Title: PROCESS FOR RECOVERING DIGLYCERIDES AND USE THEREOF

Abstract: The present invention relates to a process for recovering diglycerides comprising fractionating a glyceride mixture of mono, di- and triglycerides on an industrial scale in at least two fractionation steps at temperatures above 150 °C and pressures between 0.15 and 10 Pa. One of said steps separates triglycerides from mono- and/or diglycerides and the other one of said steps separates monoglycerides from di- and/or triglycerides. Diglycerides are recovered as a product of said fractionation steps. The process can be used for the providing of target diglycerides having a controlled fatty acid composition.
Process for recovering diglycerides and use thereof

The invention relates to a process for recovering diglycerides. The invention also relates to the use of the process for producing of target diglycerides according to customer requirements. The invention is advantageously used for producing diglyceride distillate with a diglyceride content of 80% or more.

Background
The functionality and the properties of partial glycerides depend on the ratio and type of fatty acid chains in the molecule. Therefore, partial glycerides are used in several ways in the food, nutraceutical, pharmaceutical and plastic/polymer industry depending on their properties.

Partial glycerides are compounds of the formula

\[
\begin{align*}
\text{CH}_2 - \text{OR}^1 \\
\text{CH} - \text{OR}^2 \\
\text{CH}_2 - \text{OR}^3
\end{align*}
\]

wherein one or two of the groups R^1, R^2, and R^3 represent hydrogen and the other represent fatty acid residues. Partial glycerides with one fatty acid residue are monoglycerides and partial glycerides with two fatty acid residues are diglycerides. Glycerides having fatty acid residues at all three R positions are triglycerides. Most natural fats of both vegetable and animal origin are triglycerides.

In the prior art monoglycerides are typically produced in substantially pure form, i.e. with a purity of 90 to 95 % by weight. Diglycerides are more difficult to produce in high purity because the typical processes for producing diglycerides also produce an abundance of mono- and triglycerides. Some attempts in the prior art at producing diglycerides in high purity are described below.

EP 0307154 discloses an enzymatic method for preparing a diglyceride from a saturated or unsaturated fatty acid having 4 to 22 carbon atoms, or a lower alcohol ester thereof, and glycerol, which comprises the step of reacting at least 1.5 moles of the fatty acid or lower alcohol ester thereof with one mole of glycerol in the presence of an immobilized lipase or an endo-lipase that reacts with glycerides preferentially at their 1st or 3rd position, while water or lower alcohol produced by the reaction is removed under reduced pressure.
WO 03/060139 discloses an enzymatic process for the production of diglycerides which comprises reacting a fatty acid or lower alkyl ester thereof with glycerin in the presence of an immobilized partial glyceride lipase while removing water or lower alcohol, which is generated upon reaction, out of the reaction system.

EP 10005517 disclosed a process for producing diglycerides comprising the steps of conducting a partial hydrolysis of a fat or oil to obtain a partial hydrolyzate having 67 to 96 % by weight of decomposed fatty acids and being inhibited from discoloring and, without distillation, then esterifying the partial hydrolyzate with glycerol.

WO 03/029392 discloses a chemical method for producing 1,3-diglyceride oils. The method comprises mixing triglyceride containing oil with glycerol and a catalyst comprising an alkali metal salt or alkali earth metal salt of a mono-carboxylic acid or a dicarboxylic acid, or a mixture thereof, to achieve glycerolysis, wherein 1,3-diglyceride oil is produced. In a preferred embodiment of the process, the diglyceride oil product is cleaned by the removal of monoglycerides by molecular distillation at 200 to 210 °C and 0.001 to 0.010 millibars (0.1-1 Pa). The document also suggests that an additional molecular distillation step could increase the purity and improve the colour of the diglyceride product by removing a triglyceride residue containing catalyst.

A.T. Erciyes and H. Civelecoglu describe in Chimica Acta Turcica, 11, (1983), pp 191-199 the molecular distillation of some specific Turkish oils to provide products containing diglycerides as the main component. According to the authors, it is imperative that the distillation is carried out at a pressure of $1 \times 10^{-3}$ mmHg (0.133 Pa) or less. In the process, the monoglycerides are removed by circulating the feed stream twice over a heater at 140 °C. The diglycerides are recovered by a similar circulation at 200 °C and the triglycerides are obtained at the same temperature by a third circulation.

The present inventors have found that the process described by Erciyes et al. is difficult to operate on an industrial scale since there is a tendency for the pressure to rise above the indicated low level. It has now been found that it is possible to provide an industrially advantageous process which does not need to perform the distillation at the suggested low pressure. On the contrary, the inventors have found that when diglycerides are distilled on an industrial scale, a technically more advantageous process is provided by the use of a higher pressure than in said prior art. Thus, the present process comprises an industrially useful process for recovering diglycerides.
Summary of the invention

The present invention concerns a process for recovering diglycerides. The process is suitable for being operated on an industrial scale. The process is defined in the appended claims. The present invention also concerns the industrial use of said process for supplying customers with their desired target diglycerides in a technically feasible way. The use is defined in the appended claims. The invention also relates to a process for producing a diglyceride distillate with a minimum diglyceride content of 80 %, preferably 85 %, more preferably 90 % by weight. It is also possible to recover monoglycerides as a further product of the present fractionation process. The contents of the claims are considered as being part of this specification.

In the process according to the invention diglycerides are recovered by fractionating a glyceride mixture of mono-, di- and triglycerides on an industrial scale in at least two fractionation steps at temperatures above 150 °C and pressures between 0.15 and 10 Pa, wherein one of said steps separates triglycerides from mono- and/or diglycerides at a temperature between 220 and 300 °C and the other one of said steps separates monoglycerides from di- and/or triglycerides at a temperature between 150 and 250 °C, and recovering diglycerides as a product of said fractionation steps.

In the process, the triglyceride-separating step is typically performed at a temperature of 240 to 280 °C. The monoglyceride-separating step is typically performed at a temperature of 180 to 240 °C.

Target diglycerides as well as optional monoglycerides having different content of fatty acids are recoverable from said two fractionation means, respectively, as end products.

The process of the invention may, in addition to the actual diglyceride recovery steps, also contain an additional purification step in order to increase the purity of the diglyceride product. In the invention this purification step preferably comprises a third fractionation step, which is performed on the diglyceride product. The third fractionation may remove monoglyceride or triglyceride. In a preferred removal of monoglycerides the fractionation is performed at a temperature of 150 to 250 °C, preferably 180 to 240 °C, in order to effectively remove monoglycerides from said diglyceride product.

In a preferred embodiment at least one of said fractionation steps is performed in a fractionation means, such as a distillation unit, like a short path distillation column, a falling film short path evaporator, a centrifugal still and/or a high vacuum wiped film evaporator, preferably a short path distillation column. Fractionation steps are preferably performed in one or in two or more
separate short path distillation columns. In a preferred embodiment a fluid from one of the columns is treated in another fractionation means at a temperature above 150 °C.

Based on a control of the glycerides in the feed mixture, on the temperature of the fractionation means and on the flow path of the liquids, the target diglycerides, as well as optional monoglycerides, are obtained in high purity. In order to obtain a desired target glyceride, the composition of the feed mixture is preferably designed to provide a glyceride mixture containing the desired diglyceride and/or monoglyceride molecules. The specific fractionation process of the invention provides the final diglycerides for the intended use, such as for food ingredient, nutritional, nutraceutical and for pharmaceutical use, use as additive for plastics and polymers as well as for other uses. The process of this invention makes it possible to produce diglycerides in a substantially pure form for the interested industry to test. In this way the present invention makes it possible to provide new diglycerides, which have potentially useful and surprising properties.

In the process according to the present invention a mixture of glycerides is fractionated in order to obtain the desired diglycerides. The mixture of glycerides used as a feed stream in the present invention may be prepared in any conventional manner. Thus, the mixture may be provided by transesterification of glycerol and triglycerides in a reaction system using conventional chemistry and/or enzymatic process, by enzymatic or chemical esterification of glycerol with fatty acids. The person skilled in the art will be aware of other ways to provide mixtures of partial glycerides for the feed mixture.

Thus, the glycerides comprising the feed stream may be provided e.g. by transesterification of glycerol and triglycerides containing the desired fatty acid moieties of the desired product partial glycerides. The mixture obtained from a conventional or enzymatic esterification process contains a mixture of glycerides comprising a different number of fatty acids depending on the feeds used for the process as well as on the used process itself.

In case the feed stream is made by transesterification, the composition of the feed stream may be optimised by selecting the ratio between glycerol and triglycerides in the reaction to provide the highest yield in kg/hr of the desired product in the fractionation according to the invention. When the feed stream is provided by transesterification of glycerol and triglycerides, or by other processes producing glycerol, the present process requires the removal of glycerol prior to the actual fractionation of the partial glycerides.

It is also possible to provide the desired feed stream mixture by enzymatic techniques. By enzymatic techniques it is, for instance, possible to obtain partial glycerides containing
polyunsaturated fatty acids. The enzymatic techniques also make it possible to provide a more exact distribution of partial glycerides. The enzymatic techniques make it possible to produce partial glyceride mixtures wherein the concentration of essential fatty acids e.g. polyunsaturated fatty acids like linoleic, α-linolenic acid, DHA and EPA is higher than in a partial glyceride mixture owing from chemical transesterification or esterification reactions.

In the present invention, the composition of the final product is controlled mainly by the temperature used in the fractionation steps. The monoglyceride, diglyceride and triglyceride molecules are separated from the mixture in an order and in fractions which depend on the temperature used in the fractionation step in question. The number of the fractionation steps is selected according to the desired purity of diglyceride end product.

The fatty acids in the glyceride mixture are derived from natural or hydrogenated or selectively hydrogenated oils and fats including oils and fats having vegetable, animal or micro organism origin or mixtures thereof.

The fatty acids of the present invention are preferably C8 to C30 saturated or unsaturated, cyclic or branched or hydroxyl fatty acids. More preferably, the fatty acids are saturated C8 to C30 acids, most preferably saturated C12 to C24 acids. The acids may be selected according to the desired known properties of the product which may be low caloric or other nutritional use, pharmaceutical use, use in plastics etc. The acids may also be selected according to a pattern for obtaining target diglycerides with unknown properties which may prove beneficial in any field of industry.

Saturated long chain fatty acids include e.g octanoic, decanoic, lauric, myristic, palmitic, stearic, arachidicic, behenic, lignoceric acid, etc. Unsaturated long chain fatty acids include palmitoleic, oleic, gadoleic, arachidonic acids and polyunsaturated fatty acids (PUFA) such as linoleic, α-linolenic, DHA (C22:6 ω3) and EPA (C20:5 ω3) etc. Fatty acids included in glycerides from animal or vegetable oils and fats and micro-organisms, such as lard, tallow, palm, rapeseed, soybean, cottonseed, linseed, sunflower, coconut, palm kernel, fish, algae etc. The fat and oils may be hydrogenated, selectively hydrogenated or non hydrogenated. Preferable fatty acids are C12 to C24 acids, like palmitic, stearic and behenic acids.

The diglyceride used in the specification and claims means a partial glyceride having two fatty acid chains. The monoglyceride contains one fatty acid chain. The triglyceride has three fatty acid chains.
The process according to the present invention enables production of diglycerides at a high purity. The process can be described in short as follows:

- providing a feed stream containing a desired mixture of glycerides;
- optionally stripping off glycerol from said feed stream;
- subjecting the substantially glycerol-free feed stream to a first partial glyceride fractionation step in a first fractionation means at a temperature above 150 °C;
- subjecting a fluid from said first fractionation means to a second partial glyceride fractionation step in a second fractionation means at a temperature above 150 °C wherein said fluid is either a distillate or a residue of said first fractionation step;
- recovering target partial glyceride(s) of desired composition from at least one of said first and said second fractionation means.

At least one of the fractionation steps is preferably performed at a temperature above 220 °C, preferably between 220 and 300 °C, whereby the yield of the monoglyceride and diglyceride fractions is improved and whereby the diglyceride concentration of the diglyceride fraction is increased. The temperature used in said step is preferably between 240 and 280 °C.

The pressure in the fractionation step is lowered, preferably to a value between 0.15 and 10 Pa more preferably to a value of 0.15 to 5 Pa.

In the present invention the fractionation is performed in two steps which improves the product purity and enables obtaining distilled products having more than 80 % by weight diglycerides at a high yield. It should be noted that the glyceride percentage in the present specification and claims is calculated by weight of the total product, while in the prior art, diglyceride purity is often calculated as the percentage of diglyceride based on the sum of diglyceride and triglyceride. For providing a desired target monoglyceride and/or diglyceride product, the feed glyceride mixture is tailored accordingly to provide a suitable end product after fractionation.

The present invention enables the obtaining of a product having a purity, which is higher than the purity obtainable in the prior art. The purity of the monoglyceride and/or diglyceride product of the present invention is preferably at least about 80 %, more preferably at least about 85 %, most preferably at least about 90 % by weight of the respective glyceride product.

A mixture of glycerides obtainable from most conventional partial glyceride production processes is suitable for being treated in the process according to the present invention. However, in case the mixture contains glycerol, this should be substantially removed before the mixture is subjected to the process of the invention. The mono-, di- and triglycerides are each
separated from the mixture in an order, which depends on the flow design of the process as well as on the temperatures used in the process. The process according to the invention may be designed using conventional separation and fractionation equipment, such as distillation means and evaporators. Short path distillation units are preferred as separation means. The process preferably also includes strippers for further purification of the products.

In the preferred embodiment of the invention the two fractionation steps are performed in two separate fractionation means. It is, however, also possible to provide the two fractionation means in one and the same physical equipment. Thus it is possible to provide one short path distillation column, which has two or more separate heat sections. The separate sections may operate at different temperatures, thus providing distinct fractionation steps. The columns and/or sections may be provided with separate distillate residue collection points for recovery of the different triglycerides.

The fractionation is most preferably performed in at least two separate short path distillation columns. Depending on the desired product composition the distillation is performed at a selected temperature and with a flow design that gives the desired composition. In case short path distillation columns are used in the process according to the present invention, the fractionation is generally operated according to one of two main principles.

In one preferred process according to the invention both the mono- and the diglycerides are distilled off on the first column at temperatures above about 220 °C, preferably between 240 and 280 °C and then the monoglycerides are removed from the distillate on the second column at temperatures from about 150 to 250 °C, preferably between 180 and 240 °C. The monoglycerides and diglycerides obtained are preferably each further purified in separate steps after the fractionation.

Another preferred way to operate the columns of the process according to the invention is to distil the majority of the monoglycerides on the first column. Then the diglycerides are distilled from the remaining mixture on the second column. A diglyceride content of more than about 80 %, preferably more than 85 %, more preferably above about 90 % by weight is obtained with the rest being substantially monoglycerides and/or triglycerides. The temperature in the second column is between 220 and 300 °C, preferably between 240 and 280 °C. A higher purity of the diglyceride is obtained if a third fractionation step is used.

The respective monoglyceride and diglyceride products from the fractionation means are preferably stripped with water vapour in packed columns in order to ensure a good organoleptic quality and remove any traces of glycerol.
The present invention makes it possible to design diglycerides, and optionally monoglycerides, for any desired need and also for testing for potential beneficial properties. The process of the invention can thus be used for providing of target diglycerides and/or monoglycerides having a controlled composition, said use comprising the steps of
- defining at least one target fatty acid of the target diglyceride;
- optionally defining the target position(s) of said fatty acid(s);
- providing a glyceride starting material containing a significant amount of the target diglyceride having a desired fatty acid composition;
- at need, removing glycerol from said starting material to provide a feed stream substantially free of glycerol;
- treating said feed stream in at least two fractionation steps at temperatures above 150 °C and pressures between 0.15 and 10 Pa in order to fractionate between mono-, di and triglycerides; and
- recovering the target diglyceride containing at least one of said target fatty acid(s) having the desired composition.

In the process, triglycerides are separated at a temperature of 220 to 300 °C, typically at 240 to 280 °C. Monoglycerides are separated at a temperature of 150 to 250 °C, typically at 180 to 240 °C. The target diglycerides are then recovered at high purity.

It is possible to recover also monoglyceride having the target fatty acid from the process. The target di- and/or monoglyceride(s) is/are preferably recovered at a purity above 80 %, more preferably above 85 %, most preferably above 90 % by weight.

The target fatty acid(s) and/or composition of the target di- and/or monoglyceride are also defined in response to customer requirements.

The partial glycerides obtained by the present invention may be used e.g. in nutritional compositions in nutraceuticals and pharmaceuticals, etc. The partial glycerides may also be used in various food industry applications, e.g. in low caloric products, in baked products, cooking oils, coatings and snack food products, as well as for emulsifiers, plasticizers, anti-static additive for plastic/polymers etc. The diglyceride obtained may be mixed with one or more ingredients for end products, and if desired the mixed diglyceride and ingredient(s) are processed into a respective end product.

The partial glycerides of the present invention may be incorporated in a composition comprising a thermoplastic polymer. A typical thermoplastic polymer may be or comprise a
polycarbonate. Polycarbonates are understood to include both homo- and copolycarbonates as well as aromatic and non-aromatic polycarbonates. The polycarbonates may be linear or branched. A portion of the carbonate groups in the polycarbonate may be replaced by aromatic dicarboxylic acid ester groups.

The partial glycerides/products of the present invention may be used as – or in the preparation of - a food. Here, the term “food” is used in a broad sense – and covers food for humans as well as food for animals (i.e. a feed). In a preferred aspect, the food is for human consumption.

As used herein the term “food ingredient” or “feed ingredient” includes a formulation, which is or can be added to functional foods or foodstuffs as a nutritional supplement. As used herein, the term “functional food” means food, which is capable of providing not only a nutritional effect, but is also capable of delivering a further beneficial, preferably health effect to consumer.

Some functional foods are nutraceuticals. Here, the term “nutraceutical” means a food which is capable of providing not only a nutritional effect and/or a taste satisfaction, but is also capable of delivering a therapeutic (or other beneficial) effect to the consumer. Nutraceuticals cross the traditional dividing lines between foods and medicine.

The partial glycerides/products of the present invention may also be used in pharmaceutical preparations or for combination into foodstuffs in order to provide some pharmaceutical effect.

When used as – or in the preparation of - a pharmaceutical, the partial glycerides/products of the present invention may be used in conjunction with one or more of: a pharmaceutically acceptable carrier, a pharmaceutically acceptable diluent, a pharmaceutically acceptable excipient, a pharmaceutically acceptable adjuvant, a pharmaceutically active ingredient.

The term “emulsifier” as used herein refers to an ingredient (e.g. a food product ingredient) that prevents the separation of emulsions.

There are many other applications which are known to those skilled in the art. Additionally, the present invention enables the production of novel compounds having properties, which are not yet known. Because the present invention provides new possibilities to obtain partial glycerides with desired composition, new and hitherto unknown partial glycerides with new and surprising properties may be produced. Thus, the present invention makes it possible to prepare partial glycerides which could be beneficial for lowering cholesterol absorption, reducing fatty tissue,
reducing tumor growth rate, enhancing renal, liver or colon function or reducing the risk of infections, etc.

**Detailed description of the invention**

The invention will now be described in greater detail with reference to the drawings, wherein:

Figure 1 discloses a fractionation system for the process according to the present invention.
Figure 2 discloses another fractionation system for the process according to the present invention.

In the preferred embodiment of the process disclosed in Figure 1 a mixture 1 of glycerides obtained from a conventional or non-conventional reaction system is supplied to a first stripping column 2 where substantially all of the glycerol is removed from the reaction mixture 1 at a temperature of about 150-240 °C and a pressure of about 10-1000 Pa depending on the amount of glycerol in the reaction mixture 1. In this stage about 1-30 % by weight, preferably about 5-20 % of the mixture is stripped off. It is preferred to remove as much as possible of the glycerol and the feed to the next step generally contains less than 2 weight-% preferably less than 1 weight-% glycerol most preferably less than 0.5 weight-%. The stripped glycerol 3 may be recycled back to the process for preparing the mixture 1 of partial glycerides.

The glycerol-striped mixture of glycerides from the first stripping column 2 is used as a feed mixture 4 according to the invention. The feed mixture is first fed into a first short path distillation unit 5. The temperature of the feed is preferably adjusted to about 140-200 °C before feeding into the short path distillation unit. The first short path distillation is performed at a temperature of 220 °C to 300 °C, preferably at a temperature of 240 °C to 280 °C in order to distill both the mono- and diglycerides. The pressure in the distillation unit is about 0.15-10 Pa. Triglycerides are not distilled under these conditions and the residue 6 containing the triglycerides is removed and may be recycled as a feed into the reaction for preparing the mixture 1 of partial glycerides.

The distillate 7 containing both mono- and diglycerides is then supplied to a second short path distillation unit 8. The temperature used in the second short path distillation unit is about 150-250 °C, preferably 180-240 °C, in order to distill the monoglycerides. The pressure in the distillation unit is about 0.15-10 Pa.

The residue 10 from the second short path distillation unit 8 is recovered as a product containing mostly diglycerides. It is preferably fed to a second stripping column 14 through a
heat exchanger. This stripping unit purifies the diglycerides and removes the odors. The temperature of the column is about 180-240 °C and the pressure is about 10-1000 Pa. The residue 15 contains finished product comprising diglycerides at a high yield and desired purity.

The distillate 9 from the second short path distillation unit 8 may be supplied into a third stripping column 11 for the purification of the product. The temperature of such a column is about 180-240 °C and the pressure is about 10-1000 Pa. The residue 13 contains finished product comprising monoglycerides at a high yield and desired purity.

In another process according to the present invention disclosed in Figure 2, a mixture 1 of partial glycerides obtained from a conventional or non-conventional reaction system is supplied to a first stripping column 2 where substantially all glycerol is removed from the reaction mixture 1 at a temperature of about 150-240 °C depending on the amount of glycerol in the reaction mixture.

The glycerol-stripped mixture of glycerides is used as a feed mixture 4 to a first short path distillation unit 5. The temperature of the feed is adjusted to about 140-200 °C. The first short path distillation is performed at a temperature of about 180-240 °C. The pressure in the distillation unit is about 0.15-10 Pa. The monoglycerides are distilled off the mixture at this stage.

The distillate 7 from the first short path distillation having a temperature of about 40-100 °C may be supplied to a second stripping column 14 for purification. The temperature of the column is about 180-240 °C and the pressure is about 10-1000 Pa. The distillate is removed and the residue 15 contains finished product comprising purified monoglycerides.

The residue 6 from the first short path distillation unit 5 is heated to a temperature of about 140-200 °C. It is then supplied to a second short path distillation unit 8. The temperature used in the second short path distillation unit is about 220-300 °C, preferably about 240-280 °C. The pressure in the distillation unit is about 0.15-10 Pa. The residue 10 contains the triglycerides which may be discarded or recycled as a feed into the reaction for preparing the mixture 1 of partial glycerides.

The distillate 9 from the second short path distillation unit 8, having a temperature of about 40-100 °C may be supplied to a third stripping column 11 for purification. The temperature of the column is about 180-240 °C and the pressure is about 10-1000 Pa. The stripped part 12 is removed and the residue 13 contains finished product comprising diglycerides.
The temperature and/or flow of the distillation are selected depending on the desired product composition. This is controlled by the distillation cut defined as the distillate flow rate in kg/hr divided by the feed flow rate in kg/hr. The mixture of glycerides used as a feed into the fractionation process affects the amount of different partial glycerides obtained as well.

A person skilled in the art will be capable of determining the appropriate temperatures and flows for each desired product depending on the composition of the feed stream as well as the process according to the present invention.

In the following the present invention will be illustrated by some examples, which describe some embodiments of the invention. The percentages in the Examples are calculated by weight unless otherwise specified.

**Example 1**

A glyceride mixture based on a transesterification of glycerol and safflower oil having the following composition (%) after substantially removing the excess glycerol:

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerol</td>
<td>0.3</td>
</tr>
<tr>
<td>free fatty acid</td>
<td>0.6</td>
</tr>
<tr>
<td>monoglyceride</td>
<td>42.8</td>
</tr>
<tr>
<td>diglyceride</td>
<td>45.2</td>
</tr>
<tr>
<td>triglyceride</td>
<td>11.5</td>
</tr>
</tbody>
</table>

was separated in a first fractionation in a short path distillation column in accordance with the principles shown in Figure 1 at a temperature of 260 °C and a pressure of 0.75 Pa. 77.7 % of the feed was recovered as distillate with a composition (%) of

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerol</td>
<td>0.30</td>
</tr>
<tr>
<td>free fatty acid</td>
<td>0.10</td>
</tr>
<tr>
<td>monoglyceride</td>
<td>52.6</td>
</tr>
<tr>
<td>diglyceride</td>
<td>46.7</td>
</tr>
<tr>
<td>triglyceride</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The rest was a residue with the following composition (%):

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerol</td>
<td>0.0</td>
</tr>
<tr>
<td>free fatty acid</td>
<td>0.1</td>
</tr>
<tr>
<td>monoglyceride</td>
<td>1.8</td>
</tr>
<tr>
<td>diglyceride</td>
<td>29.3</td>
</tr>
<tr>
<td>triglyceride</td>
<td>68.9</td>
</tr>
</tbody>
</table>
The distillate was treated further in a second distillation in a short path distillation column at 205 °C and a pressure of 0.15 Pa. 52.4 % was removed as distillate. The composition (%) of the distillate was

- glycerol: 0.3
- free fatty acid: 0.1
- monoglyceride: 96.1
- diglyceride: 3.5
- triglyceride: 0.0

The composition of the residue was

- glycerol: 0.0
- free fatty acid: 0.0
- monoglyceride: 4.4
- diglyceride: 94.1
- triglyceride: 1.4

The residue from the second fractionation was recovered as a high purity diglyceride product.

**Example 2**

A glyceride mixture based on a transesterification of glycerol and fully hydrogenated tallow with the following composition (%) after substantially removing the excess glycerol:

- glycerol: 0.3
- free fatty acid: 0.2
- monoglyceride: 40.1
- diglyceride: 47.3
- triglyceride: 12.1

was separated in a first fractionation in a short path distillation column in accordance with the principles shown in Figure 1 at a temperature of 265 °C and a pressure of 0.2 Pa. 83.5 % of the feed was recovered as distillate with a composition (%) of

- glycerol: 0.20
- free fatty acid: 0.4
- monoglyceride: 51.2
- diglyceride: 45.5
- triglyceride: 2.7

The rest was a residue with the following composition (%):

- glycerol: 0.0
- free fatty acid: 0.3
monoglyceride  2.1  
diglyceride  12.0  
triglyceride  85.6  

The distillate was treated further in a second distillation in a short path distillation column at 205 °C and a pressure of 0.15 Pa. 52.8 % was removed as distillate. The composition (%) of the distillate was  
glycerol  0.3  
free fatty acid  0.6  
monoglyceride  89.2  
diglyceride  9.9  
triglyceride  0.0  

The composition of the residue was  
glycerol  0.0  
free fatty acid  0.1  
monoglyceride  2.5  
diglyceride  87.4  
triglyceride  10.0  

The residue from the second fractionation was recovered as a high purity diglyceride product.  

**Example 3**  
A glyceride mixture based on a transesterification of glycerol and safflower oil with the following composition (%) after substantially removing the excess glycerol:

glycerol  0.3  
free fatty acid  0.6  
monoglyceride  41.6  
diglyceride  44.8  
triglyceride  12.7  

was separated in a first fractionation in a short path distillation column in accordance with the principles shown in Figure 2 at a temperature of 190 °C and a pressure of 0.3 Pa. 35.8 % of the feed was recovered as distillate with a composition (%) of  
glycerol  0.60  
free fatty acid  0.6  
monoglyceride  97.6  
diglyceride  1.2  
triglyceride  0.0  

The distillate from the first fractionation was recovered as a high purity monoglyceride.

The rest was a residue with the following composition (%):
- glycerol: 0.0
- free fatty acid: 0.2
- monoglyceride: 8.0
- diglyceride: 70.8
- triglyceride: 21.0

The residue was treated further in a second distillation in a short path distillation column at 245 °C and a pressure of 0.3 Pa. 47.5 % was removed as distillate. The composition (%) of the distillate was:
- glycerol: 0.0
- free fatty acid: 0.2
- monoglyceride: 16.3
- diglyceride: 83.4
- triglyceride: 0.1

The composition of the residue was:
- glycerol: 0.0
- free fatty acid: 0.2
- monoglyceride: 0.4
- diglyceride: 54.1
- triglyceride: 45.3

The distillate from the second fractionation was recovered as a diglyceride product.

Example 4
A glyceride mixture substantially free of glycerol was subjected to a two-step fractionation in accordance with the invention. The glyceride mixture was obtained from a reaction between glycerol and fully hydrogenated rapeseed oil (consisting approximately 90% stearic acid). In the first fractionation the partial glyceride mixture with the following composition (in weight %)
- monoglyceride: 43
- diglyceride: 47
- triglyceride: 10
underwent fractionation in a short path distillation column in accordance with the principles
shown in Figure 2 at 215°C and a pressure of 0.2 Pa. 49% of the feed was removed as distillate with a composition (%) of
monoglyceride  86
diglyceride     14
triglyceride    0

The rest was a residue with the following composition (%):
monoglyceride  1
diglyceride    79
triglyceride   20

The residue from the first fractionation underwent a second fractionation in a short path
distillation column at 245°C and a pressure of 0.2 Pa. 52% of the feed was removed as distillate
with a composition (%) of:
monoglyceride  1
diglyceride    98
triglyceride   1

This product was recovered as a diglyceride product.

The residue from the second fractionation had the following composition (%):
monoglyceride  0
diglyceride    50
triglyceride   50

Example 5

The diglyceride product obtained in Example 2 and containing 87.4 % by weight of diglyceride
and 10.0 % by weight of triglyceride is subjected to a third fractionation step to increase its
purity. The fractionation is performed in a short path distillation column at a temperature of 280
°C and a pressure of 0.2 Pa. 55 % of the feed is recovered as a high purity diglyceride distillate
having a diglyceride content of 95 % by weight.
**Example 6**

The diglyceride product obtained in Example 2 and containing 87.4 % by weight of diglyceride and 2.5 % by weight of monoglyceride is subjected to a third fractionation step to increase its purity. The fractionation is performed in a short path distillation column at a temperature of 200 °C and a pressure of 0.15 Pa. 90 % of the feed is recovered as a high purity diglyceride residue having a diglyceride content of 89 % by weight.

The present invention has been illustrated in detail by the above examples. It is evident to those skilled in the art that the invention may be used in many different ways and many different applications.
Claims

1. A process for recovering diglycerides comprising fractionating a glyceride mixture of mono-, di- and triglycerides on an industrial scale in at least two fractionation steps at temperatures above 150 °C and pressures between 0.15 and 10 Pa, wherein one of said steps separates triglycerides from mono- and/or diglycerides at a temperature between 220 and 300 °C and the other one of said steps separates monoglycerides from di- and/or triglycerides at a temperature between 150 and 250 °C, and recovering diglycerides as a product of said fractionation steps.

2. A process according to claim 1, wherein said triglyceride-separating step is performed at a temperature of 240 to 280 °C.

3. A process according to claim 1, wherein said monoglyceride-separating step is performed at a temperature of 180 to 240 °C.

4. A process according to claim 1, wherein said diglyceride product has a purity of 80 % or more, preferably 85 % or more, most preferably 90 % or more by weight.

5. A process according to claims 1, 2, 3 or 4, wherein a third fractionation step is performed on said diglyceride product in order to increase the purity of the product.

6. A process according to claim 5, wherein said third fractionation step is performed at a temperature of 150 to 250 °C in order to remove monoglycerides from said diglyceride product.

7. A process according to claim 1 or 6, wherein monoglycerides are recovered as a further product of said fractionation.

8. A process according to claim 1 wherein at least one of said fractionation steps is performed in a fractionation means, selected from a distillation unit, a short path distillation column, a centrifugal still and a high vacuum wiped film evaporator, a falling film short path evaporator, preferably a short path distillation column.

9. A process according to claim 8 wherein said fractionation steps are performed in one or in two or more separate short path distillation columns.

10. A process according to any one of the claims 1 to 9 wherein the glyceride mixture derives from a transesterification of glycerol and triglycerides containing a mixture of fatty acid chains corresponding to a desired end product partial glyceride.
11. A process according to claim 1 wherein the glyceride mixture has been stripped of glycerol in a stripping column to remove glycerol from said partial glycerides before said fractionation steps.

12. A process according to claim 11 wherein the stripped glycerol is about 1-30 %, preferably 5-20 % by weight of the triglycerides before stripping.

13. A process according to any one of the claims 1 to 9 wherein the glyceride mixture derives from an enzymatic process using the fatty acid chains of a desired end product partial glyceride.

14. A process according to claim 1 wherein glycerol stripping is performed after said fractionation steps, preferably with water vapour, preferably at a temperature of about 180-240 °C and preferably at a pressure of about 10-1000 Pa.

15. A process according to claim 1, wherein both monoglycerides and diglycerides are distilled in a first fractionation step at a temperature between 220 and 300 °C to provide a separation from triglycerides.

16. A process according to claim 15 wherein the distillate from said first fractionation step containing both mono- and diglycerides is supplied to a second fractionation step in order to recover the monoglycerides as distillate and the diglycerides as residue at a temperature from about 150 to 250 °C.

17. A process according to claim 1 or 7 wherein the monoglycerides and/or diglycerides are recovered and purified in a stripping step.

18. A process according to claim 1 wherein the majority of the monoglycerides are distilled off in a first fractionation step.

19. A process according to claim 7 wherein the monoglyceride product has a purity of 80 % or more, preferably 85 % or more, most preferably 90 % or more.

20. A process according to claim 18 wherein the residue from the first fractionation step is processed in a second fractionation step at a temperature between 220 and 300 °C, preferably at a pressure of about 0.15-10 Pa, in order to recover the diglycerides.
21. A process according to any of the preceding claims wherein the glyceride mixture is obtained from enzymatic or chemical processes.

22. A process according to any of the preceding claims wherein the purity of both the monoglyceride and diglyceride product is at least about 80 %, preferably at least about 85 %, more preferably at least about 90 % by weight.

23. A process according to any of the preceding claims wherein the fatty acids in the glyceride mixture contain from 8 to 30 carbon atoms and are selected from the group consisting of octanoic, decanoic, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, palmitoleic, oleic, gadoleic, arachidonic, linoleic, α-linolenic acids and, DHA and EPA.

24. A process according to claim 23 wherein the fatty acids in the diglyceride are saturated fatty acids.

25. A process according to claim 24 wherein the fatty acids in the diglyceride are stearic or palmitic or behenic acids.

26. A process according to any of the preceding claims wherein the fatty acids in the glyceride mixture are derived from natural or hydrogenated or selectively hydrogenated oils and fats including oils and fats having vegetable or animal or micro organism origin or mixtures thereof.

27. A process according to any one of claim 1 to 26, wherein said diglyceride is mixed with one or more ingredients for end products selected from the group consisting of ingredients for nutritional, nutraceutical, pharmaceutical, plastics and polymer products.

28. A process according to claim 27, wherein said mixed diglyceride and ingredient(s) are processed into an end product selected from the group consisting of nutritional, nutraceutical, pharmaceutical, plastics and polymer products.

29. Use of the process according to claim 1 for the providing of target diglycerides having a controlled fatty acid composition, said use comprising the steps of

- defining at least one target fatty acid of the target diglyceride;

- optionally defining the target position(s) of said fatty acid(s);
- providing a glyceride starting material containing a significant amount of the target diglyceride having a desired fatty acid composition;

- at need, removing glycerol from said starting material to provide a feed stream substantially free of glycerol;

- treating said starting material in at least two fractionation steps at temperatures above 150 °C and pressures between 0.15 and 10 Pa in order to fractionate between mono-, di- and triglycerides; and

- recovering the target diglyceride containing at least one of said target fatty acid(s) having the desired composition.

30. The use according to claim 29, wherein monoglyceride having the target fatty acid is additionally recovered.

31. The use according to claim 29 or 30, wherein the target di- and/or monoglyceride(s) is/are recovered at a purity above 80 %, preferably above 85 %, most preferably above 90 % by weight.

32. The use according to claim 29 or 30 wherein said defining of the target fatty acid(s) and/or composition of the target di- and/or monoglyceride is done in response to customer requirements.
INTERNATIONAL SEARCH REPORT

PCT/EP2006/060833

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11B3/12  C11B7/00  C07C7/04  C11C1/10

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)
C11B  C07C  C11C

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Y</td>
<td>WO 03/029392 A (ARCHER-DANIELS-MIDLAND COMPANY) 10 April 2003 (2003-04-10) cited in the application claims 22,24,25; figure 1; examples 11,12</td>
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<tr>
<td>Y</td>
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search
2 June 2006

Date of mailing of the international search report
22/06/2006

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Authorized officer
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<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>YANG TIANKUI; ZHANG HONG; MU HUILING; SINCLAIR ANDREW J; XU XUEBING: &quot;Diacylglycerols from butterfat: production by glycerolysis and short-path distillation and analysis of physical properties&quot; JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, vol. 81, no. 10, 2004, pages 979–987, XP008064608 US page 980, column 1, paragraph 4; table 1 page 981, column 2, paragraph 2 – page 983, column 1, paragraph 3 page 986, column 1, paragraph 2 – column 2, paragraph 1</td>
<td>29–32</td>
</tr>
<tr>
<td>A</td>
<td>GB 2 031 290 A (TAIYO OIL &amp; FAT MFG CO LTD) 23 April 1980 (1980-04-23) the whole document</td>
<td>1–32</td>
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<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
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<tr>
<td>WO 03029392</td>
<td>10-04-2003</td>
<td>BR 0213118 A</td>
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<td>CA 2462884 A1</td>
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<td>CN 1585814 A</td>
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<td>EP 1451279 A1</td>
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<td>US 2005054621 A1</td>
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