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(54) METHOD OF CONTROLLING LEVEL OF 3-CHLORO-1,2-PROPANEDIOL OR ESTERS THEREOF IN OILS AND FATS

(57) The present invention discloses a method for controlling the amount of 3-chloro-1,2-propanediol or ester thereof during the refinement of oils and fats, , comprising degumming, bleaching, contacting the resultant bleached oil with water, isolating the water phase, drying the resultant oil phase, and deodorizing.

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Description

Technical Field

[0001] The present invention relates to a method for processing edible oils and fats. In particular, the present invention relates to a modified method for processing edible oils and fats, i.e., a method for controlling the amount of 3-chloro-1,2-propanediol or ester thereof (3-MCPD/3-MCPD FE) during the refinement of oils and fats.

Background Art

[0002] Crude oil generally refers to the oils and fats extracted from plant or animal through leaching or pressing process while containing certain inedible or industrial impurities.

[0003] The main component of crude oil is a mixture of triglyceride fatty acids, which generally known as neutral oil. In addition to the neutral oil, crude oil further comprises non-glyceride substances (collectively called as impurities). The impurities can roughly be classified by their types, properties and states into three categories, i.e., mechanical impurities, fat-soluble impurities and water-soluble impurities.

[0004] Refining oil and fat generally refers to the refinement of crude oil. Impurities in crude oil not only affect the edibleness and safe storage of the oils and fats, but also make intensive processing difficult. Meanwhile, rather than removing all of the impurities, refining is aimed at the removal of the impurities that are deleterious to edibleness, storage and industrial production, etc., including gossypol, proteins, phospholipids, slimes, water and the like, while keeping the beneficial "impurities" such as tocopherol, etc. Therefore, the purpose of refining oils and fats is to remove undesirable and deleterious impurities from the oils and fats for the producing of oil products that satisfy certain quality standard(s) based on various requirements and applications.

[0005] 3-MCPD is a carcinogenic contaminant commonly acknowledged worldwide, which is mainly produced during the processing of food product. The refining process of oils and fats greatly increases the content of 3-MCPD; the presence of which in oils and fats is primarily in the forms of alcohol and ester, with ester as the dominant form. Furthermore, the amount of it varies among different oils. Chemical & Veterinary Test Agency (CVUA, Germany) classifies the amount of 3-MCPD in the common plant oils and fats into the following three levels:

1. Low level (0.5-1.5 ppm): soybean oil, rapeseed oil, sunflower oil, coconut oil, etc.;
2. Middle level (1.5-4 ppm): peanut oil, safflower oil, cottonseed oil, rice bran oil, corn oil, olive oil, etc.;
3. High level (>4 ppm): hydrogenated oils and fats, solid frying oil, palm oil, etc.

[0006] It has been found that the refined palm oil contains 4-30 mg/kg of 3-MCPD, the highest level in all of the oils.

[0007] In 2002, the European Union set a tolerable daily intake (TDI) of 2μg per kilogram of body weight per day for 3-MCPD intake from food. According to German Bundesinstitut für Risikobewertung (BfR), when assuming the complete hydrolyzing of 3-MCPD FE into free 3-MCPD by lipase, these levels will go far beyond the safety standard. For example, the amount in infant milk powder is 12.5-20 times the value of TDI, and the amount in vegetable oils and fats for adult consumption is 5-10 times the value of TDI.

[0008] In summary, it is urgent to modify the refining process of oils and fats to avoid safety problems. In "Influence of chemical refining process and oil type on bound 3-chloro-1,2-propanediol contents in palm oil and rapeseed oil" (2009), K. Franke compared effect of chemical refining process on 3-KCPD contents in crude palm oil, refined palm oil and crude rapeseed oil. The results showed that the amount of 3-MCPD was about 4.56 ppm in the re-refined palm oil, around 4.39 ppm in the refined palm oil (refined once), and nearly 1.04 ppm in rapeseed oil. These concentrations were still rather high.

[0009] Studies on the temperature and time of the bleaching and deodorizing processes showed that 3-MPCD was mainly formed in the deodorizing process, and particularly in the initial 20 minutes. It is well known in the art that the deodorizing process of oils and fats generally lasts 45-90 minutes, otherwise the indexes including smell and flavor, color and acid value, of the refined oils and fats could not be optimized. Further investigations showed that the mono- and di- glycerides may be the precursors of 3-MCPD. However, reducing the amounts of these precursors in oils and fats inevitably requires some approaches such as enzymatic reaction or molecular distillation, which are of little practice in actual processing due to the high cost or difficulties for implementation in industrial production.

[0010] Therefore, there is a burning need of a new method for reducing 3-MCPD and 3-MCPD FE in refined oils.

Summary of Invention

[0011] The present invention is to provide a method for effectively controlling 3-MCPD and 3-MCPD FE during refining oils and fats without undue increasing of the factorial production cost. The methods of the subject invention can be used in industrial production of food, thereby achieving an industrial production. Another purpose of the subject invention is to provide an optimized process and refined oils and fats of high quality produced by the optimized process.

[0012] The purposes of the subject invention can be realized through the scheme as following:

> A method for controlling the amount of 3-MCPD and 3-MCPD FE during the refining of oils and fats, said refining of oils and fats comprising a bleaching step (D), and a deodorizing step (G), wherein the method comprises:
>
> a degumming step (A) prior to the bleaching step (D),
> an alkali refining step (B) and a soap removing step (C) between the degumming step (A) and the bleaching step (D), wherein the alkali refining step (B) comprises adding an alkali solution into the oil phase obtained from step (A) to neutralize the oil phase obtained from step (A), and the soap removing step (C) comprises adding hot water to the oil phase obtained from step (B) to remove the soap stock; and
> steps (E) and (F) between the bleaching step (D) and the deodorizing step (G), wherein step (E) comprises contacting the bleached oil with water, said contacting comprising (E1) mixing with water and/or (E2) transesterification, and wherein step (F) comprises isolating the water phase and drying the oil phase obtained from step (E1) or (E2).

[0013] In one preferred embodiment, the amount of water used in step (E1) is in the range of 0.5-30 wt%, such as 0.5-20 wt%, 0.5-10 wt%, 2-20 wt%, or the like, of the bleached oil. The mixing in step (E1) is performed at a temperature of not higher than 100°C, such as not higher than 95°C. For instance, the mixing step is performed at temperature in the range of 60-100°C, preferably 70-95°C, and best 80-95°C.

[0014] In one preferred embodiment, the transesterification step (E2) comprises heating the bleached oil obtained from step (D) to 60-120°C and adding a catalyst in an amount of 0.1-2 wt% of the bleached oil. The catalyst may be sodium methoxide. The catalyst may also be (1) NaOH and (2) alkali metal (they are generally used in combination with glycerin). The transesterification step is carried out under vacuum for 15-60 minutes, such as 30 minutes, and then the reaction is terminated. After terminating the reaction, the oil is washed with water until a neutral pH is obtained.

[0015] Alternatively, the transesterification step (E2) comprises flowing the bleached oil from step (D) through a packed column (immobilized enzyme such as lipozyme TL IM, etc.) in countercurrent or warming it to 40°C-60°C, adding a transesterification enzyme in an amount of 0.1-2 wt% of the bleached oil and reacting under vacuum for 30-120 minutes (such as 30 minutes), and then the reaction is terminated. After terminating the reaction, the product is washed with hot water for 3 times until a neutral pH is obtained. The oil phase is isolated by centrifugation.

[0016] The transesterification enzyme used in the present invention includes various commercially available immobilized enzymes or the corresponding fermentation broth, such as lipozyme TL IM, Lopozyme RM and others available from Novozymes, and immobilized enzymes or the corresponding fermentation broth from AMANO Enzyme.

[0017] The degumming step includes a process of mixing the crude oil, degumming medium and water, etc. The degumming medium may be selected from the group consisting of citric acid solution, phosphoric acid solution and degummase. If a degummase is used, the reaction system is generally held at 50-80°C, with pH 5-6 for 2-4 hours. In industrial production, citric acid buffer (NaOH) may be used to adjust the pH to 5-6. The degumming medium is used in an amount of no less than 0.05 wt% of the crude oil. The water is used in an amount of no less than 0.5 wt% of the crude oil. The concentration of acid in the degumming medium is no less than 5 wt% based on the total weight of the solution.

[0018] Generally, the degumming medium is not higher than 2 wt% of the crude oil. The amount of water used in each degumming step is not higher than 30 wt% of the oil, such as in the range of 0.5-20 wt%, 0.5-10 wt%, 5-25 wt%. Said amount of water does not include the water in the degumming medium. Generally, the concentration of acid is not higher than 80 wt%, such as in the range of 5-65 wt%, 10-60 wt% or 20-50 wt%. Degumming with water only may be difficult to reduce the amount of phospholipid in the oils and fats (unable to remove non-hydratable phospholipids via the conversion to hydratable phospholipid).

[0019] Conventionally, the bleaching medium used in the bleaching step (D) may be selected from the group consisting of natural clay, activated clay, activated carbon, attapulgite clay, etc., preferably the low-acidity clay activated by sulfuric acid (having a pH close to neutral).

[0020] In a preferred embodiment, the bleaching step (D) comprises:

(i) heating the oil phase from step (C) to 80-90°C under vacuum;
(ii) adding the bleaching medium, such as clay activated by sulfuric acid;
(iii) further heating to 100-110°C for at least 10 minutes with stirring under vacuum; and
(iv) removing the bleaching medium through filtration.

[0021] In one embodiment, the amount of water used in step (E1) is equal to or larger than 0.5 wt% of the bleached oil from step (D), generally within 30 wt%, such as 0.5-20 wt%, 0.5-10 wt%, and 5-25 wt%. The mixing is carried out at

60-120°C, generally not higher than 100°C (such as 95°C). For example, the mixing is performed at 70-95°C or 80-95°C.

[0022] The present invention provides a method for controlling the formation of 3-MCPD and 3-MCPD FE as well during the deodorizing of oils and fats, including, prior to the deodorizing step, a rinsing step (E) to rinse the bleached oil with water. The rinsing step comprises a mixing step (E1) with water and/or a transesterification step (E2), and a step (F) to isolate the water phase and dry the resultant oil phase.

[0023] The bleached oil may be commercially available or obtained through conventional refining techniques.

[0024] In a preferred technical solution, the method further comprises, after the deodorizing step, a step (E) of further contacting the deodorized refined oil with water, wherein step (E) comprises (E1) mixing with water and/or (E2) transesterification step; and a step (F) of drying the resultant water-containing oil phase. Said steps (E1) and (E2) may be performed as mentioned above.

[0025] The present invention also provides a method for refining oils and fats comprising the following steps:

(A) a degumming step through acidifying and rinsing;
(A-1) drying the oil phase from step (A);
(D) bleaching the oil phase from step (A-1);
(E1) mixing the bleached oil from step (D) with water; and/or
(E2) transesterification step;
(F) isolating the water phase, drying the oil phase from step (E1) and/or (E2); and
(G) deodorizing the oil phase from step (F) by introducing nitrogen gas or vapor into said oil phase.

[0026] Preferably, the method for refining oils and fats further comprises, between step (A) and step (D), an alkali refining step (B) in which an alkali solution is added to neutralize the oil phase from step (A-1), a soap-removing step (C) in which hot water is added to the oil phase from step (B) to remove soap stock, and an isolating and drying step (C-1) in which the water phase is removed and the oil phase from step (C) is dried.

[0027] Steps (E1) and (E2) and the degumming step are as described above. The degumming medium is used in an amount of no less than 0.05 wt% of the crude oil. The water is used in an amount of no less than 0.5 wt% of the crude oil. The concentration of acid is not less than 5 wt% based on the total weight of the solution.

[0028] Generally, the degumming medium is not higher than 2 wt% of the crude oil. The amount of water used in each degumming step is not higher than 30 wt% of the oil, such as in the range of 0.5-20 wt%, 0.5-10 wt%, 5-25 wt%. Said amount of water does not include the water in the degumming medium. The concentration of acid generally is not higher than 80 wt%, such as in the range of 5-65 wt%, 10-60 wt% or 20-50 wt%.

[0029] The degumming step (D) includes:

(i) heating the oil phase from step (C-1) to 80-90°C under vacuum;
(ii) adding a clay activated by sulfuric acid;
(iii) further heating to 100-110°C for at least 10 minutes with stirring under vacuum; and
(iv) removing the clay via filtration.

[0030] In one embodiment, the amount of water used in step (E1) is equal to or larger than 0.5 wt% of the bleached oil from step (D), generally within 30 wt%, such as 0.5-20 wt%, 0.5-10 wt%, and 5-25 wt%. The mixing is carried out at 60-120°C, generally not higher than 100°C (such as 95°C). For example, the mixing is performed at 70-95°C or 80-95°C.

[0031] The crude oil or the bleached oil used in the present invention may be oils and fats extracted from plant oil material or animal through leaching or pressing processes, including but not limited to vegetable oils and fats and animal oils and fats, such as soybean oil, rapeseed oil, sunflower oil, coconut oil, peanut oil, safflower oil, cottonseed oil, rice bran oil, corn oil, olive oil, hydrogenated oils and fats, palm oil, etc., or mixtures thereof.

[0032] The refined oil obtained from the method of the present invention comprises less than 0.5 ppm of 3-MCPD and 3-MCPD FE, based on the total weight of the refined oil.

[0033] In one embodiment, a step (E) of rinsing the bleached oil is performed between the bleaching step (D) and the deodorizing step (G), wherein the step (E) is referring to a rinsing step (E1) by mixing with water or water-containing substance, such as an ethanol solution, or a chemical or physical process comprising a step of contacting the bleached oil with water, such as the transesterification step (E2).

[0034] In one embodiment, following the deodorizing step, the oil from the deodorizing step may be subjected to freezing crystallization processing.

[0035] In another embodiment, prior to the bleaching step, the oil to be bleached may be subjected to freezing crystallization processing.

[0036] The freezing crystallization processing can be performed with the methods well known in the art. Preferably, the freezing crystallization processing can be performed according to the methods described in Examples 14 and 15 herein.

Specific Embodiments

[0037] Upon extensive and intensive research, the inventors have surprisingly found that, the amount of 3-MCPD or 3-MCPD FE in the refined oil may be advantageously reduced during the refinement of oils and fats if water is incorporated into the oil phase, specifically prior to the deodorizing step, and then isolating the water phase, followed by drying the oil phase before the deodorizing processing.

[0038] The inventors have also discovered that the amount of 3-MCPD or 3-MCPD FE in the refined oil may be effectively reduced by improving the degumming step in the refining process for oils and fats. In particular, the degumming step is a step of degumming through acidifying and rinsing, which could effectively reduce the amount of the substances such as phospholipids, thereby further reducing the amount of 3-MCPD or 3-MCPD FE in the refined oil.

[0039] In the prior art refining process for oils and fats, alkali refining step (or neutralizing step) and soap-removing step are optional. However, the present inventors find that the alkali refining step and the subsequent soap-removing step may contribute to reducing the amounts of phosphorous substances and the precursors of 3-MCPD or 3-MCPD FE, such as chlorine ions, thereby further reducing the amount of 3-MCPD or 3-MCPD FE in the refined oil.

[0040] Specifically, the present invention provides a method for controlling the formation of 3-MCPD and 3-MCPD FE during deodorizing of oils and fats, and the method comprises a rinsing step (a) and a drying step (b) before a deodorizing step, in the rinsing step (a) the bleached oil is mixed with pure water for rinsing at a temperature of not higher than 95°C and then the oils and fats were isolated through centrifugation, wherein the water comprises 0.5 wt% or more of the bleached oil, and in the drying step (b) the oil phase is warmed to 80-110°C for 5-30 minutes and kept under vacuum to obtain the rinsed and dried oil.

[0041] Besides what mentioned above, the inventors point out that, effectively controlling the amount of the phosphorus-containing substances, such as phospholipid, during the refining process may advantageously reduce the amount of 3-MCPD or 3-MCPD FE in the refined oil. In particular, lower amount of the phosphorus-containing substances in the oils and fats before the deodorizing step is in favor of reducing the amount of 3-MCPD or 3-MCPD FE.

[0042] On a total weight basis, when the bleached oil mentioned in the above methods comprises less than 5 ppm, preferably less than 3 ppm, best less than 1 ppm of phosphorus (PHOS), the amount of 3-MCPD or 3-MCPD FE may be reduced to a distinguish level, such as lower than 0.5 ppm.

[0043] The bleached oil used in the present invention may be oils and fats extracted from plant or animal through leaching or pressing processes and having been subj ected to refining and bleaching, including but not limited to vegetable oils and fats and animal oils and fats, such as soybean oil, rapeseed oil, sunflower oil, coconut oil, peanut oil, safflower oil, cottonseed oil, rice bran oil, corn oil, olive oil, hydrogenated oils and fats, palm oil, etc., or mixtures thereof.

[0044] Preferably, in the above methods, steps (a) and (b) are duplicated for 1 or 2 or more times.

[0045] After step (b) of the above methods, a step (c) may be performed by introducing nitrogen gas or vapor as deodorizing medium under a vacuum degree of not higher than 25 mBarA at a suitable temperature to carry out the deodorization for 45-90 minutes. The vacuum may be released at a temperature below 50°C and the refined oil after deodorization could be obtained through filtration.

[0046] The present invention also provides a method for producing refined oils and fats, comprising the following steps:

(A) degumming through acidifying and rinsing, including mixing crude oil, degumming medium and pure water under 80-90°C, stirring for 30-40 minutes and then isolating by centrifugation to obtain oil phase 1;
(A-1) drying, comprising heating the oil phase 1 to 80-110°C and then stirring for 5-30 minutes while kept vacuum;
(D) bleaching, comprising heating to 80-90°C under vacuum, adding the bleaching agent, then further heating to 100-110°C, stirring for not less than 10 minutes under vacuum, and then removing the bleaching agent by filtration to obtain the bleached oil;
(E) rinsing, comprising adding pure water at an amount of no less than 0.5 wt% of the oil weight to the bleached oil under 75-90°C to rinse, and isolating by centrifugation to obtain oil phase 2;
(F) drying, comprising heating oil phase 2 to 80-110°C for 5-30 minutes while kept under vacuum;
(G) deodorizing, comprising introducing nitrogen gas or vapor as deodorizing medium under a vacuum degree of not higher than 25 mBarA at a suitable temperature to perform deodorization for 45-90 minutes, releasing the vacuum at a temperature below 50°C and obtaining the refined oil by filtration after deodorization.

[0047] On a total weight basis, the amount of phosphorus (PHOS) in the bleached oil obtained in step (D) is 5 ppm or less, preferably 3 ppm or less, best 1 ppm or less.

[0048] Preferably, step (A) of the above method is repeated for 2 or 3 times.

[0049] Preferably, steps (A) to (G) of the above method are repeated for 2 or 3 times.

[0050] In one preferred embodiment of the present invention, the method for refining oils comprises the following steps:

(1) degumming through acidifying and rinsing, including mixing crude oil, degumming medium and pure water under

80-90°C, stirring for 30-40 minutes and then isolating by centrifugation to obtain oil phase 1;

(2) drying, comprising heating oil phase 1 to 80-110°C and then stirring for 20-30 minutes while kept vacuum;

(3) alkali refining (neutralizing), comprising adding a suitable amount of alkali solution to the dried oil phase 1 for reaction under 80-90°C;

(4) soap-removing, comprising adding a suitable amount of hot water under 80-90°C to remove soap stock;

(5) drying, comprising heating up the light phase to 90°C and then stirring for 30 minutes while kept under vacuum;

(6) bleaching, comprising heating to 80-90°C under vacuum, adding the bleaching agent, then further heating to 100-110°C, stirring for not less than 10 minutes under vacuum, and then removing the bleaching agent by filtration to obtain the bleached oil;

(7) rinsing, comprising adding pure water at an amount of no less than 0.5 wt% of the oil weight to the bleached oil under 70-95°C to rinse, and then isolating by centrifugation to obtain oil phase 2;

(8) drying, comprising heating oil phase 2 to 80-110°C for 5-30 minutes while kept under vacuum to obtain a refined oil;

(9) deodorizing, comprising introducing nitrogen gas or vapor as deodorizing medium under a vacuum degree of not higher than 25 mBarA at a suitable temperature to perform deodorization for 45-90 minutes, releasing the vacuum at a temperature below 50°C and obtaining the refined oil by filtration after deodorization.

[0051] On a total weight basis, the amount of phosphorus (PHOS) in the bleached oil obtained in step (6) is 5 ppm or less, preferably 3 ppm or less, more preferably 1 ppm or less.

[0052] Preferably, step (1) of the above method is repeated for 2 or 3 times.

[0053] Preferably, steps (1) to (9) of the above method is repeated for 2 or 3 times.

[0054] The alkali solution in step (3) may be any alkali solution, preferably selected from the group consisting of NaOH solution and KOH solution. The alkali solution has a concentration of not higher than 35 wt%. The hot water used in step (4) may have a temperature of 50°C or higher.

[0055] In the method for preparing a refined oil of the present invention, the degumming medium used in the degumming step is a citric acid solution with the concentration of the acid not less than 5 wt% based on the total weight of the solution.

[0056] In the method for preparing a refined oil of the present invention, the degumming medium is no less than 0.05 wt% of the crude oil and water is no less than 0.5 wt% of the crude oil.

[0057] In the method for preparing a refined oil of the present invention, the bleaching step may be carried out with conventional bleaching methods in the art. The bleaching agent may contain but is not limited to natural clay, activated clay, activated carbon, attapulgite clay, etc., preferably the clay activated by sulfuric acid.

[0058] Preferably, in the method for preparing a refined oil of the present invention, a further rinsing step is carried out after the deodorizing step (9), and then the oil is dried to ensure that the final refined oil is water-free. In other words, steps including rinsing following by water isolating and oil phase drying are identical to steps (7) and (8) in the method of the present invention.

[0059] In the method for preparing a refined oil of the present invention, a step of transesterification (including rinsing) with drying may be incorporated into any stage of the process. The step of transesterification with drying may be a conventional method in the art, such as, but is not limited to mixing the oil and fat with sodium methoxide, terminating the reaction with citric acid solution, rinsing the mixture to a neutral pH, obtaining the oil phase by centrifugation, and drying the oil at an elevated temperature under vacuum.

[0060] As used herein, the "crude oil" refers to oils and fats extracted from plant or animal through leaching or pressing processes, including but not limited to vegetable oils and fats and animal oils and fats, such as soybean oil, rapeseed oil, sunflower oil, coconut oil, peanut oil, safflower oil, cottonseed oil, rice bran oil, corn oil, olive oil, hydrogenated oil and fat, palm oil, etc., or mixtures thereof. The amount of 3-MCPD in the crude oil is 0.3 ppm or more based on the total weight of the crude oil. In the present invention, crude palm oil with not higher than 3 wt% of free fatty acids is preferred.

[0061] As used herein, the term "refined oil" refers to the oils and fats comprising less than 1 ppm of 3-MCPD, based on the total weight of the refined oil.

[0062] The refined oil obtained from the method of the present invention comprises less than 0.5 ppm of 3-MCPD and/or 3-MCPD FE, based on the total weight of the refined oil.

[0063] The present invention also relates to a method for improving the quality of a refined oil and fat, including the steps of degumming through acidifying, alkali refining, rinsing and drying, wherein the method further comprises, in the following order, the steps of freezing crystallizing, bleaching and deodorizing. In some embodiments, several days, such as after 5 days or more, 10 days or more, 20 days or more, or 30 days or more after rinsing and drying, the oil and fat are subjected to freezing crystallization, re-bleaching and re-deodorizing. In one specific embodiment, 5-40 days, such as 10-30 days, after rinsing and drying, the oil and fat are subjected to freezing crystallization, re-bleaching and re-deodorizing.

[0064] The present invention also incorporates a method for transporting the oil and fat, including the steps of degumming through acidifying, alkali refining, rinsing and drying, wherein the oil and fat obtained after rinsing and drying are transported under normal temperature or with refrigeration. In some embodiments, after the above transportation, the rinsed and dried oil and fat are subjected to freezing crystallization, re-bleaching and re-deodorizing treatments. The above steps, such as degumming through acidifying, alkali refining, rinsing and drying, bleaching, and deodorizing, may be performed according to the methods described herein. The freezing-crystallization may be performed, for instance, according to the methods described in Examples 14 and 15 of the present invention.

[0065] The main advantages of the present invention include:

1. The refined oil obtained by the method for preparing a refined oil of the present invention comprises 0.5 ppm or less of 3-MCPD and 3-MCPD FE.
2. The refined oil of the present invention significantly abates the safety issue of oils and fats.
3. The method for preparing a refined oil by the present invention bears low production cost and could be readily industrialized.

[0066] The invention will be further illustrated by the following specific examples. It should be understood that the examples are for illustrative purposes only and in no way limit the scope of the invention. Unless particularly indicated, the specific conditions in the experimental methods of the following examples are generally the same as the conventional conditions or the same as the conditions recommended by manufacturer. Unless otherwise indicated, percentages, rates, ratios or parts mentioned are all calculated by weight.

[0067] The unit of the percent weight in volume is well known in the art. For example, it means the weight of a solute in 100 ml of a solution.

[0068] Unless otherwise defined, all professional and scientific terms used herein have the same meanings as those commonly known by a skilled artisan. In addition, any methods and materials that are similar or equivalent to those disclosed herein may be used in the methods of the present invention. The preferred methods and materials disclosed herein are illustrative only.

[0069] In the following examples, the quantity of 3-MCPD is determined by an indirect measuring approach which means several pre-treatments before GC-MS measurement (gas chromatography-mass spectroscopy).

Test example 1: the relationship between the amount of phospholipid and the amount of 3-MCPD in the refined oil and fat

[0070] The quality of a crude oil is shown in Table 1.

Table 1: The conventional chemical and physical indexes of a crude palm oil (about 3% FFA)

Sample	Acid value mg KOH/g	peroxide value mmol/kg	Amount of phosphorus mg/kg	Color R/Y,1"	Iodine value gI/100g	Amount of 3-MCPD ppm
Crude palm oil	6.05	0.20	10.54	20.3/30	52.63	0.52
Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane. The high purity lecithin (>95%) was used.						

[0071] The processes were as follows, 600 g crude palm oil was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50 wt%), in an amount of 0.1 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, then centrifuging at 4500 rpm for 15 minutes, followed by collecting the oil-containing light phase; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 110°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
4. Increasing the amount of the phospholipid: adding a certain amount of refined lecithin at 70°C, stirring at a uniform velocity for 1 hour;
5. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0072] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Amount of phosphorus	Amount of 3-MCPD
	ppm	ppm
Bleached oil	1.07	0.67
Bleached oil after adding lecithin	36.68	0.69
Deodorized oil	20.17	7.38

[0073] This test example shows that the amount of phospholipid is somewhat related to the amount of 3-MCPD in the refined oil and fat.

Example 1: Dry degumming (without rinsing and drying)-a control example

[0074] The quality of the crude oil is shown in Table 1.

[0075] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0076] The processes were as follows, 600 g crude palm oil was processed according to the following steps:

1. Dry degumming: mixing the oil with citric acid solution (50% concentration) in an amount of 0.1 wt% of the oil, stirring for 15 minutes at 90°C under vacuum, then obtaining the light phase by centrifugation;
2. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
3. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree about 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0077] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Color R/Y	Acid value mg KOH/g	Amount of phosphorus ppm	Amount of 3-MCPD ppm
Bleached oil	18.1/11(1")	6.13	4.38	0.67
Refined oil	2.1/20(5")	0.11	1.25	4.1

[0078] This example indicates that the formation of 3-MCPD in the bleached oil obtained from the conventional dry degumming method has substantially been enhanced upon the deodorizing step.

Example 2: Degumming through acidifying and rinsing with a combination of physical refining

[0079] The quality of the crude oil is shown in Table 1 of Test example 1.

[0080] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0081] The processes were as follows, 600 g crude palm oil was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50 wt%), in an amount of 0.1 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the oil-containing light phase; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 110°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
4. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0082] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Amount of phosphorus ppm	Acid value mg KOH/g	Amount of 3-MCPD ppm
Bleached oil	1.46	6.13	0.69
Refined oil	0.54	0.18	0.92

[0083] This example illustrates that the step of degumming through acidifying and rinsing may suppress the formation of 3-MCPD during deodorizing step.

Example 3: Dry degumming with a combination of rinsing the bleached oil

[0084] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0085] The processes were as follows, 600 g crude palm oil was processed according to the following steps:

1. Dry degumming: mixing the oil with citric acid solution (50% concentration) in an amount of 0.1 wt% of the oil, stirring for 15 minutes at 90°C under vacuum, then obtaining the light phase by centrifugation;
2. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
3. Rinsing: adding deionized water, which was pre-heated to 80°C or above, in an amount of 20 wt% of the oil to the bleached oil, stirring at 85°C for 10 minutes, and then obtaining the light phase by centrifugation;
4. Drying: heating up the light phase to 90°C and then stirring for 30 minutes under vacuum;
5. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree about 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0086] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Color R/Y	Acid value mg KOH/g	Amount of phosphorus ppm	Amount of 3-MCPD ppm
Bleached oil	13.4/18(1")	6.32	4.20	0.59
Refined oil	2.4/20(5")	0.08	1.13	3.4

[0087] As compared with Example 1, introduction of a rinsing step after the bleaching step in this Example decreases the amount of 3-MCPD in the refined oil.

Example 4: Degumming through acidifying and rinsing with a combination of rinsing the bleached oil

[0088] The quality of the crude oil is showed in Table 1 of Test example 1.

[0089] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0090] The processes were as follows, 600 g crude palm oil was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50 wt%), in an amount of 0.1 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, then centrifuging at 4500 rpm for 15 minutes, and collecting the oil-containing light phase; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil, stirring at 110°C for 30 minutes under vacuum, obtaining the bleached oil by filtration;
4. Rinsing: adding deionized water, which was pre-heated to 80°C or above, in an amount of 20 wt% of the oil to the bleached oil, stirring at 85°C for 10 minutes, and then obtaining the light phase by centrifugation;
5. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
6. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0091] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Amount of phosphorus ppm	Color R/Y	Acid value mg KOH/g	Amount of 3-MCPD ppm
Bleached oil	1.11	18.1/11(1")	6.48	0.69
Refined oil	0.23	2.1/20(5")	0.08	0.31

[0092] This example displays that degumming through acidifying and rinsing along with rinsing and drying the bleached oil may effectively control the formation of 3-MCPD in the deodorizing step.

Example 5: Secondary refining (Multiple refining)

[0093] The crude oil used in Test example 1 was employed.
[0094] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4).
[0095] The processes were as follows, 1200 g crude palm oil was processed according to the following steps:

1. Dry degumming: mixing the oil with citric acid solution (50% concentration) in an amount of 0.1 wt% of the oil, stirring for 15 minutes at 90°C under vacuum, then obtaining the light phase by centrifugation;
2. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
3. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the oil, which has been refined once, by filtration;
4. Dry degumming: mixing the oil, which has been refined once, with citric acid solution (50% concentration) in an amount of 0.1 wt% of the oil, stirring for 15 minutes at 90°C under vacuum, then obtaining the light phase by centrifugation;
5. Bleaching: adding Taiko Supreme 1B in an amount of 0.5 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
6. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 220°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtain the oil, which has been refined twice, by filtration.

[0096] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Amount of phosphorus ppm	Amount of 3-MCPD ppm
Bleached oil (once)	4.2	0.71
Refined oil (once)	3.94	2.0
Bleached (twice)	1.54	1.9
Refined oil (twice)	0.64	1.3

Example 6: Transesterification

[0097] The crude oil used in Test example 1 was employed.
[0098] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). NaOH solution with a concentration of 18 wt%, and sodium methoxide powder were used.
[0099] Pure water was prepared using reverse osmosis (R/O) membrane.
[0100] The processes were as follows, 700 g crude palm oil was processed according to the following steps:

1. Dry degumming: mixing the oil with citric acid solution (50 wt%) in an amount of 0.01 wt% of the oil, stirring for 15 minutes at 90°C under vacuum, then obtaining the light phase by centrifugation;
2. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,

the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times(1+\text{excess quantity of alkali})$, wherein the excess quantity of alkali is 20%, the amount of the alkali solution equals the amount of the alkali/0.18, that is, 20.13 g of NaOH solution was added. As used herein, the M_{oil} refers to the weight of the oil and the AV refers to the acid value.
3. Soap-removing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
4. Drying: stirring at 90°C for 1 hour under vacuum;
5. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
6. Chemical transesterification: heating the bleached oil to 90°C, adding sodium methoxide in an amount of 0.1 wt% of the oil, reacting for 30 minutes under vacuum, terminating the reaction with citric acid solution with a concentration of 15% by mass in an amount of 1.7 wt% of the oil, and then rinsing with hot water for 3 times or more until a neutral pH was reached, obtaining the oil phase by centrifugation;
7. Drying: heating the oil phase to 90°C and then stirring for 30 minutes under vacuum;
8. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0101] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Phosphorus amount ppm	3-MCPD amount ppm
Bleached oil	4.29	0.69
Refined oil	1.15	1.8

Example 7: Degumming through acidifying and rinsing + transesterification

[0102] The crude oil used in Test example 1 was employed.

[0103] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). NaOH solution with a concentration of 18% by mass, and sodium methoxide powder were used.

[0104] Pure water was prepared using reverse osmosis (R/O) membrane.

[0105] The processes were as follows, 700 g crude palm oil was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50% mass concentration), in an amount of 0.1 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the light phase, i.e., the oil; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,
the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times(1+\text{excess quantity of alkali})$, wherein the excess quantity of alkali is 20%, the amount of the alkali solution = the amount of the alkali/0.18, that is, 20.13 g of NaOH solution was added;
3. Soap-removing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
4. Drying: stirring at 90°C for 1 hour under vacuum;
5. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
6. Chemical transesterification: heating the bleached oil to 90°C, adding sodium methoxide in an amount of 0.1 wt% of the oil, reacting for 30 minutes under vacuum, terminating the reaction with citric acid solution with a concentration of 15% by mass in an amount of 1.7 wt% of the oil, and then rinsing with hot water for 3 times or more until a neutral pH was reached, obtaining the oil phase by centrifugation;
7. Drying: heating the oil phase to 90°C and then stirring for 30 minutes under vacuum;
8. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0106] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Phosphorus amount ppm	3-MCPD amount ppm
Bleached oil	1.11	0.86
Refined oil	0.37	0.64

Example 8: Rinsing the refined oil

[0107] The quality of the refined oil is shown in the table below.

Sample name	Acid value mg KOH/g	Peroxide number mmol/kg	Color R/Y,5"	3-MCPD amount ppm
Refined palm oil	0.33	4.0	3.1/30	3.34

[0108] Pure water was prepared using reverse osmosis (R/O) membrane.

[0109] The processes were as follows, 400 g refined palm oil was processed according to the following steps:

1. Rinsing: adding deionized water (pre-heated to 80°C or above) in an amount of 20 wt% of the oil to the bleached oil under 85°C and then stirring for 10 minutes;
2. Isolating: centrifuging at 4500 rpm for 15 minutes and obtaining the light phase;
3. Drying: heating to 90°C and then stirring for 30 minutes under vacuum.

[0110] The quality of the product is shown in the table below.

Sample name	Acid value mg KOH/g	Peroxide number mmol/kg	Color R/Y,5"	3-MCPD amount ppm
Refined palm oil (refined)	0.32	3.8	3.3/30	2.93

[0111] This example demonstrates that rinsing the refined oil can also control the amount of 3-MCPD in the oil and fat.

Example 9: Degumming through acidifying and rinsing + alkali refining + rinsing

[0112] The quality of the crude oil is shown in Table 1.

[0113] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0114] The processes were as follows, 800 g crude palm oil was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50% mass concentration), in an amount of 0.1 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the light phase, i.e., the oil; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,
   the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times$(1+excess quantity of alkali), wherein the excess quantity of alkali is 20%, the amount of the alkali solution = the amount of the alkali/0.18, that is, 20.13 g of NaOH solution was added;
4. Soap-removing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
5. Drying: stirring at 90°C for 1 hour under vacuum;
6. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 95°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
7. Rinsing: adding deionized water (pre-heated to 80°C or above) in an amount of 20 wt% of the oil to the bleached oil under 85°C and then stirring for 10 minutes, obtain the light phase by centrifugation;
8. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;

9. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0115] The samples obtained in each step and their qualities are shown in the table below.

Sample name	Amount of phosphorus ppm	Color R/Y	Acid value mg KOH/g	Amount of 3-MCPD ppm
Bleached oil	0.83	9.6/12(1")	0.23	0.69
Refined oil	0.44	1.3/10(5")	0.12	0.21

[0116] The amount of 3-MCPD in the final refined product could be effectively controlled by rounds of degumming through acidifying and rinsing, alkali refining, using activated clay with weak acidity and the subsequent rinsing.

Example 10: Dry degumming + rinsing + bleaching

[0117] The crude oil of Test example 1 was used.

[0118] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0119] The processes were as follows, 600 g refined palm oil was processed according to the following steps:

1. Dry degumming: mixing the oil with citric acid solution (50% mass concentration) in an amount of 0.01 wt% of the oil, stirring for 15 minutes at 90°C under vacuum, then obtaining the light phase by centrifugation;
2. Rinsing: stirring the oil with deionized water (pre-heated to 85°C or above) in an amount of 20wt% of the oil at 90°C for 10 minutes;
3. Drying: keeping stirring at 90°C and under vacuum for 1 hour;
4. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 90°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration.

[0120] The sample obtained in each step and their qualities are showed in the table below.

Sample name	Phosphorous amount (ppm)	3-MCPD amount (ppm)
Rinsed oil	6.97	0.48
Bleached oil	3.01	0.67

[0121] This experiment demonstrates that the amount of 3-MCPD in the oil and fat after bleaching will slightly increase.

Example 11: Bleaching + deodorizing VS bleaching + rinsing + deodorizing

[0122] The feed material was the material used in Test example 1.

[0123] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0124] The processes were as follows, 600 g refined palm oil was processed according to the following steps:

1. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the crude oil at 110°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
2. Rinsing: adding deionized water (pre-heated to 80°C or above) in an amount of 20 wt% of the oil to the crude oil under 85°C, stirring for 10 minutes, and then obtain the light phase by centrifugation;
3. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
4. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 260°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0125] The qualities of both oils are shown in the table below.

Sample name	Description	Phosphorus amount (ppm)	3-MCPD amount (ppm)
Refined palm oil	Bleaching+ deodorizing	6.81	2.3
Refined palm oil	bleaching + rinsing + deodorizing	5.96	2.1

[0126] This example proves that the combination of bleaching + rinsing + deodorizing could decrease the amount of 3-MCPD in the final product as compared with the combination of bleaching + deodorizing.

Example 12: crude oil → (rinsing) → deodorizing

[0127] The feed material used was the same as in Test example 1.

1. Rinsing: adding deionized water (pre-heated to 80°C or above) in an amount of 20 wt% of the oil to the crude oil at 85°C, stirring for 10 minutes, and then obtaining the light phase by centrifugation;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

(Steps 1 and 2 were practiced in only one experiment.)

[0128] The processed samples and their qualities are shown in the table below.

Name	Description	3-MCPD amount (ppm)
Deodorized oil	Directly deodorizing	5.0
Deodorized oil	Deodorizing after rinsing	3.9

Example 13: Applicability to other oil and fat

[0129] Material: corn oil having the quality as shown in the table below.

Name	Acid Value mg KOH/g	Color (1")	Phosphorus amount (ppm)	3-MCPD amount (ppm)
Crude corn oil	4.8	7.7/70	450	<0.15

[0130] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0131] The processes were as follows, 800 g crude corn oil was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50% mass concentration), in an amount of 0.5 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the light phase, i.e., the oil; repeating this step twice and the light phase proceeding to the next refining step;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,
the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times$(1+excess quantity of alkali), wherein the excess quantity of alkali is 20%, the amount of the alkali solution = the amount of the alkali/0.18, that is, 20.13 g of NaOH solution was added;
4. Soap-removing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
5. Drying: stirring at 90°C for 1 hour under vacuum;
6. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 110°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
7. Rinsing: adding deionized water (pre-heated to 80°C or above) in an amount of 20 wt% of the oil to the bleached

oil under 85°C and then stirring for 10 minutes, obtaining the light phase by centrifugation;
8. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
9. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

(Steps 7 and 8 were practiced in only one experiment.)

[0132] The processed samples and their qualities are shown in the table below.

Name	Description	Phosphorus amount (ppm)	3-MCPD amount (ppm)
Bleached corn oil	Product of step 6	2.47	0.26
Refined corn oil	Not subjected to steps 7 and 8	0.41	0.81
Refined corn oil	Subjected to steps 7 and 8	0.32	0.47

Example 14: Freezing fractionation after deodorization

The quality of the crude oil was shown in Table 1.

[0133] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0134] The processes were as follows:

1. Degumming through acidifying and rinsing: adding citric acid solution (50% mass concentration), in an amount of 0.1 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the light phase, i.e., the oil; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,
the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times(1+\text{excess quantity of alkali})$, wherein the excess quantity of alkali is 20%, the amount of the alkali solution = the amount of the alkali/0.18;
3. Rinsing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
4. Drying: stirring at 90°C for 1 hour under vacuum;
5. Bleaching: adding Taiko Supreme 1B in an amount of 1 wt% of the oil into the dried oil at 95°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by suction filtration while the processed oil was hot;
6. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 3-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration;
7. Freezing crystallization: placing the refined oil into a crystallizer and freezing crystallized according to the following:

Temperature (°C)	Time for cooling (min)	Time of constant temperature (min)	Duration (min)
65	/	/	240
65	/	60	60
50	60	/	60
40	60	/	60
30	60		60
15	120	300	420
15	/	300	300

[0135] Upon the completion of the above freezing crystallization, liquid oil and solid fat were obtained by pressure filtering through a plate-and-frame filter. The table below shows the quality of the resultant products.

Sample name	Acid value (mg KOH/g oil)	Iodine value (IV) (Ig/100g oil)	3-MCPD amount (mg/kg)
Refined palm oil	0.1	N/A	0.8
Liquid oil	0.15	59.59	1.15
Solid fat	0.12	43.37	0.58

[0136] The solid fat has a lowest amount of 3-MCPD and thus provides a higher safety.

Example 15: Freezing fractionation before bleaching

The quality of the crude oil was shown in Table 1.

[0137] Activated clay: Taiko Supreme 1B (pH=6.23, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0138] The processes were as follows:

1. Degumming through acidifying and rinsing: adding citric acid solution (50 wt%), in an amount of 0.1 wt% of the oil, and deionized water in an amount of 10 wt% of the oil into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the oil-containing light phase; repeating this step twice and the light phase proceeding to the next refining step;
2. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,
the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times(1+\text{excess quantity of alkali})$, wherein the excess quantity of alkali is 20%, the amount of the alkali solution = the amount of the alkali/0.18;
3. Rinsing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
4. Drying: stirring at 90°C for 1 hour under vacuum;
5. Freezing crystallization: placing the neutralized oil into a crystallizer and being freezing crystallized according to the following:

Temperature (°C)	Time for cooling (min)	Time of constant temperature (min)	Duration (min)
65	/	/	240
65	/	60	60
50	60	/	60
40	60	/	60
30	60		60
15	120	300	420
15	/	300	300

Upon the completion of the above freezing crystallization, liquid oil and solid fat were obtained by pressure filtering through a plate-and-frame filter.

6. Bleaching: adding 1 wt% of Taiko Supreme 1B into the resultant liquid oil and solid fat, respectively, stirring for 30 minutes at 110°C under vacuum, obtaining the bleached oils by suction filtration while the oils were hot;
7. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oils under a vacuum degree of 1-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oils by filtration;

[0139] The qualities of the resultant products are shown in the table below.

Sample name	Acid value (mg KOH/g oil)	Iodine value (IV) (Ig/100g oil)	3-MCPD amount (mg/kg)
Liquid oil	0.08	59.11	0.81

(continued)

Sample name	Acid value (mg KOH/g oil)	Iodine value (IV) (Ig/100g oil)	3-MCPD amount (mg/kg)
Solid fat	0.06	43.44	0.43

[0140] Generally, palm oil is separated into liquid oil and solid fat to ease applications with different requirements. During the refinement of palm oil, the freezing crystallization is generally performed after the deodorizing step, as described in Example 14. By comparing Example 14 with Example 15, we realize that, if the freezing crystallization is performed prior to the bleaching step and followed by deodorizing, the resultant liquid oil and solid fat will comprise lower amount of 3-MPCD and have favorable acid value and flavor. Palm oil is mainly produced outside China. With this process, the refined oil and fat could still be processed by the freezing crystallization, bleaching and deodorizing even after 30 days of transportation for the purpose of acquiring excellent product qualities in various aspects. Therefore, the above process could solve the problem about poor quality of the refined palm oil obtained from the refining process as a result of the quality deterioration during long term transportation.

Example 16: Clay with strong acidity as the bleaching medium

[0141] Activated clay: Tonsil 215FF (pH = 4.35, activated by H_2SO_4). Pure water was prepared using reverse osmosis (R/O) membrane.

[0142] The processes were as follows, 600 g crude palm oil (its quality is shown in Table 1) was processed according to the following steps:

1. Degumming through acidifying and rinsing: adding citric acid solution (50% mass concentration), in an amount of 0.5 wt% of the oil, and deionized water, in an amount of 10 wt% of the oil, into the oil, stirring at 80°C for 30 minutes, centrifuging at 4500 rpm for 15 minutes, and collecting the light phase, i.e., the oil; repeating this step twice and the resultant light phase proceeding to the next refining step;
2. Drying: heating the light phase to 90°C and then stirring for 30 minutes under vacuum;
3. Alkali refining: adding an alkali solution and reacting under 90°C for 30 minutes, and then obtaining the light phase by centrifugation,
   the amount of the alkali = $7.13\times10^{-4}\times M_{oil}\times AV\times(1+\text{excess quantity of alkali})$, wherein the excess quantity of alkali is 20%, the amount of the alkali solution = the amount of the alkali/0.18, that is, 18.25 g of NaOH solution was added;
4. Soap-removing: stirring the oil with deionized water in an amount of 20 wt% of the oil at 90°C for 10 minutes, wherein the deionized water needs to be pre-heated to 85°C;
5. Drying: stirring at 90°C for 1 hour under vacuum;
6. Bleaching: adding Tonsil 215FF in an amount of 1 wt% of the oil into the dried oil at 110°C, stirring for 30 minutes under vacuum, obtaining the bleached oil by filtration;
7. Deodorizing: introducing nitrogen gas (as a stirring and deodorizing medium) into the bleached oil under a vacuum degree of about 10-20 mBarA, maintaining at 240°C for 1 hour and then removing the heating jacket, releasing the vacuum at 50°C or below and then stopping the introduction of nitrogen gas, obtaining the refined oil by filtration.

[0143] The processed sample and its quality are shown in the table below.

Sample name	3-MCPD amount (ppm)
Refined palm oil	1.21

[0144] As compared with the previous examples, this example indicated that using clay with a near neutral pH may control the amount of 3-MCPD in the refined oil and fat more effectively.

[0145] The above examples are only preferred embodiments of the subject invention, and in no way limiting the scope of the substantive technical contents of the present invention. The substantive technical contents of the present invention are broadly defined in the claims. It is noted that, any technical means or method performed by any other parties, may it be completely identical to or equivalent to the technical means and method defined in the appended claims, will be deemed within the scope of the claims.

Claims

1. A method for controlling the amount of 3-MCPD or 3-MCPD FE during a process of refining oil and fat, said process of refining oil and fat comprising a bleaching step (D), and a deodorizing step (G), wherein said method includes:

   a step (E) and a step (F) between the bleaching step (D) and the deodorizing step (G), wherein the step (E) is to contact the oil from the bleaching step with water, comprising (E1) mixing with water and/or (E2) transesterification, and wherein the step (F) is to isolate the water phase and to dry the oil phase from step (E).

2. The method according to claim 1, wherein the amount of water used in step (E1) is equal to or greater than 0.5 wt% of the bleached oil from step (D).

3. The method according to claim 1, wherein the transesterification (E2) comprises heating the bleached oil from step (D) to 90-120°C and adding a catalyst in an amount of 0.1-2 wt% of the bleached oil, preferably reacting under vacuum for 15-60 minutes, terminating the reaction and then rinsing to reach a neutral pH;
   the catalyst is selected from the group consisting of sodium methoxide, a mixture of NaOH and glycerin, or a mixture of alkali metal and glycerin; or
   the transesterification (E2) comprises heating the bleached oil from step (D) to 40-60°C and adding a transesterification enzyme in an amount of 0.1-2 wt% of the bleached oil, preferably reacting under vacuum for 30-120 minutes, and terminating the reaction.

4. The method according to claim 1, wherein a degumming step (A) is performed before the bleaching step.

5. The method according to claim 4, wherein the degumming step comprises mixing the crude oil, degumming with the medium and water; and the degumming medium is selected from the group consisting of citric acid solution, phosphoric acid solution and degummase; the degumming medium is used in an amount of no less than 0.05 wt% of the crude oil; the water is used in an amount of no less than 0.5 wt% of the crude oil; the degumming medium comprises acid at a concentration of not less than 5 wt% based on the total weight of the degumming medium solution; preferably, the reaction is performed at 50-80°C, pH 5-6 for 2-4 hours.

6. The method according to any of claims 1-6, wherein the method comprises an alkali refining step (B) and a soap removing step (C) between the degumming step (A) and the deodorizing step (D), wherein the alkali refining step (B) comprises adding an alkali solution into the oil phase obtained from step (A) to neutralize the oil phase obtained from step (A); the soap removing step (C) comprises adding hot water into the oil phase obtained from step (B) to remove the soap stock.

7. The method according to claim 6, wherein the method further comprises, before the bleaching step (D), freezing crystallization of the oil phase from the soap removing step (C).

8. The method according to any of claims 1-6, wherein the method further comprises, after the deodorizing step, freezing crystallization of the oil from the deodorizing step.

9. The method according to claim 6, wherein the bleaching step (D) comprises:

   (i) heating the oil phase from step (C) to 80-90°Cunder vacuum;
   (ii) adding a bleaching medium;
   (iii) further heating to 100-110°C and stirring under vacuum for at least 10 minutes; and
   (iv) removing the bleaching medium by filtration.

10. The method according to claim 9, wherein the bleaching medium is selected from the group consisting of natural clay, activated clay, activated carbon, and attapulgite clay.

11. A method for controlling formation of 3-MCPD or 3-MCPD FE during deodorizing oil and fat, comprising a step (E) and a step (F) before the deodorizing step; the step (E) is to contact the bleached refined oil with water, which comprises a step (E1) of mixing with water and/or a transesterification step (E2), and the step (F) is to isolate the water phase and to dry the resultant oil phase.

12. The method according to claim 11, wherein the phosphorous of the bleached oil and fat is less than 5 ppm, preferably

less than 3 ppm, best less than 1 ppm.

13. The method according to claim 11, wherein the transesterification (E2) comprises heating the bleached refined oil to 90-120°C and adding a catalyst in an amount of 0.1-2 wt% of the bleached oil, preferably reacting under vacuum for 30 minutes, terminating the reaction and then rinsing to reach a neutral pH;
the catalyst is selected from the group consisting of sodium methoxide, a mixture of NaOH and glycerin, or a mixture of alkali metal and glycerin; or
the transesterification (E2) comprises heating the bleached refined oil to 40-60°C and adding a transesterification enzyme in an amount of 0.1-2 wt% of the bleached oil, preferably reacting under vacuum for 30 minutes, and terminating the reaction.

14. The method according to claim 12, wherein the amount of water used in step (E1) is equal to or greater than 0.5 wt% of the bleached refined oil.

15. The method according to claim 11, wherein the method further comprises, after the deodorizing step, freezing crystallization of the oil from the deodorizing step.

16. A method for refining oil and fat, comprising the following steps:

(A) degumming;
(D) bleaching the oil phase from step (A);
(E) contacting the bleached oil from step (D) with water, comprising:
(E1) mixing with water; and/or
(E2) transesterification;
(F) isolating the water phase, drying the oil phase from step (E); and
(G) deodorizing the oil phase from step (F).

17. The method according to claim 16, wherein the method further comprises, between step (A) and step (D),
an alkali refining step (B) of adding an alkali solution to neutralize the oil phase from step (A);
a soap-removing step (C) of adding hot water into the oil phase from step (B) to remove soap stock, and
an isolating and drying step (C-1) of removing the water phase and drying the oil phase from step (C).

18. The method according to claim 17, wherein the transesterification (E2) comprises heating the bleached oil from step (D) to 90-120°C and adding a catalyst in an amount of 0.1-2 wt% of the bleached oil, preferably reacting under vacuum for 30 minutes, terminating the reaction and then rinsing to reach a neutral pH;
the catalyst is selected from the group consisting of sodium methoxide, a mixture of NaOH and glycerin, or a mixture of alkali metal and glycerin; or
the transesterification (E2) comprise heating the bleached oil from step (D) to 40-60°C and adding a transesterification enzyme in an amount of 0.1-2 wt% of the bleached oil, preferably reacting under vacuum for 30 minutes, and terminating the reaction.

19. The method according to claim 17, wherein the degumming step comprises mixing the crude oil, degumming with the medium and water; the degumming medium is selected from the group consisting of citric acid solution, phosphoric acid solution and degummase; the degumming medium is used in an amount of not less than 0.05 wt% of the crude oil; the water is used in an amount of not less than 0.5 wt% of the crude oil; the degumming medium comprises acid at a concentration of not less than 5 wt% based on the total weight of the degumming medium solution;
preferably, the reaction is performed at 50-80°C, pH 5-6 for 2-4 hours.

20. The method according to claim 17, wherein the bleaching step (D) comprises:

(i) heating the oil phase from step (C-1) to 80-90°C under vacuum;
(ii) adding a bleaching medium;
(iii) further heating up to 100-110°C and stirring under vacuum for at least 10 minutes; and
(iv) removing the bleaching medium by filtration.

21. The method according to claim 17, wherein the amount of water used in step (E1) is equal to or greater than 0.5 wt% of the bleached oil from step (D).

22. The method according to any of claims 1-21, wherein the method further comprises, after the deodorizing step, a rinsing step (E) and a drying step (F), wherein the rinsing step (E) rinses the refined oil again and comprises a step (E1) of mixing with water and/or a transesterification step (E2), and the drying step (F) dries the resultant water-containing oil phase.

23. The method according to any of claims 1-22, wherein the crude oil or the bleached oil is a plant oil and fat or animal oil and fat selected from the group consisting of soybean oil, rapeseed oil, sunflower oil, coconut oil, peanut oil, safflower oil, cottonseed oil, rice bran oil, corn oil, olive oil, hydrogenated oils and fats, palm oil, or mixtures thereof.

24. A refined oil obtained from the method according to any of claims 1-23, wherein the refined oil comprises less than 0.5 ppm of 3-MCPD and/or 3-MCPD FE, based on the total weight of the refined oil.

25. A method for improving the quality of a refined oil and fat, including the steps of degumming through acidifying, alkali refining, and rinsing and drying, wherein the method further comprises, in the following order, the steps of freezing crystallizing, bleaching and deodorizing.

26. The method for improving the quality of a refined oil and fat according to claim 25, wherein the freezing crystallization, re-bleaching and deodorizing are performed several days after obtaining the oil and fat from rinsing and drying.

27. A method for transporting an oil and fat, including the steps of degumming through acidifying, alkali refining, and rinsing and drying, wherein the oil and fat obtained after rinsing and drying is transported under normal temperature or with refrigeration.

28. The method for transporting the oil and fat according to claim 27, wherein after transported under normal temperature or in with refrigeration, the rinsed and dried oil and fat are subjected to freezing crystallization, re-bleaching and re-deodorizing treatments.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/077096

A. CLASSIFICATION OF SUBJECT MATTER

C11B 3/00(2006.01)i

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)

IPC: C11B, A23D, A23L

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)

CNABS,CPRSABS,DWPI,CJFD: oil, fat, refinement, sodium methoxide, methylatesodium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN101455242A（HENAN HUATAI GRAIN&OIL MECHANICAL ENG CO LT）17 Jun. 2009（17.06.2009）claims 1-2	1-2，4-12，14-17，19-28
X	CN101305974A（GUANGDONG XINDADI BIOLOGICAL SCI & TECHN）19 Nov. 2008（19.11.2008）claims 1-3	1-2，4-12，14-17，19-28
A	CN101168501A（UNIV NANJING TECHNOLOGY）30 Apr. 2008（30.04.2008）claims 1-10	1-28
A	CN101665742A（CHEN, Jun）10.3 月 2010（10.03.2010）claims 1-7	1-28

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&”document member of the same patent family

Date of the actual completion of the international search 29 Sep. 2011（29.09.2011）	Date of mailing of the international search report 20 Oct. 2011（20.10.2011）
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. (86-10)62019451	Authorized officer ZHAO, Shihua Telephone No. (86-10) **62411183**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN101455242A	17.06.2009	CN101455242B	04.05.2011
CN101305974A	19.11.2008	CN101305974B	14.04.2010
CN101168501A	30.04.2008	CN101168501B	07.04.2010
CN101665742A	10.03.2010	NONE	

Form PCT/ISA /210 (patent family annex) (July 2009)