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(71) Applicant: **Feyecon Development & Implementation B.V.**
3542 GH Utrecht (NL)

(72) Inventors:
- **Woerlee, Geert Feye**
  1019 RW Amsterdam (NL)
- **Pellikaan, Hubert Clemens**
  3511 HL Utrecht (NL)
- **Peters Rit, Antonius Wilhelmus Petrus Gerardus**
  5531 VH Bladel (NL)

(74) Representative: **Jorritsma, Ruurd**
Nederlandsch Octrooibureau
Scheveningseweg 82
P.O. Box 29720
2502 LS Den Haag (NL)

(54) A method of processing lipid materials

(57) The present invention is concerned with a new method of processing lipid materials, such as triglycerides and waxes, which process involves contacting such lipid materials with a reactive granulate in the presence of a gas in near supercritical state. More particularly the present invention relates to a method of processing lipid material comprising the steps of

a) dissolving into the lipid material from 5-95 wt.% of a gas selected from the group consisting of carbon dioxide, ethane, propane, or nitrous oxide and mixtures thereof, at a temperature and a pressure at which the gas *per se* would be near its supercritical state,
b) contacting the lipid material containing the dissolved gas with a reactive granulate,
c) separating the granulate from the lipid material and
d) allowing the gas to evaporate from the lipid material by reducing the pressure.

The reactive granulate employed in the present process may suitably be a catalyst, such as bleaching earth or hydrogenation catalyst, or an adsorbent, such as active carbon.

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Description

TECHNICAL FIELD

[0001] The present invention is concerned with a new method of processing lipid materials, such as triglycerides and waxes, which process involves contacting such lipid materials with a reactive granulate in the presence of a gas in near supercritical state. The reactive granulate employed in the present process may suitably be a catalyst, such as bleaching earth or hydrogenation catalyst, or an adsorbent, such as active carbon. Examples of gases that can advantageously be used in the present method include carbon dioxide, ethane, propane and nitrous oxide.

[0002] The present invention specifically relates to methods of processing in which the composition of the lipid material is altered as a result of the interaction between the lipid material and the reactive granulate. This interaction may incite certain chemical reactions to occur in the lipid material and/or it may lead to selective adsorption of lipid material components onto the granulate. The present invention is not concerned with an extraction or fractionation processes wherein a lipid material is separated into 2 or more lipid material fractions by means of extraction with a supercritical solvent.

BACKGROUND OF THE INVENTION

[0003] Lipid materials such as triglycerides, waxes and fosfolipids all have in common that they are obtained from natural sources in a crude quality which is often unsuitable for human consumption or other commercial uses. Hence such crude lipid raw materials are usually subjected to a sequence of refining and other processing steps to upgrade the quality and/or applicability thereof. Processes commonly applied in the upgrading of crude lipid materials include bleaching, deodorisation, fractionation, hydrogenation, interesterification, hydrolysis etc.

[0004] The aforementioned methods of processing lipid materials are well known in the art and are normally conducted at elevated temperatures and in some cases also at elevated pressures. Some of these processes may apply processing aids such as organic solvents, adsorbents and catalysts. Examples of adsorbents commonly used in the processing of lipid materials are active carbon and silica. Catalysts widely employed in oil processing include bleaching earth, hydrogenation catalysts and interesterification catalysts. Both chemical and enzymatic catalysis are used in the field of oil processing. Enzymatic interesterification, for instance, is applied on an industrial scale.

[0005] The application of supercritical gases in the processing of lipid materials is known in the art. The known areas of application are extraction of lipid materials from plant materials and isolation of lipid fractions through supercritical extraction. These techniques have in common that the supercritical gas is added to the lipid material in an excess amount so that it may function as an extraction solvent. The supercritical gas containing dissolved components is separated from the bulk of the material after which the extract is recovered by reducing the pressure and allowing the gas to escape through evaporation. This cycle is normally repeated several times, often as part of a semi-continuous process. The following 2 prior art documents describe the use of supercritical gases in the processing of lipid materials, wherein said supercritical gas acts as an extraction solvent.

[0006] DE-A 4 306 303 (Schulmeyer et al.) relates to a process for obtaining vegetable oils by extraction with liquid or supercritical carbon dioxide, wherein the solvent flows through the comminuted oil seed or a crude oil and is subsequently passed through a bed of bleaching agent.

[0007] US 4,548,755 (Stahl et al) concerns a process for the extractive production of waxes from fossil, vegetable or animal starting material, by extraction with a gas at supercritical pressure and temperature conditions wherein the separation of the extract-containing gas is achieved in a separator part by pressure reduction and/or temperature change.

[0008] The use of supercritical gases in a process for bleaching textiles is known from DE-A 3 906 735 (Buschmann et al.). In this application a process is described for bleaching silk, wool, linen and/or cellulose fibre materials by treating the materials with a supercritical fluid containing oxidative bleaching chemicals such as hydrogen peroxide. It is noted that in the proces described, the bleaching chemicals are dissolved in the supercritical fluid, i.e. they are not present in the form of reactive granulates.

[0009] Conventional methods of processing lipid materials tend to be rather time-consuming, i.e. typically it takes several hours to bring them to completion. This is mainly due to the fact that the chemical phenomena governing these processes occur at a rather slow rate. Given the enormous scale at which these processes are operated, even a slight improvement in terms of processing time may generate very significant benefits, particularly in terms of savings.

SUMMARY OF THE INVENTION

[0010] The present invention relates to methods of processing lipid materials that are more efficient than the corresponding conventional methods. The present method was developed starting from the insight that in many existing processing methods, particularly in those cases where a reactive granulate is employed, the rate limiting factor is the rate of diffusion of the reactants in the lipid material. Surprisingly it was found that the diffusion rates of these reactants could be increased significantly by dissolving into the lipid material a gas at near supercritical conditions. The inclusion of a near su-

percritical gas was found to be particularly advantageous in processing methods that employ a reactive granulate, such as a catalyst or an adsorbent.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Hence one aspect of the invention is concerned with a method of processing lipid material comprising the steps of

a) dissolving into the lipid material from 5-95 wt.% of a gas selected from the group consisting of carbon dioxide, ethane, propane, or nitrous oxide and mixtures thereof, at a temperature and a pressure at which the gas *per se* (i.e. without lipid material) would be near its supercritical state,
b) contacting the lipid material containing the dissolved gas with a reactive granulate,
c) separating the granulate from the lipid material and
d) allowing the gas to evaporate from the lipid material by reducing the pressure.

[0012] The term "lipid material" as used herein encompasses lipophilic materials that are largely, e.g. for at least 60 wt.%, made up of molecules that contain one or more long chain alkyl or alkenyl groups. Usually these long chain groups comprise at least 10 carbon atoms. The aforementioned lipid materials normally possess a density which is lower than that of water and are not miscible water. Hence when admixed to water, these lipid materials will form a floating layer on top of the water surface.

[0013] In a preferred embodiment of the present method steps c) and d) are carried out consecutively. An important advantage of carrying out the method in this fashion is that the separation of granulate and lipid material is more easily achieved at elevated pressure, as under such conditions the lipid material is less viscous and displays a lower surface activity than at ambient. Preferably essentially all of the gas that is dissolved into the lipid material is removed therefrom through evaporation, i.e. not by separating the gas from the lipid material when said gas in liquid, supercritical or near supercritical form, as this might lead to the extraction of lipid material components, which is not an aim of the method according to the invention.

[0014] Best results are obtained with the present method if the lipid material is liquid when it is contacted with the reactive granulate and also when it is separated therefrom. In order to ensure that the material is liquid it is advisable to operate the method at a temperature well above the melting point of said lipid material.

[0015] It is an essential element of the present invention that the gas is dissolved into the lipid material and not the reverse, i.e. when the lipid material is dissolved into the gas. Particularly good results are obtained with the present method if the lipid material contains 10-90 wt.%, more preferably if 30-70 wt.% of the dissolved gas. In case an excess amount of gas is used the percentage of dissolved gas will simply be determined by the applied temperature and pressure. It is noted, however, that it is also possible to operate the method of the invention by mixing together a stream of lipid material and a stream of near supercritical gas in such a ratio that the amount of dissolved gas is less than the equilibrium concentration at the given temperature and pressure. Naturally in such an embodiment of the invention it is crucial that the streams are mixed in such a ratio that the amount of dissolved gas is maintained within the range needed to obtain the benefits of the present invention.

[0016] It is a critical aspect of the present method that step b) is carried out at a temperature and pressure at which the gas *per se* would be near its supercritical state. In a preferred embodiment of the invention, during steps a) and b) the temperature of the gas is at least T_c-60 °C and the pressure is at least $0.5xP_c$ (i.e. $P_c/2$), wherein T_c and P_c represent the critical temperature and critical pressure of the gas. More preferably the temperature of the gas is between T_c-60 °C and T_c+150 °C and the pressure is between $0.8xP_c$ and $12xP_c$.

[0017] The critical temperatures and pressures for the (pure) gases that are preferentially used in the present method are listed in the table below.

	T_c in °C	P_c in bar
Carbon dioxide	31	74.9
Ethane	32.2	48.8
Propane	96.7	42.6
N_2O	36.5	72.7

[0018] For a number of reasons, such as efficiency, safety and environmental impact, carbon dioxide is the gas which is preferentially used in the presence method, optionally in combination with one or more other gases. Preferably the lipid material is contacted with the reactive granulate in the presence of carbon dioxide at a pressure of at least 40 bar, and a temperature between 0° and 200°C. More preferably the carbon dioxide is at a pressure of between 70 and 800 bar. Furthermore the carbon dioxide is preferably applied at a temperature between 40° and 120°C.

[0019] The reactive granulate used in the present method is preferably selected from the group consisting of catalysts, adsorbents and mixtures thereof. In the case of catalysts the present method offers the advantage that, due to the increased diffusion rates, at the catalyst surface reactants be replenished more quickly and, in addition, reaction products will disappear more quickly. Both these effects will increase catalytic effectiveness. In the case of adsorbents the present method offers the advantage that components dissolved in the

lipid material will be captured more quickly by the absorbent than is the case for conventional methods employing the same adsorbent.

[0020] Reactive granulates which can be used in accordance with the present invention are preferably selected from the group consisting of bleaching earth, active carbon, hydrogenation catalyst and mixtures thereof. Most preferably the reactive granulate is bleaching earth. In a particular embodiment of the invention the method comprises contacting bleaching earth and the lipid material, wherein as a result of step b) and after separation of the granulate, the Lab L-value of the lipid material is increased by at least 10 and/or the absolute Lab a-value isreduced by at least 2 and/or the absolute Lab b-value is reduced by at least 2.

[0021] In order to achieve sufficient interaction between the lipid material and the reactive granulate, it is advisable to maintain the lipid material in contact with the reactive granulate for at least 30 seconds. Preferably contact-time is at least 45 seconds, more preferably at least 60 seconds. Most preferably contact time is at least 2 minutes. Usually contact-time will be less than 60 minutes, preferably less than 30 minutes and most preferably less than 15 minutes.

[0022] The lipid material processed by the present method is preferably selected from the group consisting of triglycerides, diglycerides, monoglycerides, fatty acids, fosfolipids, waxes and mixtures thereof. All these lipid materials are derived from lipid materials which are obtained in crude qualities from natural sources. In particular crude (i.e. unrefined) qualities of triglycerides, fosfolipids and waxes can suitably be processed through the present method. Waxes that can advantageously be used in the method include beeswax, carnauba wax, wool wax, montan wax and jojoba oil. Most preferably the wax used in the present method is beeswax.

[0023] In a specific and particularly advantageous embodiment of the present method the liquid lipid material is contacted with the reactive granulate by suspending the granulate into the lipid material and passing the lipid material upwards through a column whilst allowing the granulate to move downwards under the influence of gravity. Thus the effective contact-time between lipid material and granulate is increased and in addition the separation of the lipid material and the granulate is greatly facilitated.

[0024] In another preferred embodiment the reactive granulate is separated from the lipid material by means of filtration at elevated pressure, preferably a pressure of at least 70 bar. As mentioned herein before the separation at such an elevated pressure offers the advantage that separation is achieved more easily or that less lipid material is lost because it remains stuck to the granulate.

[0025] It can be advantageous to include solvents in the mix of lipid material and near supercritical gas as these solvents may assist in further improving processing yields and/or minimising losses of lipid material. Preferably, in the present method prior to step b) solvent is added to the lipid material in an amount of at least 2 %, preferably at least 8% by weight of the lipid material. The solvent used may suitably be selected from the group consisting of acetone, ethanol, di-ethylether, hexane, water and mixtures thereof.

[0026] The invention is further illustrated by means of the following examples

EXAMPLES

Example 1

[0027] The colour of refined yellow sunflower oil at room temperature was determined with a spectrophotometer. Expressed in Lab values the colour was (77.9, 0.55, and 7.39). 100 gram of sunflower oil was put in an autoclave of 323 ml.

[0028] The vessel is pressurised with 158 gram carbon dioxide using a positive displacement pump. The whole vessel is put in a thermostatic bath and heated to 45°C, while the vessel is mixed continuously. The end pressure becomes 170 bar. The autoclave now contains a liquid and gaseous carbon dioxide. The liquid contains approximately 30 wt.% carbon dioxide and 70 wt.% sunflower oil.

[0029] The liquid is subsequently contacted, under continuous mixing, with 1 gram of activated coal and 2.5 gram of bleaching earth for 15 minutes. After this the liquid is filtered and subsequently depressurised. The yellow colour had largely disappeared and the Lab values of the treated sunflower oil were determined as (79.8, -0.22, 0.3).

Example 2

[0030] The colour of refined greenish olive oil at room temperature was determined with a spectrophotometer. Expressed in Lab values the colour was (75.2, -0.69, and 6.63).

[0031] 99 gram of olive oil was put in an autoclave of 323 ml. The vessel is pressurised with 161 gram carbon dioxide using a positive displacement pump. The whole vessel is put in a thermostatic bath and heated to 45°C, while the vessel is mixed continuously. The end pressure becomes 192 bar. The autoclave now contains a liquid and gaseous carbon dioxide. The liquid contains approximately 35 wt.% carbon dioxide and 65 wt.% olive oil.

[0032] The liquid is subsequently contacted, under continuous mixing, with 1 gram of activated coal and 2.5 gram of bleaching earth for 15 minutes. After this the liquid is filtered and subsequently depressurised. The greenish colour was found to have largely disappeared and the Lab values of the treated olive oil were determined as (77.2, -0.18, 1.74).

Example 3

[0033] The colour of yellow beeswax was determined with a spectrophotometer. Expressed in Lab values the colour was (30.9, 4.71, and 21.9).

[0034] 50 gram of beeswax was put in an autoclave of 323 ml. The vessel is pressurised with 155 gram carbon dioxide using a positive displacement pump. The whole vessel is put in a thermostatic bath and heated to 75°C, while the vessel is mixed continuously. The end pressure becomes 188 bar. The autoclave now contains a liquid phase and gaseous carbon dioxide. The liquid contains approximately 23 wt.% carbon dioxide and 77 wt.% beeswax.

[0035] The liquid is subsequently contacted, under continuous mixing, with 0.5 gram of activated coal and 1.25 gram of bleaching earth for 5 minutes. After this the liquid is filtered and subsequently depressurised. The yellow colour largely disappeared and the Lab values of the treated beeswax were determined as (39.1, -2.39, 3.22). The amount of granulate recovered after processing was 2.09 grams, meaning that it contained only 0.34 grams of beeswax.

Comparative Example A:

[0036] Example 3 was repeated except that the process was carried out at ambient pressure, the temperature applied was 80 °C and contact time was increased to 20 minutes. Despite the fact that a longer contact time and higher temperature were applied, the yellow colour of the processes was not removed as effectively as in experiment 3. This observation was confirmed by the Lab values of the treated beeswax which were determined as (36.4, -0.54, 8.34).

[0037] The amount of granulate recovered after processing was 2.28 grams, meaning that it contained 0.53grams of beeswax. This shows that the used granulate obtained in this example holds 56% more beeswax than the granulate of example 3.

Example 4

[0038] 50 gram of beeswax as described in example 3 was put in an autoclave of 323 ml. The vessel is pressurised with 218 gram carbon dioxide using a positive displacement pump. The whole vessel is put in a thermostatic bath and heated to 74°C, while the vessel is mixed continuously. The end pressure becomes 370 bar. The autoclave now contains a liquid phase and gaseous carbon dioxide. The liquid contains approximately 52 wt.% carbon dioxide and 48 wt.% beeswax.

[0039] The liquid is subsequently contacted, under continuous mixing, with 0.5 gram of activated coal and 1.25 gram of bleaching earth for 15 minutes. After this the liquid is filtered and subsequently depressurised. The yellow colour was found to have disappeared and the Lab values of the treated beeswax were determined as (38.1, -2.21, 0.61).

Example 5

[0040] 50 gram of beeswax as described in example 3 and 5 grams of acetone were put in an autoclave of 323 ml. The vessel is pressurised with 205 gram carbon dioxide using a positive displacement pump. The whole vessel is put in a thermostatic bath and heated to 75°C, while the vessel is mixed continuously. The end pressure becomes 350 bar. The autoclave now contains a liquid phase and gaseous phase. The liquid contains approximately 42 wt.% carbon dioxide, 55 wt.% beeswax and 3 wt.% acetone.

[0041] The liquid is subsequently contacted, under continuous mixing, with 0.5 gram of activated coal and 1.25 gram of bleaching earth for 15 minutes. After this the liquid is filtered and subsequently depressurised . The yellow colour had disappeared and the Lab values of the treated beeswax were determined as (37.1, -1.95, 2.64).

Example 6

[0042] 50 gram of beeswax as described in example 3 was put in an autoclave of 323 ml. The vessel is pressurised to 375 bar. The whole vessel is put in a thermostatic bath and heated to 75°C, while the vessel is mixed continuously. The end pressure becomes 350 bar. The autoclave now contains a liquid phase and gaseous carbon dioxide. The liquid contains approximately 50 wt.% carbon dioxide, 50 wt.% beeswax.

[0043] The liquid is subsequently contacted, under continuous mixing, with 2.5 gram of bleaching earth for 20 minutes. After this the liquid is filtered and subsequently depressurised. The yellow colour largely vanished and the Lab values of the treated beeswax were determined as (36.3, -1.57, 0.38).

Example 7

[0044] Example 3 was repeated, except that the contact time with activated coal and bleaching earth was reduced to 3 minutes. The yellow colour of the processes beeswax so obtained, had largely disappeared and the Lab values of the treated beeswax were determined as (39.3, -2.63, 4.78).

Example 8

[0045] Again Example 3 was repeated, but this time the contact time with activated coal and bleaching earth was reduced to 50 seconds. The yellow colour of the processed beeswax had largely disappeared. The Lab values of the treated beeswax were determined as (37.8, -2.85, 9.89).

Claims

1. A method of processing lipid material comprising the steps of

   a) dissolving into the lipid material from 5-95 wt. % of a gas selected from the group consisting of carbon dioxide, ethane, propane, or nitrous oxide and mixtures thereof, at a temperature and a pressure at which the gas *per se* would be near its supercritical state,
   b) contacting the lipid material containing the dissolved gas with a reactive granulate,
   c) separating the granulate from the lipid material and
   d) allowing the gas to evaporate from the lipid material by reducing the pressure.

2. A method according to claim 1, wherein steps c) and d) are carried out consecutively.

3. A method according to claim 1 or 2, wherein the lipid material is liquid when it is contacted with the reactive granulate and separated therefrom.

4. A method according to any one of claims 1-3, wherein during steps a) and b) the temperature of the gas is at least T_c-60 °C and the pressure is at least 0.5xP_c, wherein T_c and P_c represent the critical temperature and critical pressure of the gas.

5. A method according to any one of claims 1-4, wherein step a) comprises dissolving into the lipid material between 10-90 wt.%, preferably between 20-70 wt.% of the gas.

6. A method according to any one of claims 1-5, wherein the lipid material is contacted with the reactive granulate in the presence of carbon dioxide at a pressure of at least 40 bar, and a temperature between 0° and 200°C.

7. A method according to any one of claims 1-6, wherein the reactive granulate is selected from the group consisting of catalysts, adsorbents and mixtures thereof.

8. A method according to any one of claims 1-7, wherein the lipid material is contacted with the reactive granulate for at least 30 seconds, preferably for 2 to 15 minutes.

9. A method according to any one of claims 1-8, wherein the lipid material is selected from the group consisting of triglycerides, diglycerides, monoglycerides, fatty acids, fosfolipids, waxes and mixtures thereof.

10. A method according to any one of claims 3-9, wherein the liquid lipid material is contacted with the reactive granulate by suspending the granulate into the lipid material and passing the lipid material upwards through a column whilst allowing the granulate to move downwards under the influence of gravity.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 20 2375

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Y	US 2 420 761 A (THOMAS CHARLES L) 20 May 1947 (1947-05-20) * claims 1-3 *	10	
A	MACHER M-B ET AL: "PARTIAL HYDROGENATION OF FATTY ACID METHYL ESTERS AT SUPERCRITICAL CONDITIONS" FETT - LIPID, WILEY-VCH VERLAG,WEINHEIM, DE, vol. 101, no. 8, August 1999 (1999-08), pages 301-305, XP000848744 ISSN: 0931-5985 * page 302, column 1, paragraph 2 - page 303, column 1, paragraph 2 * * figure 2 *	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
C11B
C11C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 November 2001	Rooney, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 20 2375

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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