Abstract: The present invention relates to a process of refining palm oil in order to produce a refined, bleached and deodorized (RBD) palm oil with reduced level of 3-monochloropropane-1,2-diol (3-MCPD) esters and equivalent RBD palm oil quality for all range of crude palm oil (CPO) feed. Accordingly, the process comprises the steps of water degumming of crude palm oil, removal of aqueous phase by centrifugation, followed by acid degumming at lower temperature. Water degumming removes 3-MCPD esters precursors while controlled acid degumming purifies the crude oil from gums and impurities. The degummed oil is then washed with certain amount of water and the aqueous phase is removed by centrifugation to remove remaining 3-MCPD esters precursors after acid degumming. Subsequently, bleaching is conducted with an activated bleaching earth and silicate adsorbent (for example magnesium silicate, calcium silicate and aluminum silicate) as filter aid and final adsorption of the 3-MCPD esters precursors prior to deodorization step. In this way, the refining process allows production of RBD palm oil with less formation of 3-MCPD esters even from low quality CPO.
AN IMPROVED PALM OIL REFINING PROCESS

Field of the Invention

The present invention relates to refining of edible oil or fat. More particularly, the present invention relates to an improved process of refining palm oil in order to produce a refined, bleached and deodorized (RBD) palm oil with reduced level of 3-monochloropropane-1,2-diol (3-MCPD) esters.

Background of the Invention

3-Monochloropropane-1,2-diol (3-MCPD) ester is a carcinogenic contaminant that forms during deodorization step in the oil refining process. Palm oil has been reported to contain highest level of 3-MCPD ester compared to other oils. Free 3-MCPD released from hydrolysis of 3-MCPD esters during intestinal digestion has been highlighted to be potentially causing adverse health effects. Free 3-MCPD ester is carcinogenic in animal studies and can induce infertility and malfunction of organs such as kidney.

The mechanism of 3-MCPD ester formation in the route of refining process has not been clearly understood. Research on mechanism of 3-MCPD ester formation is still ongoing. However, formation of 3-MCPD esters has been observed to form at elevated temperature during deodorization process from bound precursors that present in the crude oil. In addition, 3-MCPD esters precursors can be introduced in other stages of the oil refining process prior to deodorization. The introduction of acid especially at high temperature, whether from the acid degumming step or from the acidity of the bleaching clay, could lead to the formation of 3-MCPD esters precursor (Ramli et al., 2011; Schurz, 2010).

Palm oil requires a series of processing steps to transform crude oil into RBD palm oil having acceptable degree of purity and organoleptic properties. Palm oil physical refining process consists of three main steps namely, degumming, bleaching and deodorization.
WO201 0/063450 describes a method for refining oils low in 3-MCPD ester level, wherein a crude oil is first degummed in such a manner that a degummed oil is obtained, the degummed oil is admixed with a bleaching earth and bleached, wherein a bleached oil is obtained, the bleaching earth is separated off from the bleached oil, and so a filter oil is obtained and the filter oil is deodorized, characterized in that water is added to the crude oil for the degumming, and the degumming is carried out without addition of acid at a temperature of below 70°C, and the degummed oil is preferably separated off from an aqueous phase, the degummed oil is heated to a temperature in the range from 80 to 100°C and the bleaching earth is added to the heated degummed oil in an amount of greater than 1.5% by weight, and the bleaching is carried out at a temperature in the range from 80 to 100°C. This prior art utilizes water instead of acid for the degumming step that prevents activation of precursor. However, water degumming solely is not sufficient to produce good quality RBD palm oil. Non-hydratable phospholipids may bring along metal ions and other impurities can affect the final oil quality and these substances can only be removed by acid treatment.

The above prior art WO 2010/063450 is only suitable for low-phosphorus oils. Remaining phospholipids is not sufficiently removed by water degumming, which can lead to color fixation when subject to deodorization step.

WO201 1/009841 discloses a process for making a deodorized edible oil or fat having a low level of bound MCPD (monochloro propanediol esters) and/or low level of bound 3-MCPD. The process comprises a step of contacting the oil or fat to a carboxymethyl cellulose or an ion exchange resin. The carboxymethyl cellulose can be a Blanose® cellulose gum and the resin can be a cationic resin. A deodorized vegetable oil or fat and a food product made there from is described. The food product can be an infant formula. It exhibits low levels of bound MCPD and/or low level of bound 3-MCPD. In one embodiment the oil or fat has a reduced level of free fatty acid as well as a limpid aspect and no off-flavors.

This prior art basically, involves the addition of ion exchange resin to bleached oil for adsorption of 3-MCPD ester precursor prior to deodorization step. Further,
the above prior art require very good quality crude palm oil (CPO) in order to reach the claimed level of 3-MCPD ester.

Deodorization of palm oil is a vacuum-steam distillation process at an elevated temperature of 250 to 260°C, under vacuum of 2 to 4 mmHg and inert sparging agent, typically a direct steam injection of approximately 2.5 to 4.0% by weight of oil (Gibon et al., 2007). High temperature is required to allow for efficient removal of contaminants, impurities and undesired compounds from the oils such as pesticides besides the free fatty acid and odorous compounds. However, high deodorization temperature could lead to high formation of 3-MCPD esters. Modification of the deodorization step has been introduced to reduce 3-MCPD ester formation.

WO 201 1/009843 utilizes inert nitrogen gas for mild deodorization conditions and avoids generation of proton activity from steam sparging. Kim et al. (2011a) incorporates adsorbents mixture of acid clay and activated carbon (WO2011/090239) while Kim et al. (2011b) introduces citric acid as metal scavenger (WO2011/090240) during deodorization step. In these prior art teachings, deodorization step is conducted as commonly practiced with steam sparging as the stripping medium, because the deodorization step is an established system that involve complex process control. Modification of the process demands advance technology and control.

Final approach of 3-MCPD ester reduction is via post-refining treatments for direct removal of 3-MCPD esters from refined oil without disturbing the refining process. Among earlier mitigation solutions that has been proposed are disclosed in WO201 1/005081 by Zieverink et al. (2011b) that contacts unused triglyceride oils with highly porous silicate adsorbents and WO201 1/036072 by Bornscheuer and Hesseler (2011) that utilizes enzymatic conversion of 3-MCPD into mono- and diglycerol. Sodium aluminum silicate, calcined zeolite and synthetic magnesium silicate can decrease level of 3-MCPD esters when applied to RBD palm oil after refining process (Strijowski et al., 2011). However, post-refining treatment requires very good quality oil that contains low level of 3-MCPD ester.
Quality of crude palm oil is one of the factors that contribute to formation of 3-MCPD ester during oil refining. Poor quality CPO (DOBI<2.4) produces RBD palm oil with high 3-MCPD ester level. However, not all milling factories can provide such good quality CPO with free fatty acid (FFA) of less than 1.5% and diacylglycerol (DAG) of less than 4.5%. A robust processing is needed to produce RBD palm oil with acceptable quality and safety, particularly on 3-MCPD esters contaminant.

In view of the above, it is desirable to provide an improved oil refining process that is capable of reducing 3-MCPD ester content in crude palm oil, including in low/poor quality crude palm oil.

**Summary of the Invention**

The present invention relates to a process of refining palm oil in order to produce a refined, bleached and deodorized (RBD) palm oil with reduced level of 3-monochloropropane-1,2-diol (3-MCPD) esters and equivalent RBD palm oil quality for all range of crude palm oil (CPO) feed.

Accordingly, the process comprises the steps of water degumming of crude palm oil, removal of aqueous phase by centrifugation, followed by acid degumming at lower temperature. Water degumming removes 3-MCPD esters precursors while controlled acid degumming purifies the crude oil from gums and impurities. The degummed oil is then washed with certain amount of water and the aqueous phase is removed by centrifugation to remove remaining 3-MCPD esters precursors after acid degumming. Subsequently, bleaching is conducted with activated bleaching earth and silicate adsorbent (for example magnesium silicate, calcium silicate and aluminum silicate) as filter aid and final adsorption of the 3-MCPD esters precursors prior to deodorization step. In this way, the refining process allows production of RBD palm oil with less formation of 3-MCPD esters even from poor quality CPO.

In present invention, both water and acid degumming steps are incorporated for reduction of 3-MCPD esters level yet produced oil with equivalent quality. The removal of 3-MCPD esters precursors can also take place during the bleaching...
stage, whereby selected bleaching adsorbents have the ability to adsorb large amount of the precursors than others.

Brief Description of the Drawing

Figure 1 illustrates the process flow of refining palm oil according to the present invention.

Detailed Description of the Invention

The present invention relates to a series of palm oil refining stages that produce refined, bleached and deodorized (RBD) palm oil with reduced level of 3-MCPD esters and maintained similar RBD palm oil quality. The process flow of the refining is shown in Figure 1.

Crude palm oil is degummed with water, between 2% and 5% wt, preferably 3% and 4% at temperature ranging from 40°C to 60°C for 10 to 15 minutes under vacuum. The moisture and impurities are subsequently removed from the oil by centrifugal separation, for the oil to contain less than 1% moisture, preferably 0.5% moisture. The oil is then added with phosphoric acid at 0.05 to 0.1% by wt of oil, and acid degummed at a temperature less than 80°C, preferably at 50°C to 70°C for 15 to 30 minutes under vacuum.

After acid degumming, the degummed oil is washed with water again, 1 to 2% by wt oil to remove remaining 3-MCPD esters precursors if present after acid degumming. The moisture and impurities are then removed from the oil to less than 1% moisture, preferably 0.5% by centrifugal separation. The degummed oil is bleached with a silicate adsorbent (for example magnesium silicate, calcium silicate and aluminum silicate) at 0.5 to 1% by wt of oil to help in 3-MCPD esters precursor adsorption and activated bleaching earth at 0.1 to 1% by wt of oil as filter aid, conducted under vacuum at 90 to 100°C.

Subsequently, the bleached oil is deodorized at 260 to 265°C under vacuum with sparging steam as the stripping medium.
The 3-MCPD ester contents of the RBD palm oil are determined using the modified BfR Method 008 (BfR, 2009). The determination of 3-MCPD esters was carried out based on an indirect method using acid trans-esterification, which involves the release of 3-MCPD from its esters, purification by ammonium sulphate extraction, PBA derivatisation and quantification using gas chromatography with tandem mass spectrometry detection (GC-MS/MS).

The free fatty acid level, peroxide value and colour of the RBD palm oil are determined according to the AOCS Official Methods (2009) Ca5a-40, Cd 8b-90 and Cc 13e-92, respectively. The oil stability index (OSI) is determined according to the AOCS Official Method (2009) Cd 12b-92 with a Rancimat 743 apparatus (Metrohm Ltd., Herisau, Switzerland) by measuring the induction periods of the oils at 110°C based on a conductometric method. The principle of this test is to purge a stream of air through heated oil and then continuously monitor the conductivity of the water in which this effluent gas was trapped. The oxidation process was monitored in 3 g oil samples at an air velocity of 20 L/h.

The present invention will now be described in further detail by way of examples.

**EXAMPLE 1**

The refining was conducted in a laboratory scale refining flask equipped with a stirrer and heating mantle that was connected to a vacuum pump and a laboratory scale deodorizer mimicking industrial scale deodorizer connected to a vacuum pump (<5 mtorr) through three stages of water-jacketed traps and two empty flask traps to hamper the volatiles entering the pump. Stripping steam was produced from distilled water and evaporated in a glass steam generator that was connected directly to the deodorizer steam inlet.

Crude palm oil, in the amount of 1 L (from Golden Jomalina Food Industries, Selangor, Malaysia) was water degummed with 3.5% water at 50°C. The aqueous phase together with the gums and impurities was separated from the oil by centrifugation. The oil was then heated to 60°C and acid degummed with \( \text{H}_3\text{PO}_4 \) (0.1% wt) for 20 minutes, followed by washing with 1% water for 10 minutes. The aqueous phase was removed by centrifugation to remove
remaining 3-MCPD esters precursors if present. The degummed oil was bleached with 0.3 wt% bleaching earth and 1% magnesium silicate at 90°C for 30 minutes under vacuum. The bleached oil was then deodorized at 260°C under vacuum below 5 mtorr for 90 minutes with sparging steam as the stripping medium.

The refined palm oil had a 3-MCPD ester content of 0.377 mg/kg, having a FFA content of less than 0.01%, color of 2.4 Lovibond Red and oil stability index (OSI) of 14.3 hours. This resulted in 87% reduction of 3-MCPD esters when compared to a conventional palm oil refining process that contained 2.948 mg/kg 3-MCPD esters.

EXAMPLE 2

The refining was conducted in a laboratory scale refining flask equipped with a stirrer and heating mantle that was connected to a vacuum pump and a laboratory scale deodorizer mimicking industrial scale deodorizer connected to a vacuum pump (<5 mtorr) through three stages of water-jacketed traps and two empty flask traps to hamper the volatiles entering the pump. Stripping steam was produced from distilled water and evaporated in a glass steam generator that was connected directly to the deodorizer steam inlet.

Crude palm oil, in the amount of 1 L (from Golden Jomalina Food Industries, Selangor, Malaysia) was water degummed with 3.5% water at 50°C. The aqueous phase together with the gums and impurities were separated from the oil by centrifugation. The oil was then heated acid degummed with $H_3PO_4$ (0.1% wt) for 20 minutes, followed by washing with 1% water for 10 minutes. The aqueous phase was removed by centrifugation to remove remaining 3-MCPD esters precursors.

The degummed oil was bleached with 0.3 wt% bleaching earth and 0.5% magnesium silicate at 90°C for 30 minutes under vacuum. The bleached oil was then deodorized at 260°C under vacuum below 5 mtorr for 90 minutes with sparging steam as the stripping medium.
The refined palm oil had a 3-MCPD ester content of 0.494 mg/kg, having a FFA content of less than 0.01%, color of 2.1 Lovibond Red and oil stability index (OSI) of 21.7 hours. This resulted in 83.2% reduction of 3-MCPD esters when compared to a conventional palm oil refining process that contained 2.948 mg/kg 3-MCPD esters.

Table 1. Level of 3-MCPD and other quality characteristics of RBD palm oil of the conventional treatment compared with the process of the present invention

<table>
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<tr>
<th>Treatments</th>
<th>3-MCPD (mg/kg)</th>
<th>Color</th>
<th>OSI (hours)</th>
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<tr>
<td>Conventional refining</td>
<td>2.948</td>
<td>2.1 R 20 Y</td>
<td>24.1</td>
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<tr>
<td>Modified refining with</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1% H$_3$PO$_4$ and 1% Magnesol R60</td>
<td>0.377</td>
<td>2.4 R 40 Y</td>
<td>14.3</td>
</tr>
<tr>
<td>Modified refining with 0.1% H$_3$PO$_4$ and 0.5% Magnesol R60</td>
<td>0.494</td>
<td>2.1 R 30 Y</td>
<td>21.7</td>
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<tr>
<td>Modified refining with 0.05% H$_3$PO$_4$ and 1% Magnesol R60</td>
<td>0.366</td>
<td>2.6 R 40 Y</td>
<td>7.5</td>
</tr>
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</table>

The processing is applied specifically to palm oil. However, the process can also be applied to other type of oil with conditions that may vary in certain range generally plays in the technical field of the refinement process of edible oil and fat. Appropriate changes of certain condition of the pre-treatment steps may be needed according to the material and skill of the person known to the art.

INDUSTRIAL APPLICATION

The refined palm oil has various applications in food industry especially as fat ingredients, functional fat and as carrier for lipid-soluble nutrients that made up food product including infant milk and children's food. Production of refined palm oil with minimum level of 3-MCPD esters leads to production of safer finished product. The potential application will be on food product development using refined palm oil with reduced 3-MCPD esters content.
CLAIMS

1. A process of refining palm oil in order to produce a refined, bleached and deodorized (RBD) palm oil with reduced level of 3-monochloropropane-1,2-diol (3-MCPD) esters, the process comprises the steps of:
   i. degumming of crude palm oil with water;
   ii. subjecting the degummed oil to centrifugation in order to separate oil from moisture and impurities;
   iii. degumming the separated oil with acid;
   iv. washing the degummed oil of step (iii);
   v. subjecting the washed degummed oil of step (iv) to centrifugation in order to separate aqueous phase containing remaining 3-MCPD esters precursors from the oil;
   vi. bleaching the separated oil of step (v) with an activated bleaching earth and silicate adsorbent; and
   vii. deodorizing the bleached oil.

2. A process according to claim 1, wherein step (i) is carried out at 40°C to 60°C under vacuum.

3. A process according to claim 1, wherein step (iii) includes reacting the separated oil with phosphoric acid at 50°C to 70°C.

4. A process according to claim 1, wherein step (vi) is carried out under vacuum at 90 to 100°C.

5. A process according to claim 1, wherein the silicate adsorbent of step (vi) includes magnesium silicate, calcium silicate and aluminum silicate.
6. A process according to claim 1, wherein step (vii) is carried out at 260°C to 265°C under vacuum with sparging steam as the stripping medium.

7. A refined, bleached and deodorized palm oil produced by the process of claim 1.

8. A refined, bleached and deodorized palm oil of claim 7 having a free fatty acid (FFA) content of less than 0.01%, color of less than 2.1 Lovibond Red and oil stability index (OSI) of more than 20 hours.

9. A food product comprising refined, bleached and deodorized palm oil according to claim 7 or 8.
Figure 1
# INTERNATIONAL SEARCH REPORT

**International application No**

PCT/2013/000221

### A. CLASSIFICATION OF SUBJECT MATTER

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### ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

- EPO-Internal
- WPI Data
- FSTA

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 2 502 500 AI (NESTEC SA [CH]) 26 September 2012 (2012-09-26) claims 1-13</td>
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* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance.
- "A" document defining the general state of the art which is not considered to be of particular relevance.
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- "Z" document member of the same patent family.

Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search: 29 April 2014

Date of mailing of the international search report: 09/05/2014

Name and mailing address of the ISA:

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Authorized officer:

Adechy, Miriam
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