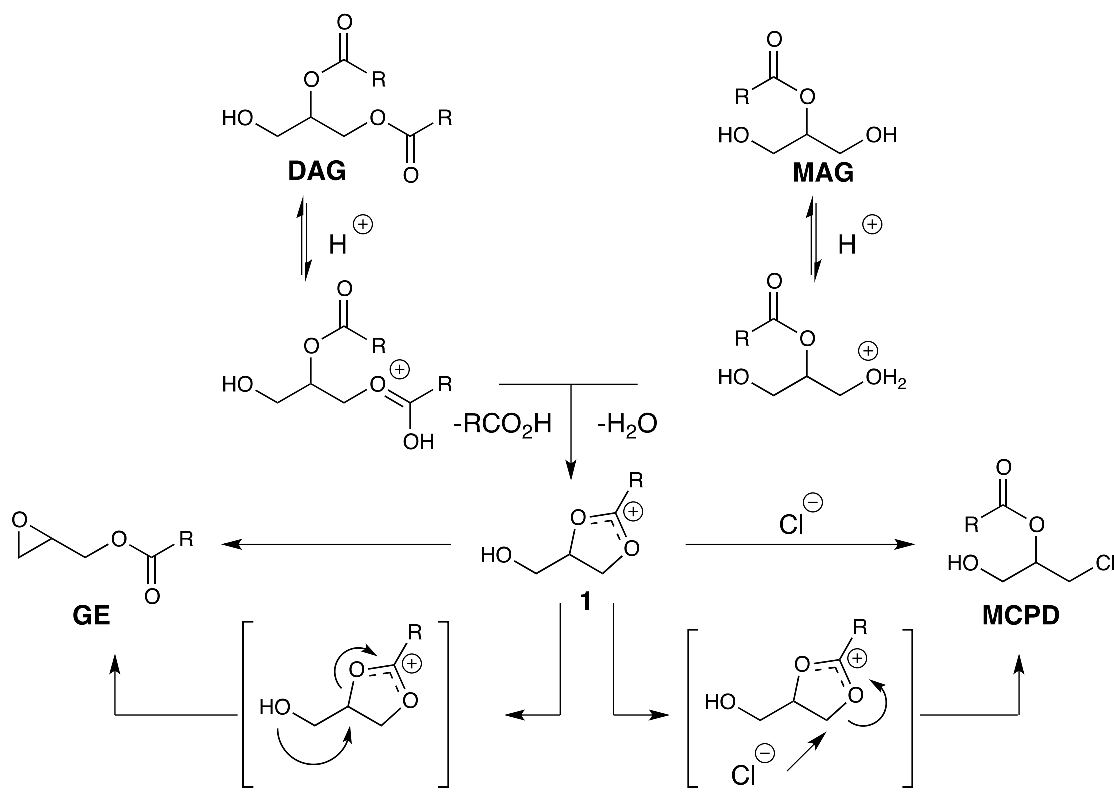
Since the discovery of the toxic and potentially carcinogenic 3-MCPDs and GEs in refined palm oils, these molecules have become closely monitored by the palm oil industry.[1] Target specifications for 3-MCPDs and GEs are typically below 1.0 mg/kg and 0.5 mg/kg, respectively, with more stringent restrictions in place for use in baby foods.[2]

The formation of GEs occurs during the deodorization process at high temperatures (>230 °C) with a strong correlation observed between GEs and diglycerides (DAGs) present in the crude oil.[3] Fortunately, GEs may be reduced in the refined oil through a mild secondary bleaching process utilizing an acidic bleaching clay followed by a secondary soft deodorization.[4]

The formation of 3-MCPDs also occurs during the deodorization process when chloride anions are present at high temperatures (>180 °C) under acidic conditions.[3] The chloride anions may be derived from inorganic chloride species or from organochloride molecules which breakdown during the deodorization process to the reactive inorganic species.[5] Unlike GEs, 3-MCPDs are difficult to remove from refined palm oil, making mitigation the primary strategy for their reduction in refined palm oil.

Various mechanisms for the formation of GEs and MCPDs have been proposed from DAG and MAG precursors.[6,7,8] One plausible mechanism for both the formation of GEs and MCPDs is shown in **Scheme 1**. DAG or MAG precursors may be protonated to give the corresponding acyloxonium ion or the oxonium ion intermediates, which may then undergo intramolecular substitution reactions to provide the cyclic acyloxonium ion intermediate **1** in **Scheme 1**. The MCPDs may then be formed through an intermolecular nucleophilic substitution reaction between the cyclic acyloxonium species and a chloride nucleophile. While an intramolecular substitution reaction followed by proton transfer provides the corresponding GE.

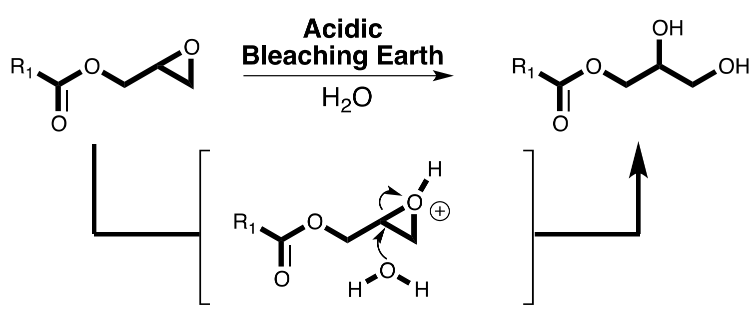
Scheme 1.



Recently there have been strategies put in place in the agricultural stage of the palm oil production process to maximize fruit quality in efforts towards preventing the formation of deleterious precursors for both MCPDs and GEs. Agricultural methods include limiting the entry of chlorine containing substances (fertilizers, pesticides, etc.) into the palm oil life cycle and decreasing the time from harvest to processing to limit the enzymatic cleavage of triglycerides and subsequent rise in free fatty acids.[8]

The palm oil refining process has many processing steps that may be optimized to limit the formation of MCPDs and GEs.[9] Palm oil refining steps may include water washing, degumming, bleaching, and deodorization. Additional post-treatment bleaching and soft deodorization may also be employed to bring the oil within the desired specifications. Water washing crude palm oil (CPO) is a MCPD mitigation technique, which works through the removal of chloride salts present in the extracted oil. Bleaching with larger quantities of bleaching clay is known to impede 3-MCPD formation during deodorizations when sufficient but economically unfavorable clay dosages are applied. Two-stage deodorization has become commonly implemented to mitigate the formation of GEs, where the bleached oil is first heated to 260 °C to strip off free fatty acids and then cooled to <230 °C for deodorization. GEs can also be degraded to MAGs during the additional post-treatment bleaching with an acid-activated bleaching earth (**Scheme 2**). Post-treatment bleaching is followed by a post-deodorization at lower temperatures <230 °C to achieve a minimum GE in the refined oil.

Scheme 2.



MATERIALS AND METHODS

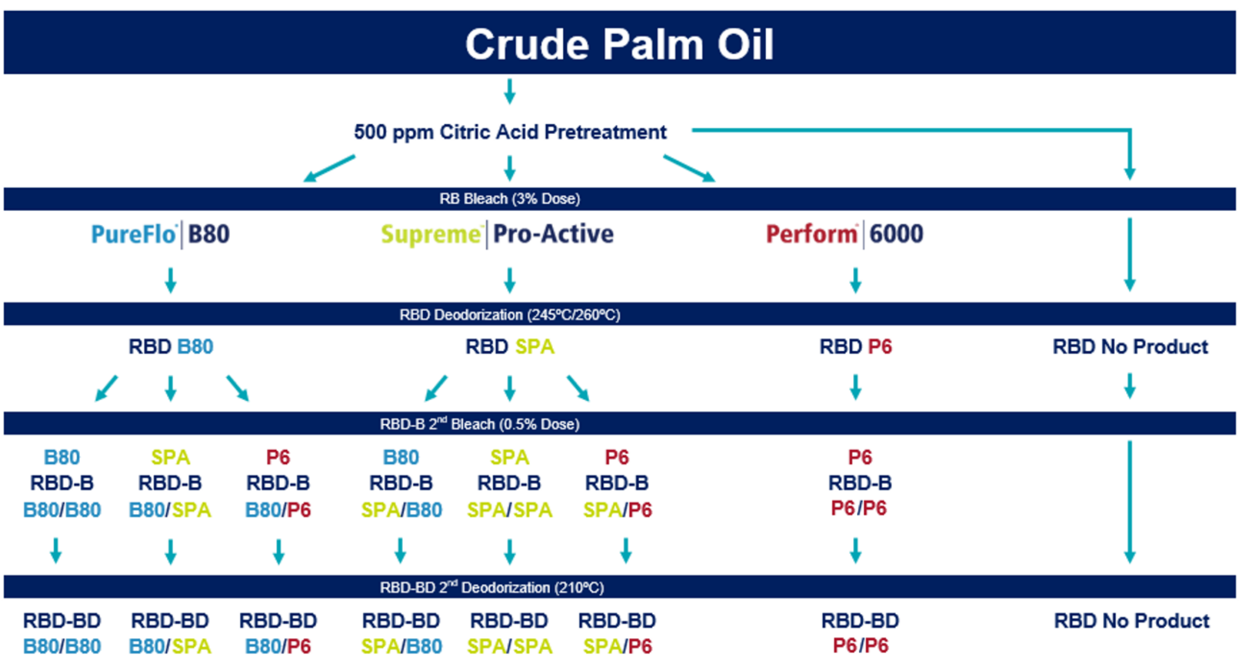
Bleaching Clay Characteristics

The Oil-Dri Corporation of America bleaching clays employed in this study were a highly acidified clay, Perform 6000 (P6) with a pH of 2.8, a mildly acidified clay, Supreme Pro-Active (SPA) with a pH of 3.5, and a non-acidified clay, Pure-Flo B80 (B80) with a pH of 8.4.

Sample Generation

The generation and reduction of 3-MCPDs and GEs were monitored throughout the palm oil refining process. The testing protocol is outlined in Figure 1 below.

Figure 1: Experimental Design Outline



Lab-Scale Bleach

The dry-degummed oil (200 g) was heated to 50 ºC and slurried with bleaching clay. The oil slurry was heated to a maintained temperature of 90 ºC while under a vacuum of 26" Hg for 30 minutes. The heated slurry was then transferred to a Baroid filter press and filtered through a sheet of 541 Whatman filter paper under 40 psi of N_2. The clay dosages of the first and second bleaching were 3% and 0.5% respectively or as indicated in the table.

Micro-Deodorization:

Standard Deodorization (RBD)

In a lab micro deodorizer, 90 mL of bleached oil was heated to a maintained temperature of 245 ºC under a < 2 mmHg vacuum with steam stripping for 30 minutes. The oil was further heated to 260 ºC and maintained for 30 minutes and cooled.

Soft Deodorization (RBD-BD)

In a lab micro deodorizer, 90 mL of bleached RBD oil was heated to a maintained temperature of 210 ºC under < 2 mmHg vacuum with steam stripping for 60 minutes.

RBD Oil

Crude palm oil (CPO) was dry-degummed (using a 50% citric acid solution), bleached, and deodorized. Clay dosage and process conditions were designed to achieve typical oil specifications for palm oil, specifically a 3.0 RBD red color. The dry-degummed oil was bleached with one of the bleaching earths. The samples were then deodorized, creating samples labeled RBD B80, RBD SPA, and RBD P6 (see Figure 1).

RBD-BD Oil

The RBD oils were subsequently post-treated with another bleach and deodorization for GE reduction. The RBD oils were treated with each of the three bleaching earths. The samples were then deodorized, creating samples with every permutation of bleaching earths used (i.e. RBD-BD B80/B80, RBD-BD B80/SPA, RBD-BD SPA/B80) (see Figure 1).

3-MCPD and Glycidyl Ester Analysis

Determination of 3-MCPDs and GEs was based on the AOCS Official Method Cd 29b-13. The derivatives were separated through gas chromatography and analyzed via selective ion monitoring mass spectrometry.

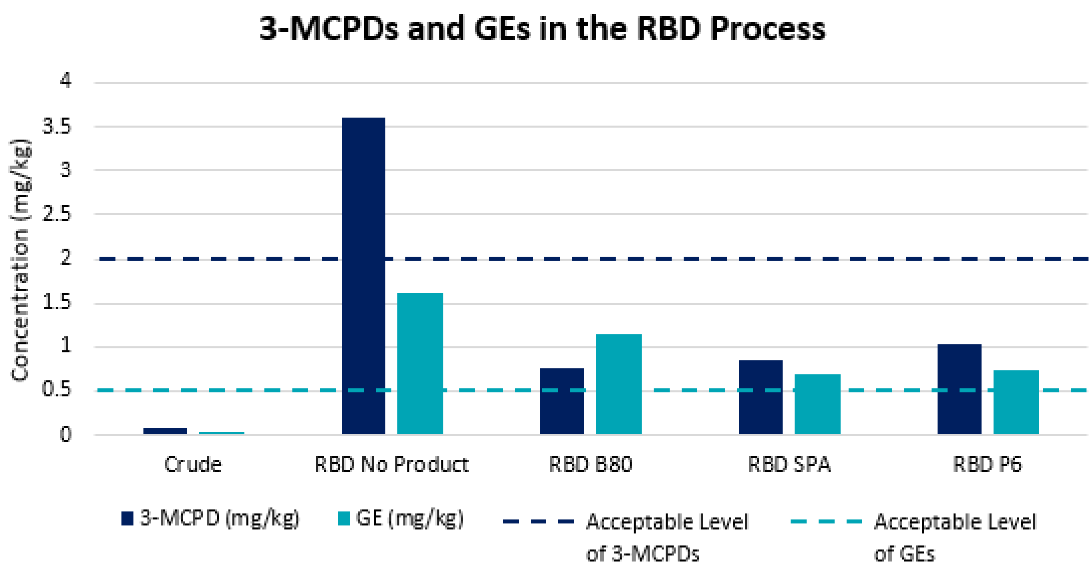
RESULTS AND DISCUSSION

CPO and RBD Oil

Crude palm oil contains little to no 3-MCPDs and GEs with analysis results below the limit of quantification for the analysis (0.1 mg/kg). A reference was used to compare the potential 3-MCPD and GE generation when the oil is processed without using clay to remove the unwanted precursors (See **Figure 2**). Acidified clays further reduced the level of GEs found in the oil but the acidity lead to an increased amount of 3-MCPDs compared to the natural bleaching clay. All three bleaching clays reduced the amount of 3-MCPDs to acceptable levels (< 2 mg/kg), however failed to achieve acceptable levels of GEs (< 0.5 mg/kg) as RBD oils (MacMahon, 2014).

The results established that a direct relationship exists between clay acidity and MCPD formation and an inverse relationship exists between clay acidity and GE formation or stability.

Figure 2: 3-MCPD and GE levels during the RBD Process

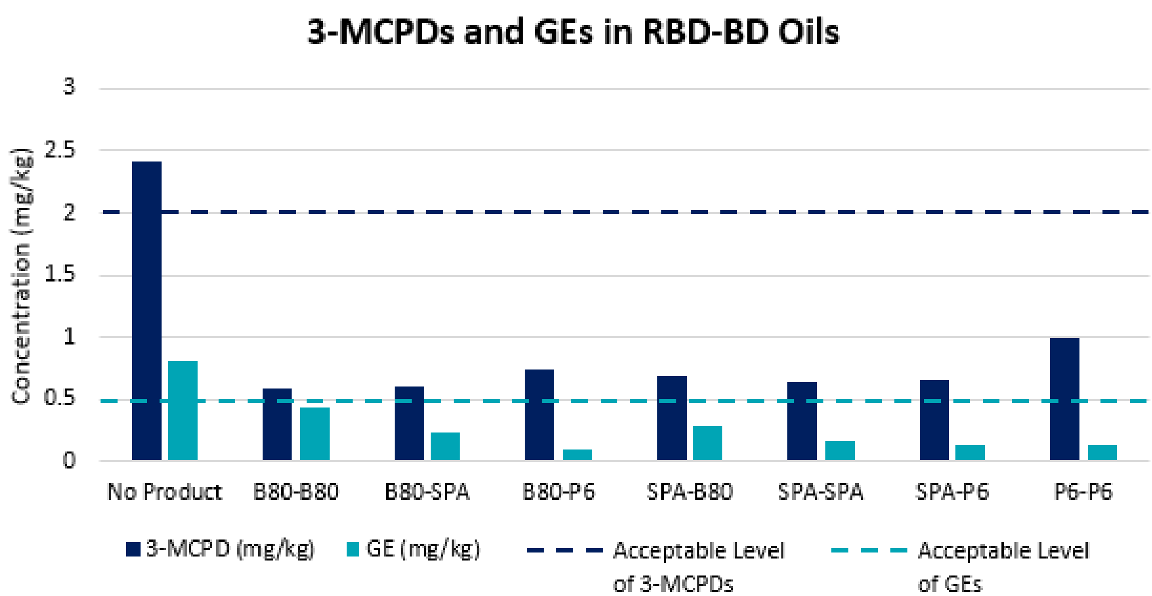


RBD-BD Oil

The RBD oils were then bleached followed by soft deodorization (at 210 ºC) to minimize GE generation. A deodorization temperature of 210 ºC was chosen based previous work where we lower observed GE results when deodorization was compared at two different temperatures. Similar trends were found in the results of the RBD-BD post-treatment (**Figure 3**). All three bleaching clay combinations decreased both MCPDs and GEs levels well within target specifications. The use of acidified clays further reduced the level of GEs found in the RBD-BD oil and directionally increased the amount of 3-MCPDs compared to the natural bleaching clay. Of the three clays employed in this experiment, the combination of Pure-Flo B80 and Supreme

Pro-Active gave better overall results than Perform 6000; reducing GEs with minimal increase of 3-MCPDs.

Figure 3: 3-MCPD and GE levels of RBD-BD Samples



Alkaline adsorbents or additives in bleaching

A major hurdle in developing new methods for the mitigation of 3-MCPDs is finding an effective outcome that does not degrade the oil. Chemical refining is one of the most effective means for mitigating MCPDs, however due to the high concentration of free fatty acids in palm oil, this method leads to significant oil losses, and a large soap stock stream that must be further processed. The formation of MCPDs is catalyzed by acid, and when alkaline adsorbents or additives are applied to the bleaching process a positive impact on the mitigation of MCPDs may often be observed, however these alkaline species have a negative impact on the bleaching process (See **Table 1**). Alkaline species competitively inhibit the adsorption of the undesired species (phospholipids, nitrogenous species, etc.) in crude palm oil and their introduction into the bleaching process leads to an increase in phosphorus levels and color of RBD oil.

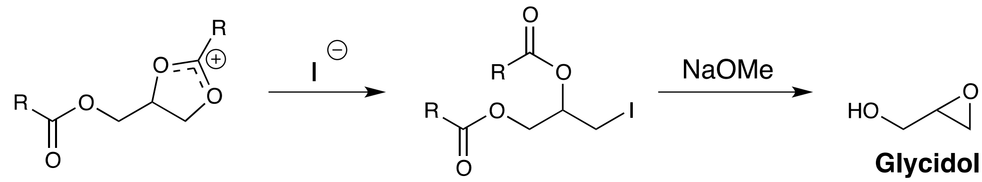
Table 1: Effect of Alkaline or iodide additives on MCPDs and GEs.

Additive (amt)	**MCPD (ppm)**	**GE (ppm)**	**RBD Red**	**RBD Yellow**
N/A	2.33	2.05	2.7	38.0
Sodium Acetate (500 ppm)	1.02	2.23	5.0	70.0
Sodium Aluminate (2500 ppm)	0.58	1.11	6.5	70.0
Potassium carbonate (1500 ppm)	0.33	3.80	Too Dark	Too Dark
Sodium Metasilicate (1500 ppm)	0.86	0.56	10.4	70.0
[1]Sodium Hydroxide	0.82	1.07	8.1	70.0
NaI (125 ppm)	1.61	34.16	2.4	32.0
NaI (250 ppm)	1.62	93.68	2.8	38.0
NaI (750 ppm)	1.86	217.48	3.2	50.0
NH_4I (750 ppm)	2.12	114.24	2.4	34.0
Pretreatment: 1500 ppm H_2O, 500 ppm of 50% citric acid, 85 °C, 15 min. Bleach: B80 3 wt% dosage, 100 °C, 30 min, 26" Hg. Deodorization: 245 °C, 30 min; 260 °C, 30 min. Additives were added during the bleaching stage of the process. [1]Clay was washed with NaOH and then water to give a clay with a pH of 11.05.				

The effect of iodide on MCPD and GE formation

In an attempt to competitively inhibit the formation of MCPDs, we found that when iodide sources (sodium iodide or ammonium iodide) are introduced into palm oil during the bleaching stage, large amounts of GEs were measured post-deodorization. Unfortunately, the formation of MCPDs were not inhibited and remained unchanged. Iodohydrin esters are likely the precursors to the GEs which may then be converted to the respective GEs during the deodorization or through the derivatization reactions during analysis (**Scheme 3**). The iodohydrins are hypothesized to be generated through similar manner mechanism to MCPD formation outlined in **Scheme 1**, however iodides are the reactive nucleophile (See **Scheme 3**).

Scheme 3.



Conclusion

3-MCPD and GE level may be effectively reduced by employing natural to mildly acidified bleaching clays prior to deodorization and mild to strongly acidified clays and soft deodorization conditions in post-treatment. However, with increasing stringent regulations on 3-MCPDs and GEs new methods for the mitigation of these process contaminants will need to be developed. One of the major challenges in developing these processes will be the balancing of meeting traditional oil quality specifications with the specifications put in place for 3-MCPDs and GEs. Although not yet realized, Oil-Dri is actively working toward developing a direct approach of mitigating the formation of 3-MCPDs by utilizing specialty bleaching clays.

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