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(54) **PROCESS FOR PRODUCING FATTY ACID ALKYL ESTERS**

(57) The present invention primarily concerns a process for producing fatty acid alkyl esters by catalytic transesterification of triglycerides from an oil and / or fat based crude feedstock containing triglycerides and free fatty acids.

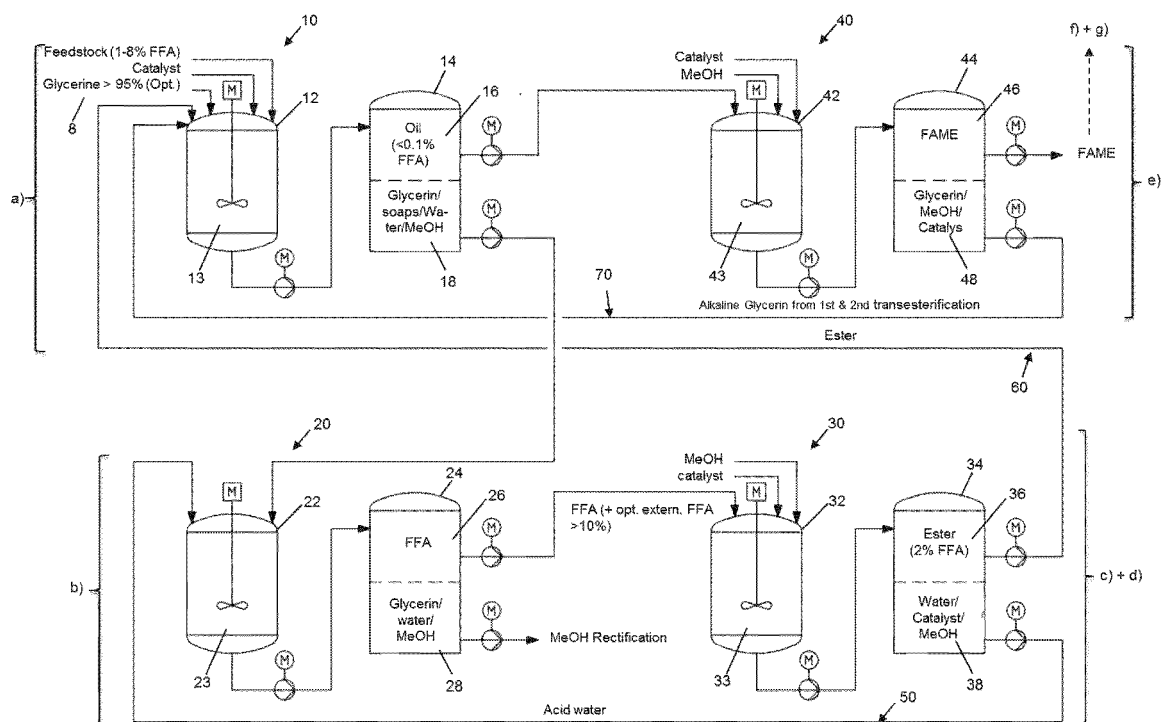


Fig. 1

Description

[0001] The present invention relates to a process for producing fatty acid alkyl esters.

[0002] Fatty acid alkyl esters are widely used in the chemical and pharmaceutical industries both as raw materials and as intermediates. In addition, such compounds are also used in the food industry and, more recently, as diesel fuel (biodiesel).

[0003] For the production of these compounds, different ways have been proposed starting from crude oil or renewable raw materials. In practice, the production of such esters from vegetable or animal oils and fats is of particular importance, not least for environmental reasons.

[0004] The known processes are generally based on base-catalyzed transesterification of fatty acid glycerides (cf., e.g., J. Am. Oil Chem. Soc. 61 (1984), 343 or Ullmann, Enzyklopädie der Technischen Chemie, 4th edition, volume 11, page 432).

[0005] Processes for the production of fatty acid alkyl esters by base-catalyzed transesterification of fatty acid esters of triglycerides are for instance described in DE 3932514 and DE 4209779. These processes can however only be carried out economically on an industrial scale from about 50,000 tons per year and more as they involve a high invest for equipment and/or work under cost-intensive conditions, i.e. at high temperature and/or high pressure, and often include complex processing steps such as distillation. They are hence not suitable for small plants of about 500-5,000 tons per year.

[0006] Other processes based on the transesterification aim at simplification in order to reduce costs and thus to be able to work economically even on a small scale. Such processes are for instance known from AT 386222, AT 397966, AT 387399, DE 3727981, DE 3020612, DE 3107318 and WO 92/00268. They particularly avoid energy-intensive and complex separation steps such as distillation. Phase separation has established itself as the method of choice for the separation of the product or intermediate products.

[0007] However, when unrefined oils such as native oils are used in the known processes as starting material, two major problems arise. Native oils, especially those of vegetable origin, usually contain mucilages / gums such as phosphatides. These substances are surface-active and are therefore partly used as emulsifiers in the food industry. This property gives rise to the problem that phase separation is adversely affected. Accordingly, processes involving phase separation are required to use already degummed starting oils or additional process steps, increasing plant costs and process complexity.

[0008] Furthermore, unrefined oils often contain considerable amounts of free fatty acids, the presence of which negatively impact the transesterification reaction. The free fatty acids react with the basic transesterification catalyst, thereby neutralizing the catalyst, which is then no longer available for the transesterification reaction.

[0009] These problems have at least been partly solved by the process disclosed in EP 1 183 225 B1. In this process, the oils and/or fats are first treated with a non-miscible basic glycerol phase so that the free fatty acids are neutralized and pass into the glycerol phase, and then the triglycerides, after separation from the glycerol phase, are transesterified with monohydric alcohols using a base as catalyst in a stirred vessel to give the fatty acid esters. Further, the basic glycerol phase resulting from the transesterification of the triglycerides is used, after separation of the fatty acid esters, for the treatment of the oils and/or fats to remove the free fatty acids.

[0010] The inventors of the present invention noticed that there is still room for improvement. For instance, it was noted that the process known from EP 1 183 225 B1 is limited to moderate free fatty acid contents. When the starting material contained high amounts of free fatty acids, an unacceptable large part of catalyst was neutralized. Moreover, it was noted that a considerable amount of waste accumulated during the process without adding value.

[0011] A problem to be solved by the present invention was thus the provision of an improved process for the production of fatty acid alkyl esters. In particular, it was an object to render the process more suitable to accept unrefined oils and fats with varying amounts of free fatty acids and / or to increase the economy, while at the same time keep the complexity of the process low.

[0012] This problem is solved by a process for producing fatty acid alkyl esters by catalytic transesterification of triglycerides from an oil and / or fat based crude feedstock containing triglycerides and free fatty acids, comprising the steps:

a) neutralizing free fatty acids contained in a mixture that further comprises oil and / or fat as well as triglycerides with alkaline glycerine to enrich triglycerides in a first light phase and neutralized free fatty acids in a first heavy phase;

b) separating the first light phase and the first heavy phase and acidifying the separated first heavy phase to enrich free fatty acids in a second light phase and glycerine in a second heavy phase;

c) separating the second light phase and the second heavy phase and esterifying free fatty acids in the separated second light phase in the presence of an alcohol to enrich fatty acid esters in a third light phase and the alcohol in a third heavy phase;

d) separating the third light phase and the third heavy phase and recycling the separated third light phase to the neutralization reaction of step a); and

e) forming fatty acid alkyl esters by catalytic transesterification of the triglycerides contained in the separated first light phase;

wherein the crude feedstock is fed to the neutralization reaction in step a) and / or to the esterification reaction in step c).

[0013] Moreover, it was a problem to be solved by the present invention to provide a process for lowering the free fatty acid content in an oil and / or fat based crude feedstock containing triglycerides and free fatty acids with the aim of providing a processed feedstock that can be used to form fatty acid alkyl esters by catalytic transesterification of the triglycerides, whereby the process is particularly suited to accept unrefined oils and / or fats with varying amounts of free fatty acids, is economic, and / or has little complexity.

[0014] This problem is solved by a process for lowering free fatty acid content in an oil and / or fat based crude feedstock containing triglycerides and free fatty acids, comprising the steps:

a) neutralizing free fatty acids contained in a mixture that further comprises oil and / or fat as well as triglycerides with alkaline glycerine to enrich triglycerides in a first light phase and neutralized free fatty acids in a first heavy phase;

b) separating the first light phase and the first heavy phase and acidifying the separated first heavy phase to enrich free fatty acids in a second light phase glycerine in the second heavy phase;

c) separating the second light phase and the second heavy phase and esterifying free fatty acids in the separated second light phase in the presence of acid, water and alcohol to enrich fatty acid esters in a third light phase and water, acid and alcohol in a third heavy phase;

d) separating the third light phase and the third heavy phase and recycling the separated third light phase to the neutralization reaction of step a);

wherein the crude feedstock is added to the neutralization reaction in step a) and / or to the esterification reaction in step c).

[0015] The present invention is based on the innovation of the inventors that a crude feedstock can be fed to different process steps. Thereby, it is possible to process with the same process different crude feedstocks, in particular crude feedstocks having relatively low as well as rather high amounts of free fatty acids as further explained herein. In comparison to the process of EP 1 183 225 B1, where only feedstocks can be economically processed that do not contain too much free fatty acids (otherwise more than catalytic amounts of catalyst would be necessary), it is possible to directly use feedstocks with higher free fatty acid contents.

[0016] Moreover, it is not necessary to subject a crude feedstock to a pretreatment step in order to bring down the free fatty acid content to an adequate level.

[0017] The advantages achieved are particularly due to the fact that an increased flexibility exists with respect to the crude feedstock, which can be used, that a product with high purity and in very good yield can be obtained and that only catalytic quantities of catalyst are required. The latter point means that additional expenditure on catalyst material for neutralizing the free acids is generally not necessary.

[0018] In addition, by recycling the separated third light phase, it is possible to decrease losses of fatty acid esters and hence increase the yield. Then, by feeding the separated third light phase specifically to the neutralization reaction of step a), it is possible to remove non-converted fatty acids, thus optimizing the following transesterification by minimizing catalyst usage.

[0019] In the process according to the invention, a crude feedstock of any origin can be generally processed as starting material as long as the crude feedstock contains triglycerides. However, it is apparent that the benefits of the invention will be achieved only when the crude feedstock also contains free fatty acids, usually as unwanted by-products. Examples include: rapeseed oil, soybean oil, sunflower oil, tallow, palm oil and palm fat, olive oil, peanut oil, safflower oil, linseed oil, pure nut oil, cottonseed oil, rice oil, pork fat. The process according to the invention is suitable for a large number of crude feedstocks of varying quality, the palette ranges from vegetable oils of edible oil quality to unrefined oils to animal fats or fat wastes, such as used hydraulic oils based on fat, and used edible oils, waste food fats, animal fats category I, II and III, trap grease from waste water treatment, POME (Palm oil mill effluent) and further side strains from the oleochemical industry. Preferred crude feedstocks are selected from the group consisting of animal or vegetable fats and oils, in particular as they are traditionally used for the production of fatty acid esters. Rapeseed oil, soybean oil and tallow are particularly suitable as crude feedstock, whereby the transesterification produces rapeseed oil fatty acid methyl ester, soybean fatty acid methyl ester and tallow fatty acid methyl ester if methanol is used as the alcohol.

[0020] An interesting variant of the process according to the invention for waste management reasons is that waste oil and / or waste fat, such as used cooking oil and / or deep-frying fat or used hydraulic oils based on fat, is / are used as crude feedstock.

[0021] According to a preferred embodiment, the crude feedstock is fed to the neutralization reaction in step a) and / or to the esterification reaction in step c), depending on the amount of free fatty acids contained in the crude feedstock.

[0022] The free fatty acid content should not be too high, when the crude feedstock is fed to the neutralization reaction. Thus, it is preferred that the crude feedstock is fed to the neutralization reaction in step a), if the crude feedstock contains free fatty acids in an amount of 8.0 wt.-% or less, preferably 7.5 wt.-% or less, more preferably 7.0 wt.-% or less, yet more preferably 6.5 wt.-% or

less, most preferably 6.0 wt.-% or less, relative to the total weight of the crude feedstock, and /or if the crude feedstock contains free fatty acids in an amount 0.2 wt.-% or more, preferably 0.4 wt.-% or more, more preferably 0.6 wt.-% or more, yet more preferably 0.8 wt.-% or more, most preferably 1.0 wt.-% or more, relative to the total weight of the crude feedstock.

[0023] On the other hand, if the free fatty acid content is relatively high, the crude feedstock is preferably fed to the esterification reaction. Accordingly, a process is preferred, wherein the crude feedstock is fed to the esterification reaction in step c), if the crude feedstock contains free fatty acids in an amount of 10 wt.-% or more, preferably 15 wt.-% or more, more preferably 20 wt.-% or more, yet more preferably 25 wt.-% or more, most preferably 30 wt.-% or more, relative to the total weight of the crude feedstock.

[0024] In the following drawings:

Fig. 1 illustrates a process scheme for producing fatty acid alkyl esters according to a preferred embodiment of the present invention.

Fig. 2 illustrates a process scheme for lowering free fatty acid content in an oil and / or fat based crude feedstock according to a preferred embodiment of the present invention.

[0025] Referring to Fig. 1, the processes for producing fatty acid alkyl esters by catalytic transesterification of triglycerides from an oil and /or fat based crude feedstock containing triglycerides and free fatty acids of the invention as well as further embodiments thereof will be described below.

[0026] The process comprises the step:

a) neutralizing 10 free fatty acids contained in a mixture 13 that further comprises oil and / or fat as well as triglycerides with an alkaline glycerine phase to enrich triglycerides in a first light phase 16 and neutralized free fatty acids in a first heavy phase 18.

[0027] It is to be understood that the mixture 13 used in step a) comprises oil and / or fat as well as free fatty acids and triglycerides primarily originating from the crude feedstock, which may be directly fed to the neutralization reaction 10 of step a) and / or indirectly fed to the neutralization reaction 10 of step a) via the esterification reaction 30 in step c) and recycling 60 the separated third light phase 36 to the neutralization reaction of step a).

[0028] The neutralizing reaction preferably comprises mixing the mixture 13 with the alkaline glycerine phase. Mixing may be carried out in a first stirred tank reactor 12. Thereby, free fatty acids and residual water, if present, are largely extracted into the glycerine phase.

[0029] A preferred embodiment pertains to a process as described herein, wherein the neutralization 10 in step

a) comprises mixing for less than 1 minute, preferably less than 55 seconds, more preferably less than 50 seconds and most preferably less than 45 seconds and/or wherein step a) comprises mixing for at least 10 seconds, preferably at least 15 seconds, more preferably at least 20 seconds, even more preferably at least 25 second and most preferably at least 30 seconds. As an advantage of this relatively short mixing step, a decreased process time and an enhanced process economy are obtained.

[0030] The reaction conditions during neutralization 10 are primarily limited by the solidification point of the components present in step a), in particular the oil and / or fat as well as free fatty acids and triglycerides originating from the crude feedstock. From an economic point of view, the neutralization 10 should be carried out at moderate temperatures, for instance at a temperature of 20 to 65 °C, preferably 25 to 60 °C, more preferably 30 to 55 °C. As the reaction preferably takes place in a pipe against a large vessel, e.g. a full vessel of 15 m height, the pressure preferably ranges between 0 and 3 bar.

[0031] The alkaline glycerine phase preferably contains enough free base to neutralize substantially all or the free fatty acids. For example, the base content may be 1 to 30 %, preferably 3 to 8 % (w/w). The glycerine content can be 20 to 99 %, preferably 50 to 70 % (w/w). Preferably, the alkaline glycerine phase resulting from the transesterification reaction 40 of step e) is recycled to the neutralization reaction 10 in step a), as set forth further below. In this case, the content of transesterification alcohol may be 5 to 40 % (w/w), preferably 15 to 25 % (w/w).

[0032] The amount of added alkaline glycerine phase, relative to the amount of added crude feedstock, may vary in a range of 1 to 100 % (w/w), preferably 5 to 20 % (w/w). If necessary, the alkaline glycerine phase can be supplemented by adding solid base or an alcohol/base mixture. It is possible to use any grade of glycerine, from technical to pharmaceutical grade as well as mixtures of different grades. Moreover, the base may be used with or without an alcohol. All base catalysts used for the transesterification reaction 40 of step e) can also be used as base in the neutralization reaction 10 in step a). Preferred bases / catalysts are described further below.

[0033] Following the neutralization 10, the mixture 13 is allowed to settle in order to allow the light phase and the heavy phase to separate from each other. For this purpose, the mixture 13 can be transferred into a first settling tank 14. Phase separation preferably occurs by sedimentation. Usual sedimentation times are 1 to 72 h, preferably 5 to 10 h. The sedimentation temperature is preferably between 0 to 100 °C, preferably 45 to 60 °C, more preferably 47 to 55 °C. The skilled person will further appreciate that the temperature is limited by the solidification point of the components contained in the mixture / crude feedstock. For instance, in the case of vegetable oils such as rapeseed, soybean and sunflower oil, the temperature should be at least 30 °C, in the case of an-

imal body and deep-fryer fats, the temperature should be 40 to 50 °C. Phase separation results in formation of the first light phase 16 and the first heavy phase 18. In the first light phase 16 triglycerides are enriched. It may further contain up to 0.5 %, preferably up to 0.2 %, more preferably up to 0.1 % (w/w) free fatty acids, relative to the total weight of the first light phase 16. In the first heavy phase 18, neutralized free fatty acids (also referred to herein as soaps or fatty acid salts) are enriched. It further contains glycerine and optionally one or more of water and alcohol.

[0034] The process further comprises the step:

b) separating the first light phase 16 and the first heavy phase 18 from each other, and acidifying 20 the separated first heavy phase 18. For this purpose, the separated first heavy phase 18 may be transferred in a second stirred tank reactor 22 (alternatively, a static mixer can be used) and mixed with an acidic solution. During acidification 20, the pH value is preferably decreased to 1 to 4, preferably 2 to 3. To this step other side streams like washing water (from washing step h), methanol containing condensate (from esterification 30 and or from drying step g) etc. also may be added. In the neutralization reaction 10, a glycerine-rich phase 18 is obtained as a by-product. This phase also contains soaps. In order to separate these fatty acid compounds from the glycerine phase, the glycerine phase is treated with an acid. This treatment releases the fatty acids from the soaps. The released fatty acids and the fatty acid esters themselves are not miscible with glycerin and therefore separate from the glycerin phase as a separate phase.

[0035] Following acidification 20, the reaction mixture 23 is allowed to settle in order to allow the light phase and the heavy phase to separate from each other. For this purpose, the mixture 23 can be transferred into a second settling tank 24. Phase separation preferably occurs by sedimentation. Usual sedimentation times are 1 to 48 h, preferably 3 to 8 h. The sedimentation temperature is preferably between 0 to 100 °C, preferably 45 to 60 °C, more preferably 47 to 55 °C. Phase separation results in formation of the second light phase 26 and the second heavy phase 28. In the second light phase 26 free fatty acids are enriched, whereas the second heavy phase 28 is rich in glycerine. Further components of the second heavy phase 28 include water and alcohol.

[0036] The process further comprises the step:

c) separating the second light phase 26 and the second heavy phase 28 from each other, and esterifying 30 free fatty acids in the separated second light phase 26 in the presence of an alcohol to enrich fatty acid esters in a third light phase 36 and the alcohol in a third heavy phase 38.

[0037] The esterification 30 allows both reacting the free fatty acids present in the processed feedstock having a relatively high free fatty acid content, e.g., above 10 %, to form fatty acid esters, and recovering the fatty acid compounds from all streams that were added to the reaction mixture 23.

[0038] The esterification 30 can be carried out by known processes. An esterification 30 in the presence of an acid catalyst is preferred. Preferably, the separated second light phase 26 is mixed with the alcohol and the acid catalyst, for instance in a third stirred tank reactor 32. The acid catalyst is not particularly limited and can, for example, be selected from the group consisting of sulfuric acid, paratoluenesulfonic acid, ion exchangers in H⁺ form and methanesulfonic acid. Sulfuric acid or methanesulfonic acid is particularly preferred.

[0039] The alcohol added in step c) is preferably a linear, branched or cyclic alkyl alcohol with 1 to 10 carbon atoms, preferably 1 to 8 carbon atoms. Examples include: methanol, ethanol, propanol, i-propanol, butanol, sec-butanol, pentanol, hexanol, heptanol and octanol. It is further preferred that the alcohol has 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms. Most preferably, the alcohol is methanol, ethanol and / or propanol; methanol is particularly preferred. The alcohol added in step e) is preferably independently selected from the aforementioned alcohols. The same or a different alcohol may be used. Preferably, the same alcohol is used in steps c) and e).

[0040] As mentioned above, it is possible to add to the esterification reaction 30 a crude feedstock, which has a relative high content of free fatty acids. In this case, the total amount of free fatty acids, which will undergo esterification 30, is the sum of the free fatty acids present in the separated second light phase 26 and the free fatty acids present in the crude feedstock.

[0041] The esterification reaction may take place at about 40 to 160 °C, preferably 50 to 140 °C, more preferably 60 to 75 °C and / or at a pH value of 0 to 1. The pressure preferably ranges between 900 to 1200 mbar, whereas at 160 °C the pressure can be up to or even more than 4 bar. The reaction may be allowed to proceed for 1 to 8 hours, preferably 4 to 6 hours and / or until the desired content decrease of free fatty acids has been achieved. It is further preferred that the reaction proceeds under mixing e.g. stirring.

[0042] If desired, the separated second heavy phase 28 can be further processed. In particular, if the second heavy phase 28 includes an alcohol, it may be separated from the glycerine-rich phase. A convenient way of separation is by means of thermal separation, in particular rectification. The separated alcohol may further be recovered and / or recycled to the esterification reaction 30 in step c) and / or to the transesterification reaction 40 in step e).

[0043] Following the esterification reaction 30, the reaction mixture 33 is allowed to settle in order to allow the light phase and the heavy phase to separate from each other. For this purpose, the reaction mixture 33 can be transferred into a third settling tank 34. Phase separation preferably occurs by sedimentation. Usual sedimentation times are 1 to 72 h, preferably 5 - 10 h. The sedimentation temperature is preferably between 0 to 100 °C, preferably 30 to 60 °C, more preferably 40 to 50 °C. Phase separation

ration results in formation of the third light phase 36 and the third heavy phase 38. In the third light phase 36, fatty acid esters are enriched. It may further contain up to about 5 % (w/w), preferably up to about 2 % (w/w), free fatty acids. In the third heavy phase 38, the alcohol is enriched. It may further contain the acid catalyst and water.

[0044] In step d) the third light phase 36 and the third heavy phase 38 are separated and the separated third light phase 36 is recycled 60 to the neutralization reaction 10 of step a). Due to the recycling step 60, it is possible to add the crude feedstock to the esterification reaction 30 in step c) and, thus, to process crude feedstocks with an increased free fatty acid content.

[0045] In step e) fatty acid alkyl esters are formed by catalytic transesterification 40 of the triglycerides contained in the separated first light phase 16. Transesterification is to be understood as an alcoholysis of triglycerides, that is to say a reaction with alcohols, preferably alkyl alcohols, in particular methanol and ethanol, whereby monoesters of fatty acids and glycerol are formed via di- and monoglycerides as intermediates. The fatty acids are not miscible with glycerin and therefore separate from the glycerin phase as a separate phase.

[0046] In a preferred embodiment, the process comprises the step:

f) recycling 50 the separated third heavy phase 38 to the acidification 20 in step b).

[0047] Thereby, it is possible to reuse (a fraction of) the acid catalyst and the alcohol, which are required in the esterification reaction 30 in step c).

[0048] According to a further preferred embodiment of the present invention, the separated third light phase 36 is not recycled to step e). This offers the advantage that free fatty acids that are present in the separated third light phase 36 do not neutralize the transesterification catalyst. For this reason, a higher free fatty acid content can be accepted in the separated third light phase 36. Preferably, the separated third light phase is not recycled to steps e) and b). More preferably, the separated third light phase is only recycled to the neutralization reaction of step a). The advantages achieved by this embodiment include the possibility to save the fatty acid esters contained in the separated third light phase 36, and to further reduce the fatty acid content in order to not waste transesterification catalyst by neutralization.

[0049] According to a preferred embodiment, the catalyst used in step e) is selected from the group of alkaline catalysts. Preferably, the catalyst is selected from the group of metal hydroxides, metal alcoholates and combinations thereof. The metals used in this group are preferably selected from the first to third main groups of the periodic system. More preferably, the catalyst is selected from the group of sodium hydroxide, potassium hydroxide, sodium alcoholates, potassium alcoholates, such as sodium methylate, sodium ethylate, sodium butylate, potassium methylate, potassium ethylate, potassium butylate, and combinations thereof. Most preferred is a

process, wherein the catalyst comprises or is potassium methylate. The advantages associated with potassium methylate include lower reaction temperatures, less side reactions and a higher solubility of K-soaps in glycerine.

[0050] According to a further preferred embodiment, step e) comprises:

e-1) treating the separated first light phase 16 with an alkyl alcohol and a base as a catalyst to form fatty acid alkyl esters and glycerine by transesterification 40 of triglycerides, wherein the fatty acid alkyl esters are enriched in a fourth light phase 46 and the glycerine is enriched in a fourth heavy phase 48, and

e-2) separating the fourth light phase 46 and the fourth heavy phase 48 and optionally recovering the fatty acid esters from the separated fourth light phase 46.

[0051] In this step, the triglycerides contained in the separated first light phase 16 is mixed with a base as transesterification catalyst and an alkyl alcohol to carry out transesterification 40 of the triglycerides to fatty acid alkyl esters. Hereto forth, the required components may be added to and mixed in a fourth stirred tank reactor 42.

[0052] The total amount of alkyl alcohol used for the transesterification reaction 40 may be distributed among several transesterification stages, for instance 1 to 5 stages, preferably 2 stages. In total, about 1.05 to 2 mol, preferably 1.2 to 1.4 mol, alkyl alcohol per mol of bound fatty acid function may be used in this step. In a two-stage process (as further described below), 40 to 99%, preferably 90 to 95%, are used in the first stage and 0 to 60%, preferably 0 to 10%, in the second stage.

[0053] The type of alkyl alcohol that can be employed in step e) is not limited. However, linear, branched or cyclic alkyl alcohols with 1 to 10 carbon atoms, in particular 1 to 4 carbon atoms, are preferred; methanol is particularly preferred.

[0054] If desired, the base can be dissolved in alcohol and added as an alcoholic solution. In such case, those containing 25 to 50 % by weight of base, based on the total weight of the solution, are preferred. It shall be understood that the amount of alcohol introduced in this way is taken into account when calculating the total amount of alkyl alcohol.

[0055] The total amount of base (transesterification catalyst) added in this process step depends, on one hand, on the further process steps (e.g. the further transesterification stages) and, on the other hand, on the nature (i.e. composition) of the crude feedstock. In the case of a single-stage transesterification, the total amount of base is used in this single stage, whereas in the case of a two-stage transesterification, only 20 to 95%, and preferably 80 to 90%, of the total quantity is used in the first stage.

[0056] The minimum amount of base at low free fatty acid content (low acid number) is primarily determined

by the transesterification reaction 40. At higher acid numbers, the amount of free fatty acids to be neutralized primarily determines the required catalyst amount. The required amounts can be routinely determined by a person skilled in the art, for example by the method disclosed in EP 1 183 225 B1. Usually, 0,088 mol base / 1000 g oil ensures an acceptable reaction rate. Of this amount, 0,084 mol base / 1000 g oil is available for the neutralization reaction 10 of free fatty acids.

[0057] From an economic point of view, 10 times the theoretical minimum amount should not be exceeded. The use of 1 to 4 times the theoretical minimum quantity of basic transesterification catalyst has proven to be particularly advantageous.

[0058] Preferably, the transesterification 40 is performed at 40 to 65°C, preferably 45 to 60°C, more preferably 50 to 55°C and/or the transesterification 40 is performed for 10 to 100 min, preferably 30 to 80 min, more preferably 35 to 60°C, most preferably 40 to 50 min.

[0059] After conclusion of the transesterification reaction 40, the reaction mixture 43 can be worked up in a suitable manner, whereas phase separation has proven to be particularly advantageous. For this purpose, the obtained reaction mixture 43 may be fed into a fourth settling tank 44. Herein, the reaction mixture 43 is allowed to settle in order to allow the light phase and the heavy phase to separate from each other. Phase separation preferably occurs by sedimentation. Usual sedimentation times are 1 to 72 h, preferably 5 to 10 h. The sedimentation temperature is preferably between 0 to 100 °C, preferably 45 to 60 °C, more preferably 47 to 55 °C. Phase separation results in formation of the fourth light phase 46 and the fourth heavy phase 48. In the fourth light phase 46, fatty acid alkyl esters are enriched. The fourth heavy phase 48 is rich in glycerine. It may further contain the base catalyst and the transesterification alcohol.

[0060] From the fourth settling tank 44, a fourth light phase 46 rich in fatty acid alkyl esters can be withdrawn. Optionally, the fourth light phase 46 is further processed by conventional methods or subjected to a second transesterification stage.

[0061] It is further preferred that step e-2) further comprises:

- e-3) subjecting the separated fourth light phase 46 to a further transesterification, wherein the fatty acid alkyl esters are enriched in a fifth light phase and the glycerine is enriched in a fifth heavy phase, and
- e-4) separating the fifth light phase and the fifth heavy phase and optionally recovering the fatty acid alkyl esters from the separated fifth light phase.

[0062] A further (second) transesterification stage is particularly advantageous, if the first light phase 16 contains a relatively high amount of mono-, di- and/or triglycerides and a single transesterification stage is expected to be not sufficient to achieve the desired degree of

conversion into fatty acid alkyl esters. In this case, the separated fourth light phase 46 can be transferred to a fifth stirred tank reactor in which a second transesterification stage is carried out. The second transesterification stage can be performed under the same reaction conditions as the first transesterification stage.

[0063] Because the alcohol and the base catalyst used in the first transesterification stage enrich during phase separation in the fourth heavy phase 48, additional alkyl alcohol and base should be added to the second transesterification stage. The alkyl alcohol and / or base may be added directly to the fifth stirred tank reactor and / or may be first mixed with each other and then fed into the fifth stirred tank reactor. As will be understood by a person skilled in the art, it is advantageous to use the same alcohol (or the same alcohol mixture) as in the preceding stage. Also with respect to the base catalyst, the same substance can be conveniently used as in the first transesterification stage. In terms of handling, an alcoholic solution containing 25 to 50 % (w/w) base is preferred.

[0064] It is further preferred that the further (second) transesterification in step e-3 comprises mixing for at least 1 minute, preferably for at least 2 minutes, more preferably at least 3 minutes, even more preferably at least 4 minutes and most preferably at least 5 minutes and/or mixing less than 15 minutes, preferably less than 14 minutes, more preferably less than 13 minutes, even more preferably less than 12 minutes, even more preferably less than 11 minutes and most preferably less than 10 minutes.

[0065] The reaction mixture obtained after the second transesterification stage can be worked up, whereby a phase separation carried out in the manner described above has proved advantageous.

[0066] The process may further comprise step h) washing the fourth light phase. After the final phase separation, one or more washing steps may be carried out, wherein the fourth light phase is washed with at least 5 % (w/w) water, relative to the weight of the light phase. Low-boiling components may be removed from the light phase rich in fatty acid alkyl esters. Removal may be achieved by evaporation. For instance, the light phase may be heated to 90 to 140 °C by passing over a heated surface. Thereby, the low-boiling components are evaporated and can be removed.

[0067] According to a preferred embodiment, the process further comprises the step:

- g) recycling 70 the separated fourth heavy phase 48, and / or the separated fifth heavy phase, if present, to the neutralization reaction 10 in step a).

[0068] As an advantage of this embodiment, (a fraction of) the glycerine, alcohol and base catalyst can be reused. The base catalyst coming from the transesterification 40 can thus be used for neutralizing free fatty acids in the neutralization reaction 10 of step a).

[0069] Especially at low acid numbers, a further reduction of the catalyst requirement by reusing a portion of the basic glycerol phase resulting from the transesterifi-

cation after separation of the fatty acid esters for the transesterification reaction is preferred. The circumstances under which a reuse is useful is described in EP 1 183 225, which is incorporated herein by reference in its entirety.

[0070] Preferably, steps a), b), d) and e) are performed continuously. More preferably, steps a), b), d) and e) as well as step f), if present, are performed continuously. Most preferably, steps a), b), d) and e) as well as steps f) and g), if present, are performed continuously.

[0071] It will be appreciated by the skilled person that the first, second, third, fourth and / or fifth settling tank(s) may be dimensioned larger than the respective first, second, third, fourth and / or fifth stirred tank reactor(s). The advantage of an increased dimension is that the settling tank(s) can be used as a reservoir, which means that, on the one hand, the settling times can be longer than the time required for the respective reaction and, on the other hand, a continuous withdrawal of the separated phase(s) is possible.

[0072] The settling tanks should also be designed in such a way that the light phase and the heavy phase can be removed separately from each other through outlets that are located at suitable heights of the settling tanks. It has proved to be advantageous to feed the respective reaction mixture to the settling tanks close to the interface, and to remove the respective phases remote from the interface. In this way, the phase separation can be performed efficiently.

[0073] Referring to Fig. 2, the process for lowering free fatty acid content in an oil and / or fat based crude feedstock containing triglycerides and free fatty acids of the invention as well as further embodiments thereof will be described in the following.

[0074] The process comprises the steps:

a) neutralizing 10 free fatty acids contained in a mixture 13 that further comprises oil and / or fat as well as triglycerides with alkaline glycerine to enrich triglycerides in a first light phase 16 and neutralized free fatty acids in a first heavy phase 18;

b) separating the first light phase 16 and the first heavy phase 18 and acidifying 20 the separated first heavy phase 16 to enrich free fatty acids in a second light phase 26 and glycerine in a second heavy phase 28;

c) separating the second light phase 26 and the second heavy phase 28 and esterifying 30 free fatty acids in the separated second light phase 26 in the presence of an alcohol to enrich fatty acid esters in a third light phase 36 and the alcohol in a third heavy phase 38;

d) separating the third light phase 36 and the third heavy phase 36 and recycling 60 the separated third light phase 36 to the neutralization reaction 10 of

step a);

wherein the crude feedstock is added to the neutralization reaction 10 in step a) and / or to the esterification reaction 30 in step c).

[0075] The various embodiments described in the context of the process for producing fatty acid alkyl esters form equivalent embodiments of the process for lowering free fatty acid content in an oil and / or fat based crude feedstock containing triglycerides and free fatty acids. In particular, step(s) a), b), c) and / or d) are preferably carried out as specified above or in the claims. This does also apply to one, some or all components employed in step(s) a), b), c) and / or d).

[0076] Further aspects, embodiments and advantages of the present invention become apparent from the following claims.

20 Claims

1. Process for producing fatty acid alkyl esters by catalytic transesterification of triglycerides from an oil and / or fat based crude feedstock containing triglycerides and free fatty acids, comprising the steps:

a) neutralizing free fatty acids contained in a mixture that further comprises oil and / or fat as well as triglycerides with alkaline glycerine to enrich triglycerides in a first light phase and neutralized free fatty acids in a first heavy phase;

b) separating the first light phase and the first heavy phase and acidifying the separated first heavy phase to enrich free fatty acids in a second light phase and glycerine in a second heavy phase;

c) separating the second light phase and the second heavy phase and esterifying free fatty acids in the separated second light phase in the presence of an alcohol to enrich fatty acid esters in a third light phase and the alcohol in a third heavy phase;

d) separating the third light phase and the third heavy phase and recycling the separated third light phase to the neutralization reaction of step a); and

e) forming fatty acid alkyl esters by catalytic transesterification of the triglycerides contained in the separated first light phase;

wherein the crude feedstock is fed to the neutralization reaction in step a) and / or to the esterification reaction in step c).

2. Process of claim 1, wherein, if the crude feedstock contains free fatty acids in an amount of 8.0 wt.-% or less, preferably 7.5 wt.-% or

- less, more preferably 7.0 wt.-% or less, yet more preferably 6.5 wt.-% or less, most preferably 6.0 wt.-% or less, relative to the total weight of the crude feedstock, and /or
 if the crude feedstock contains free fatty acids in an amount 0.2 wt.-% or more, preferably 0.4 wt.-% or more, more preferably 0.6 wt.-% or more, yet more preferably 0.8 wt.-% or more, most preferably 1.0 wt.-% or more, relative to the total weight of the crude feedstock,
 the crude feedstock is fed to the neutralization reaction in step a).
3. Process of claim 1 or 2, wherein,
 if the crude feedstock contains free fatty acids in an amount of 10 wt.-% or more, preferably 15 wt.-% or more, more preferably 20 wt.-% or more, yet more preferably 25 wt.-% or more, most preferably 30 wt.-% or more, relative to the total weight of the crude feedstock,
 the crude feedstock is fed to the esterification reaction in step c).
4. Process of any of the preceding claims, further comprising the step:
 f) recycling the separated third heavy phase to the acidification reaction in step b).
5. Process of any of the preceding claims, wherein the separated third light phase is not recycled to step e), preferably wherein the separated third light phase is not recycled to steps e) and b), more preferably wherein the separated third light phase is only recycled to the neutralization reaction of step a).
6. Process of any of the preceding claims, wherein step a) comprises mixing for less than 1 minute, preferably less than 55 seconds, more preferably less than 50 seconds and most preferably less than 45 seconds and/or
 wherein step a) comprises mixing for at least 10 seconds, preferably at least 15 seconds, more preferably at least 20 seconds, even more preferably at least 25 second and most preferably at least 30 seconds.
7. Process of any of the preceding claims, wherein the catalyst used in step e) is selected from the group of alkaline catalysts,
 preferably metal hydroxides, metal alcoholates and combinations thereof, wherein the metals are preferably selected from the first to third main groups of the periodic system,
 more preferably sodium hydroxide, potassium hydroxide, sodium alcoholates, potassium alcoholates, such as sodium methylate, sodium ethylate, sodium butylate, potassium methylate, potassium ethylate, potassium butylate, and combinations thereof,
- most preferably potassium methylate.
8. Process of any of the preceding claims, wherein step e) comprises:
 e-1) treating the separated first light phase with a monohydric alkyl alcohol and a base as a catalyst to form fatty acid alkyl esters and glycerine by transesterification of triglycerides, wherein the fatty acid alkyl esters are enriched in a fourth light phase and the glycerine is enriched in a fourth heavy phase, and
 e-2) separating the fourth light phase and the fourth heavy phase and optionally recovering the fatty acid esters from the separated fourth light phase.
9. Process of any of the preceding claims, wherein the transesterification is performed at 40 to 65°C, preferably 45 to 60°C, more preferably 50 to 55°C and/or wherein the transesterification is performed for 10 to 100 min, preferably 30 to 80 min, more preferably 35 to 60°C, most preferably 40 to 50 min.
10. Process of claim 8 or 9, wherein step e-2) further comprises:
 e-3) subjecting the separated 4th light phase to a further transesterification, wherein the fatty acid alkyl esters are enriched in a fifth light phase and the glycerine is enriched in a fifth heavy phase, and
 e-4) separating the fifth light phase and the fifth heavy phase and optionally recovering the fatty acid esters from the separated fifth light phase.
11. Process of claim 10, wherein step e-3) comprises mixing for at least 1 minute, preferably for at least 2 minutes, more preferably at least 3 minutes, even more preferably at least 4 minutes and most preferably at least 5 minutes and/or
 wherein step e-3) comprises mixing less than 15 minutes, preferably less than 14 minutes, more preferably less than 13 minutes, even more preferably less than 12 minutes, even more preferably less than 11 minutes and most preferably less than 10 minutes.
12. Process of any of claims 8 to 11, further comprising the step:
 g) recycling the separated fourth heavy phase, and / or the separated fifth heavy phase, if present, to the neutralization reaction in step a).
13. Process of any of the preceding claims, wherein steps a), b), d) and e) are performed continuously, preferably, wherein steps a), b), d) and e) as well as step f), if present, are performed continuously,

more preferably, wherein steps a), b), d) and e) as well as steps f) and g), if present, are performed continuously.

14. Process for lowering free fatty acid content in an oil and / or fat based crude feedstock containing triglycerides and free fatty acids, comprising the steps: 5
- a) neutralizing free fatty acids contained in a mixture that further comprises oil and / or fat as well as triglycerides with alkaline glycerine to enrich triglycerides in a first light phase and neutralized free fatty acids in a first heavy phase; 10
 - b) separating the first light phase and the first heavy phase and acidifying the separated first heavy phase to enrich free fatty acids in a second light phase and glycerine in a second heavy phase; 15
 - c) separating the second light phase and the second heavy phase and esterifying free fatty acids in the separated second light phase in the presence of an alcohol to enrich fatty acid esters in a third light phase and the alcohol in a third heavy phase; 20
 - d) separating the third light phase and the third heavy phase and recycling the separated third light phase to the neutralization reaction of step a); 25
- wherein the crude feedstock is added to the neutralization reaction in step a) and / or to the esterification reaction in step c). 30
15. Process of claim 14, wherein steps a), b), c) and / or d) are as defined in any of claims 1 to 4, 6 and 13. 35

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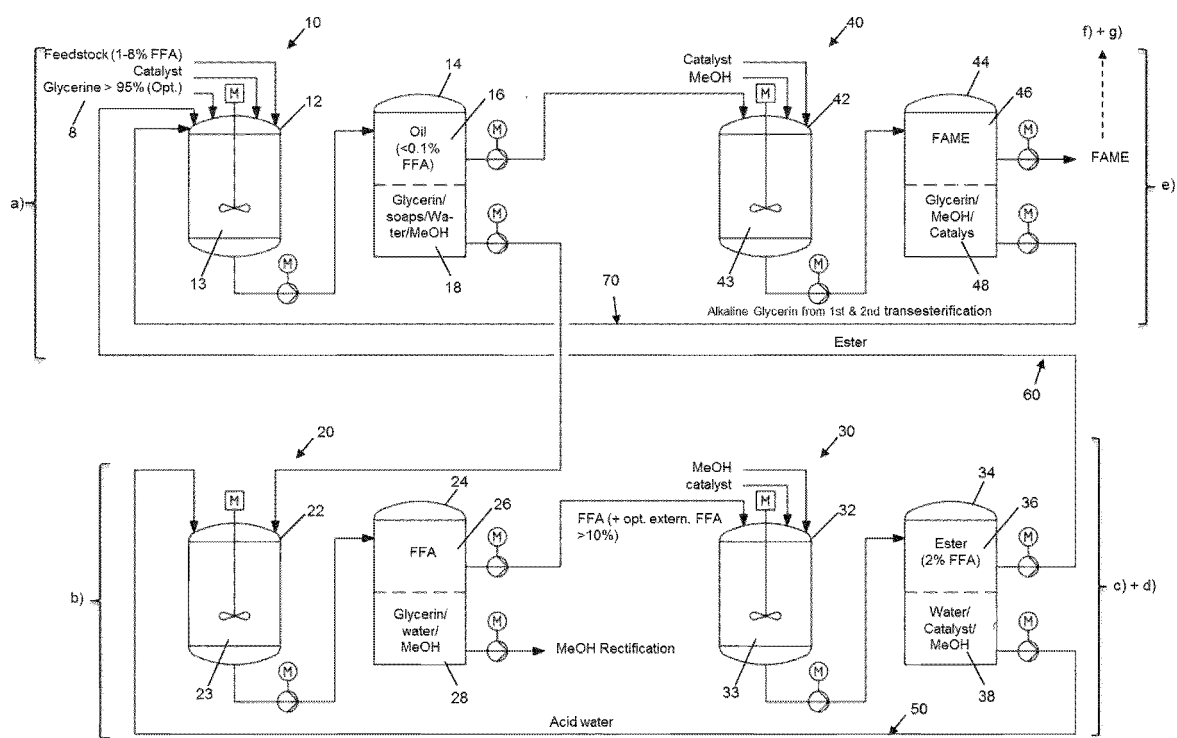


Fig. 1

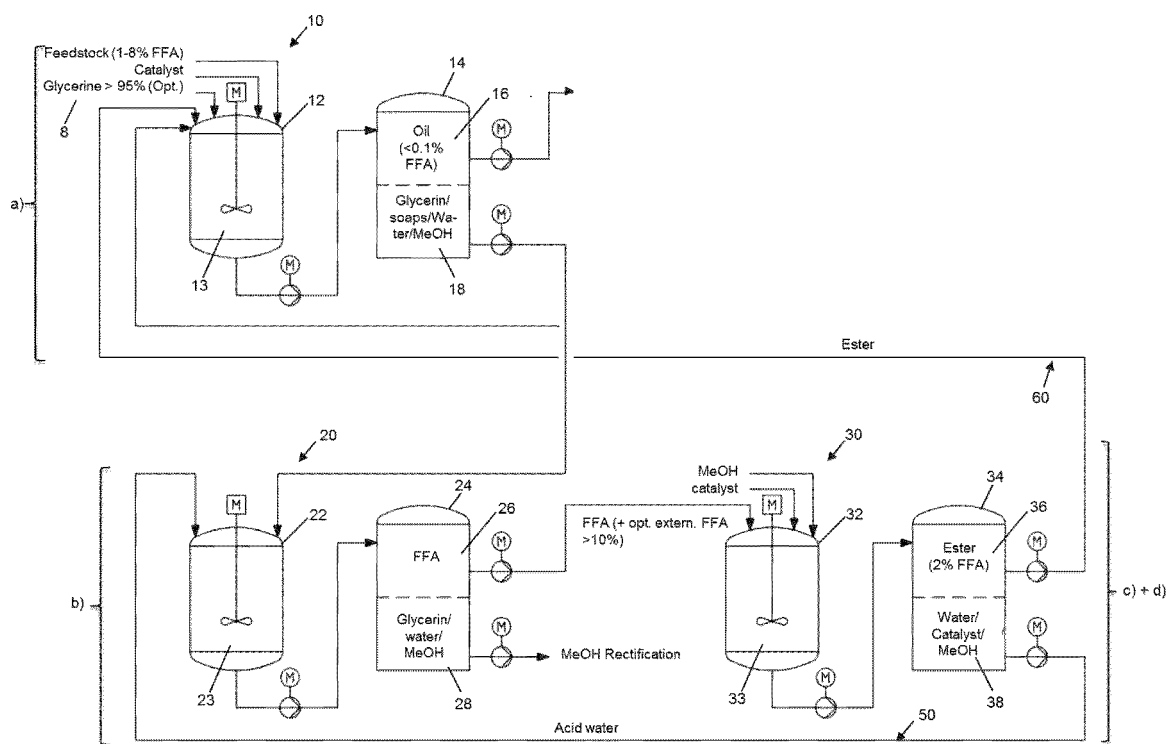


Fig. 2



EUROPEAN SEARCH REPORT

Application Number
EP 21 16 7432

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EPO FORM 1503 03/82 (P04C01)

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