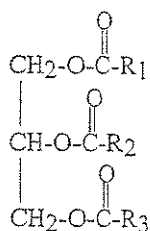


## Process for preparing alkyl esters of fatty acids and acrolein from triglycerides

The present invention relates to a process for  
5 preparing fatty acid alkyl esters and acrolein from triglycerides using suitable catalysts.

Triglycerides can be described, for example, by the following formula:



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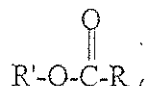
in which

$R_1$  to  $R_3$  =  $C_{10}$  to  $C_{30}$ -alkyl.

15

These triglycerides are, for example, an important constituent of synthetic and natural fats or vegetable oils, for example palm oil, sunflower oil, soya oil or rapeseed oil, which is used in biodiesel production. The triglycerides used in accordance with the invention may be present in contaminated form or in the form of  
20 mixtures.

Fatty acid alkyl esters or biodiesel are described in the present context by the following formula:



25

in which  $R = R_1$  to  $R_3$  and  $R' = C_1$  to  $C_{10}$ -alkyl or  $C_3$ - to  $C_6$ -cycloalkyl.

30

Mixtures of these fatty acid alkyl esters are the main constituent of biodiesel.  $R'$  is preferably a  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$  group, but usually a  $\text{CH}_3$  group, since methylates in methanolic solution are usually used in biodiesel

production. The transesterification of the triglycerides can also be performed with other alcohols to give corresponding fatty acid esters.

- 5 An overview of the state of use of vegetable oils and further fats for preparing biodiesel is described in G. Knothe, J. Van Gerpen, J. Krahrl, The Biodiesel Handbook, OACS Verlag, 2005.
- 10 In general, the transesterification of triglycerides to fatty acid alkyl esters can be accelerated by acidic or basic catalysis. In industry, predominantly the more rapid homogeneous base catalysis is used. Preference is given to using sodium methoxide or potassium methoxide.
- 15 In the industrial production of biodiesel, important process parameters for the optimization of the yield include the concentration of the catalyst, the temperature, the residence time, the moisture content, the
- 20 presence of free fatty acids and the alcohol excess (B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yield of fatty esters from transesterified vegetable oils, J. Am. Oil Chem. Soc., 61, 1638, 1984).
- 25 The triglycerides used contain about 10% by weight of glycerol, which is preferably isolated from the biodiesel fraction as a contaminated fraction by a phase separation or extraction after the transesterification. Both fractions are then very
- 30 substantially freed of water, acids, catalysts, alcohol, salts and by-products in multistage workup steps.
- 35 Acrolein is an important intermediate and is thus of great economic significance for the preparation of acrylic acid, D,L-methionine and the methioninehydroxy analogue (MHA, = 2-hydroxy-4-methylthiobutyric acid). Methionine is an essential amino acid which is used,

inter alia, as a supplement in feeds. Nutrition-improving feed additives are nowadays an indispensable constituent of animal nutrition. They serve for better utilization of the food available, stimulate growth and  
5 promote protein formation. One of the most important of these additives is the essential amino acid methionine, which assumes a prominent position as a feed additive in poultry breeding in particular. In this field, so-called methionine replacements such as the methionine  
10 hydroxy analogue have, though, gained not inconsiderable significance, since they have similar growth-stimulating properties to the amino acid known for this purpose.

15 According to the prior art, acrolein is synthesized by heterogeneously catalysed selective oxidation of propene over mixed oxide catalysts. EP 417723 describes the synthesis of complex mixed multimetal oxide catalysts at temperatures of 300 to 380°C and pressures  
20 of 1.4 to 2.2 bar. Ullmann's Encyclopaedia of Industrial Chemistry, 6th edition, 1999 describes the overall process including workup, in which a plurality of by-products are removed. Once the reactant mixture composed of propene, air and water has been converted  
25 at least partly over the catalyst, quenching to remove high-boiling by-products such as polymers, acrylic acid and acetic acid is effected first. In the downstream absorber, acrolein is extracted by washing. After the desorption, to recover the absorbent, the crude  
30 acrolein obtained is purified by distillation in several stages.

Scientific studies of the synthesis of acrolein from isolated glycerol are known. It is also known, for  
35 example, that glycerol can be dehydrated in the presence of acidic substances to various products.

According to Organic Synthesis I, 15-18 (1964), treatment of a mixture of pulverulent potassium hydrogensulphate, potassium sulphate and glycerol at 190 to 200°C affords acrolein in a yield between 33 and 48%. Owing to the low yields and the high salt burdens, this process is, however, unsuitable for the industrial scale.

In the course of the studies of model substances of biomass pyrolysis oils, the catalytic treatment of glycerol over H-ZSM5 zeolites at 350 to 500°C has also been studied - see Dao, Le H. et al. ACS Symp. Ser.: 376 (Pyrolysis Oils Biomass) 328-341 (1988). Hydrocarbons are formed only in low yields, but the formation of acrolein is pointed out.

WO 2006/092272 discloses a process for preparing acrylic acid or acrylic acid polymers by dehydrating glycerol to a dehydration product comprising acrolein, gas phase oxidation and subsequent isolation of acrylic acid and subsequent polymerization. However, a process for controlled acrolein preparation is not described.

DE 42 38 493 describes the acid-catalysed conversion of glycerol to acrolein in the gas phase and in the liquid phase. DE 42 38 492 further relates to the synthesis of 1,2- and 1,3-propanediol by dehydrating glycerol with high yields. The glycerol used is usually in pure form or in the form of an aqueous solution.

The glycerol obtained after the phase separation in the biodiesel production is, however, generally of low value, since it is highly contaminated, for example, by excess methanol, catalyst and soaps.

To date, the above-described steps have never been combined in order to use triglycerides directly for the

simultaneous preparation of fatty acid alkyl esters, especially of biodiesel and acrolein.

On the one hand, the separate preparation of biodiesel  
5 from triglycerides and acrolein from propene or  
glycerol gives rise to a comparatively high level of  
apparatus complexity and hence corresponding capital  
costs, since synergies in the combined preparation in  
10 an integrated system are not utilized. What also arises  
is corresponding logistical complexity and hence  
correspondingly high variable costs, for example  
transport and energy costs, in order to convey  
glycerol.

15 On the other hand, the disadvantage of the classical  
acrolein production to date, by selective oxidation  
from propene, is considered especially to be the  
complicated process in which propene has to be prepared  
in the gas phase and has to be isolated in the  
20 multistage workup, and also that propene is a  
comparatively expensive starting material whose costs  
are additionally increasing in a greater-than-  
proportional manner at the current time.

25 It was therefore an object of this invention to provide  
a process for simultaneously preparing acrolein and  
fatty acid alkyl esters, especially biodiesel, from  
triglycerides, and hence of avoiding the disadvantages  
of the prior art.

30 In particular, it was an object of the invention to  
discover a process in which the primary  
transesterification of triglycerides succeeds in a  
simple and efficient manner with inexpensive catalysts,  
35 and the glycerol obtained as the primary product can be  
removed from the fatty acid alkyl ester in an efficient  
manner. The glycerol removed should additionally be  
dehydratable catalytically to acrolein substantially

directly and again in a simple and efficient manner,  
hence avoiding the disadvantages of the prior art.

It was a further object in this connection to discover  
5 very efficient, easy-to-handle catalysts which are very  
suitable both for the primary transesterification  
(biodiesel or glycerol formation) and the dehydration  
of the glycerol to acrolein which proceeds as the  
secondary reaction.

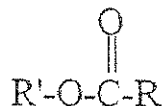
10

An additional object is directed to providing a process  
in which an aqueous acrolein solution which can be sent  
directly to its use, especially as a starting material  
for preparing methionine compounds or acrylic acid  
15 derivatives, is obtained.

#### Description of the invention

These objects and further objects which are not stated  
20 explicitly but are immediately derivable or discernible  
from the connections discussed herein are achieved by a  
process according to Claim 1. Appropriate embodiments  
and modifications of the process according to the  
invention are protected in the subclaims referring  
25 directly or indirectly back to Claim 1.

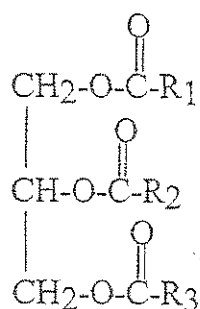
By virtue of employing a process for preparing fatty  
acid alkyl esters of the general formula I:



(I)

30

and acrolein by converting triglycerides of the general  
formula II:



(II)

which is characterized in that

- a) the triglycerides are reacted by means of alcohols  
5 R'-OH in the presence of a suitable catalyst to give the fatty acid alkyl ester and glycerol and
- b) the glycerol formed is dehydrated catalytically to  
acrolein,

10

where R is R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are all the same or some are the same or all are different and are each a straight-chain or branched and optionally mono- or polyunsaturated C<sub>10</sub>-C<sub>30</sub>-alkyl radical, preferably C<sub>12</sub>-  
15 C<sub>20</sub>-alkyl radical, and R' is a C<sub>1</sub>-C<sub>10</sub>-alkyl radical, preferably C<sub>1</sub>-C<sub>6</sub>-alkyl radical, a C<sub>3</sub>-C<sub>6</sub>-cycloalkyl radical, preferably C<sub>6</sub>-cycloalkyl radical, it is possible to avoid the disadvantages of the prior art which are specified above in detail.

20

Particular preference is given to using, in reaction step a), triglycerides in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each a C<sub>12</sub>-C<sub>18</sub>-alkyl radical.

25

Preference is additionally given to using, in reaction step a), alcohols R'-OH in which R' = methyl or ethyl. Very particular preference is given to using methanol, since the fatty acid methyl esters thus formed are most frequently used as biodiesel.

30

The simultaneous preparation of the two target products can be achieved by various variants of the process according to the invention. A distinction can be drawn between two main variants.

5

The first variant comprises a process in which reactions a) and b) are performed simultaneously in one step, i.e. in one stage, and is shown in Figure 1.

10 As a result of use of a suitable catalyst or of a mixture of catalysts, the two reactions proceed in parallel. For example, a triglyceride-catalyst mixture, optionally in the presence of a solvent, is reacted with the alcohol R'OH over an acidic catalyst in the  
15 liquid phase.

For reactions a) and b), it is possible to use a homogeneous or heterogeneous acidic catalyst and/or salts of mineral acids or optionally a suitable biocatalyst.

20

Preference is given to processes using a homogeneous acidic catalyst, especially a homogeneous catalyst with a pKa of < 7.

25 Suitable catalysts are, for example, strong Brønsted acids such as sulphuric acid, phosphoric acid, toluene-sulphonic acid or methanesulphonic acid.

Suitable salt-type catalysts are, for example,  
30 potassium sulphate, sodium sulphate or caesium sulphate, potassium hydrogensulphate, sodium hydrogensulphate or caesium hydrogensulphate, or mixtures of the hydrogensulphates and sulphates mentioned, lithium phosphate, iron phosphate, zinc sulphate, optionally in  
35 the homogeneous phase and optionally in the presence of a solvent.

In the case of use of a heterogeneous acidic catalyst, preference is given to those having an  $H_0$  of  $< +2$ , preferably  $< -3$ .

5 The  $H_0$  value corresponds to the Hammett acid function and can be determined by the so-called amine titration using indicators or by adsorption of a gaseous base (see Studies in surface science and catalysis, Vol. 51, 1989: "New solids and bases, their catalytic  
10 properties", K. Tanabe et al., Chapter 2, especially pages 5-9).

Chapter 1, pages 1-3 of the aforementioned document names numerous solid acids from which the person  
15 skilled in the art, if appropriate after determining the  $H_0$  value, can select the suitable catalyst.

Suitable heterogeneous catalysts are preferably zeolites, solid acids, mixed base metal oxide catalysts  
20 or acidic ion exchange resins.

Preferred heterogeneous catalysts include:

- 25 (i) natural or synthetic silicatic substances, especially mordenite, montmorillonite and acidic zeolites, especially HZSM-5, MCM-22 and zeolite beta,
- 30 (ii) support materials, especially oxidic or silicatic substances, preferably aluminium oxide, titanium oxide, silicon dioxide, zirconium dioxide or mixtures thereof, coated with mono-, di- or polybasic inorganic acids, especially phosphoric acid, sulphuric acid or acidic salts of inorganic  
35 acids,

- (iii) oxides and mixed oxides, especially aluminium oxides, zinc oxide-aluminium oxide mixtures or heteropolyacids, or
  - 5 (iv) polystyrenesulphonic acid resins, especially Lewatit or Aberlite resins or perfluorinated polymeric sulphonic acid resins, especially Nafion.
- 10 Suitable biocatalysts are lipases, esterases, hydratases and/or hydrolases.

The use of a solvent is preferred, since this lowers the concentration of reactive intermediate compounds and minimizes side reactions to give oligomers, polymers and other high boilers. Moreover, the addition of an alcohol is required for the ester formation. The solvents and diluents used are known to those skilled in the art and examples include methyl tert-butyl ether, ethyl tert-butyl ether, tetrahydrofuran, 1,4-dioxane, diglyme, toluene, methyl isobutyl ketone and/or the alcohol  $R'-OH$  utilized for the trans-esterification. The triglycerides used may also act as solvents, as may the glycerol which is formed as an intermediate and the fatty acid alkyl esters which form and water formed in the dehydration.

The solvent is preferably added in excess and is preferably identical to the alcohol  $R'-OH$  used for the transesterification. Methanol and/or ethanol are used with very particular preference.

A reaction temperature between 30 and 500°C, preferably between 50 and 350°C, more preferably between 70 and 300°C, is employed. The pressure is adjusted such that the liquid state of the reaction mixture is maintained. Typically, the pressure is between 1 and 300 bar,

preferably between 1 and 150 bar, more preferably between 1 and 50 bar.

5 The procedure can be performed in the reaction vessels known to those skilled in the art, for example fixed bed reactors, stirred tanks, flow tubes or combinations.

10 Acrolein formed can be removed from the resulting reaction mixture in a known manner, alone or together with a portion of the solution or dilution medium and/or water, preferably by stripping or distillation. Unconverted intermediates or glycerol remain in the reaction stage and are converted further continually.  
15 Scavenging of the acrolein removed with water (quenching) affords an aqueous acrolein solution which can be sent directly to use or to a further purification.

20 According to the intended use, impurities or by-products in the acrolein can be tolerated or should be removed by workup steps. Water, acetaldehyde, formaldehyde or acetic acid and further unreactive by-products are preferably not isolated from the acrolein.

25 The present process variant is consequently characterized in that the acrolein formed in reaction b) is removed from the reaction mixture alone or optionally together with at least a portion of the solvent.

30 The acrolein can be removed from the reaction mixture by stripping, distillation, extraction, phase separation or use of membranes.

35 Very particular preference is given to removing the acrolein from the reaction mixture by distillation during the reaction.

For the simultaneous synthesis of acrolein and biodiesel from triglycerides, as well as the involvement of dehydration steps, selective transesterification is required. Since the dehydration to acrolein forms water which, in the fatty acid alkyl ester synthesis, can likewise lead to the undesired formation of the free fatty acid, water should preferably also be removed from the reaction mixture or equilibrium as well as glycerol, which is essentially consumed by the subsequent reaction to give acrolein. This can be effected directly in the first reaction step or in a downstream stage.

The simultaneous removal of the acrolein during the chemical reactions from the reaction mixture is possible relatively easily by means of distillation and is therefore preferred. This is caused firstly by the great differences in the boiling points of acrolein on the one hand, and triglycerides, fatty acid alkyl esters and glycerol on the other hand. The immediate removal of the acrolein formed from the reaction mixture additionally allows the yield to be increased, since acrolein in the reaction mixture is a very reactive compound which can lead to undesired side reactions. The good distillative removability of the acrolein from the reaction mixture comprising fatty acid alkyl esters becomes clear in Example 2, in which acrolein has been removed quantitatively from the biodiesel by vacuum distillation.

30

In a further embodiment of the invention, acrolein is not formed immediately at the start of the esterification reaction, but rather glycerol formed is removed first after the majority of the triglycerides have been converted to fatty acid alkyl esters. The glycerol formed after the transesterification is then converted to acrolein with the aid of a dehydration catalyst. The catalysts may consist of the acidic or

35

basic components described or of components of dehydration catalysts known to those skilled in the art.

5 This further process variant comprises a process in which reactions a) and b) are performed in separate steps, and is shown in Figure 2. In this process, first reaction a) (transesterification) of triglyceride with alcohol R'OH to glycerol and fatty acid alkyl esters  
10 (biodiesel) is performed in the presence of a suitable first catalyst. Subsequently, a separation into a glycerol-containing phase and a fatty acid alkyl ester-containing phase is effected. The glycerol in the glycerol-containing phase removed is dehydrated in the  
15 presence of a suitable second catalyst to acrolein (reaction b). The fatty acid alkyl ester can be used as fuel or biodiesel directly or after suitable after-treatment, for example a substantial dewatering.

20 The use of the dehydration catalyst in a separate reaction step avoids the formation of reactive intermediates which can form at least from portions of the triglycerides or of the glycerol under the above-specified conditions. The reactive intermediates  
25 otherwise form undesired by-products to an increased degree, which lead to deactivation of the catalyst or to a reduction in the yield. When these intermediates are minimized, the yield of acrolein and fatty acid alkyl esters can be improved.

30 This can be effected firstly in a batchwise operation, in which case the dehydration catalyst, after a certain reaction time, is added to the reaction mixture which is then biphasic. For this purpose, for example,  
35 performance in a stirred tank is suitable.

Secondly, the dehydration catalyst can be fed in not until a point removed from the reactor inlet in flow

direction or in a further reactor section after a phase separation has been effected. By the time the glycerol solution and the catalyst reach this point, a portion of the glycerol may already be converted to reactive  
5 intermediates. This operation can be realized industrially, for example, in a stirred tank battery or a flow tube. In this embodiment of the invention, the phase separation can be accelerated by subsequent removal of water or by distillative removal of excess  
10 alcohol, which eases the subsequent dehydration in the glycerol phase.

A further advantage of dehydration in a second step consists in the fact that the yields of acrolein and  
15 fatty acid alkyl esters can be enhanced because a temperature profile or temperature programme optimized with reference to the reaction behaviour of the reactants can be established separately for each step. For instance, the transesterification of the tri-  
20 glycerides requires a significantly lower activation energy or reaction temperature than the activation of glycerol and its first dehydration step for the rapid preparation of intermediates, for example hydroxypropionaldehyde. The fatty acid alkyl esters formed  
25 tend, in contrast, to unselective further reactions at higher temperatures of from approx. 150 to 250°C. The performance of the combined preparation of fatty acid alkyl esters and acrolein by means of passage through two reaction stages under different reaction conditions  
30 thus constitutes a preferred embodiment.

A preferred embodiment of the process is characterized in that reaction a) is performed with the aid of an alkaline catalyst for which the pKa of the  
35 corresponding acid is > 13.

Mention should be made in particular of alkali metal alkoxides of the alcohol R'OH used for the trans-

esterification. Preference is given to the alkali metal alkoxides of the C<sub>1</sub>-C<sub>4</sub>-alcohols, especially alkali metal methoxides or ethoxides and most preferably sodium methoxide.

5

The possibility of using alkaline catalysts for the transesterification in reaction a) constitutes an additional advantage in the second process variant, because the subsequent removal of the glycerol phase  
10 here results in virtually no reaction taking place with the acidic catalysts to be used in the dehydration.

Just like in the case of reaction in one step, it is also possible here that reaction a) is performed with  
15 the aid of a homogeneous or heterogeneous acidic catalyst. This catalyst may additionally be different from the acidic catalyst to be used in the dehydration, which further increases the variability and flexibility of the process.

20

In the case of use of a homogeneous acidic catalyst in reaction a), preference is given to using catalysts with a pK<sub>a</sub> of < 7.

25 In the case of use of a heterogeneous acidic catalyst in reaction a), preference is given to using catalysts with an H<sub>0</sub> of < +2, preferably < -3.

Both the alkali- and the acid-catalysed trans-  
30 esterification a) is performed at temperatures of 20 to 150°C, preferably 25 to 100°C, preferentially of 25 to 80°C.

In this way, it is possible, through selection of  
35 optimal reaction conditions, to form glycerol as well as biodiesel in a first reaction stage and then to convert it selectively to acrolein in a second stage.

According to the invention, it is also possible that reaction a) is performed with the aid of a biocatalyst.

The biocatalysts used are preferably lipases,  
5 esterases, hydratases or hydrolases.

In the process variant with separate reaction steps a) and b), the glycerol formed as the primary product is removed completely or partly from the reaction mixture  
10 of reaction a), and dehydrated catalytically in the reaction b) proceeding separately to acrolein.

For the dehydration reaction b), it is possible in accordance with the invention to use a homogeneous or  
15 heterogeneous acidic catalyst.

In the case of homogeneous catalysts, preference is given to those having a  $pK_a$  of  $< 7$ .

20 In particular, it is possible here to use sulphuric acid, phosphoric acid, toluenesulphonic acid or methanesulphonic acid as the catalyst.

Furthermore, the homogeneous catalysts used for the  
25 dehydration reaction b) are preferably salts of mineral acids, optionally in the presence of a solvent.

Very particular preference is given to using potassium sulphate, sodium sulphate or caesium sulphate,  
30 potassium hydrogensulphate, sodium hydrogensulphate or caesium hydrogensulphate, or mixtures of the hydrogen-sulphates and sulphates mentioned, lithium phosphate, iron phosphate, zinc sulphate, optionally in the presence of a solvent, as a catalyst.

35

In the case of heterogeneous catalysts, preference is given to those having an  $H_0$  of  $< +2$ , preferably  $< -3$ .

Preference is given to using zeolites, solid acids, mixed base metal oxide catalysts or acidic ion exchange resins as the heterogeneous catalyst.

5    Suitable heterogeneous catalysts include in particular:

- 10    (i)    natural or synthetic silicatic substances, especially mordenite, montmorillonite and acidic zeolites, especially HZSM-5, MCM-22 and zeolite beta,
- 15    (ii)   support materials, especially oxidic or silicatic substances, preferably aluminium oxide, titanium dioxide, silicon dioxide, zirconium dioxide or mixtures thereof, coated with mono-, di- or polybasic inorganic acids, especially phosphoric acid, sulphuric acid or acidic salts of inorganic acids,
- 20    (iii)   oxides and mixed oxides, especially aluminium oxides, zinc oxide-aluminium oxide mixtures or heteropolyacids, or
- 25    (iv)   polystyrenesulphonic acid resins, especially Lewatit or Aberlite resins or perfluorinated polymeric sulphonic acid resins, especially Nafion.

30    The reaction conditions to be established with preference correspond to those which are employed in the above-described first one-stage process variant. Only the reaction temperature of the second reaction, of the dehydration b), compared to the first reaction, the transesterification a), is at higher temperatures  
35    of 50 to 400°C, preferably 100 to 350°C.

Preference is equally given to performing the dehydration reaction b) with the aid of a biocatalyst.

The biocatalysts used are, for example, dehydratases, hydratases or hydrolases.

- 5 The reaction step b) is performed preferably in the presence of a solvent.

Preferred solvents are methyl tert-butyl ether, ethyl tert-butyl ether, tetrahydrofuran, 1,4-dioxane,  
10 diglyme, toluene, methyl isobutyl ketone and/or the alcohol R'-OH already utilized in reaction step a).

One possibility is that the glycerol is removed from the reaction mixture a) by distillation.

15

The glycerol can be removed in a distillation column attached to the first reaction apparatus by a vacuum distillation of reaction mixture a).

- 20 A particularly advantageous embodiment of the process consists in removing glycerol from the reaction mixture a) by reactive distillation and, at the same time, dehydrating it to acrolein over the simultaneously present acidic catalyst (reaction step b)).

25

In this case, a heterogeneous dehydration catalyst, preferably of the type (i) to (iv) described in detail above, which simultaneously accelerates the conversion of the glycerol to be removed to acrolein, is present  
30 in the distillation column. The temperature in the downstream column is between 50 and 300°C, preferably between 80 and 250°C, more preferably between 100 and 200°C. The pressure there is between 0.1 and 1500 mbar, preferably between 0.5 and 1000 mbar, more preferably  
35 between 2 and 100 mbar.

The solid, generally insoluble acidic dehydration catalyst is installed within the distillation column as a bed or as a coating.

5 The advantage of performing reactions a) and b) in two separate steps also consists in the fact that the stability of the process is improved owing to delimited process steps in continuous operation.

10 In addition to distillation or reactive distillation, it is also possible to use further means of removing the glycerol.

A further preferred embodiment of the process according to the invention is characterized in that glycerol is removed from the reaction solution by simple phase separation after a lipophilic phase A comprising fatty acid alkyl esters and a glycerol-containing hydrophilic phase B have formed.

20 This phase separation can additionally be enabled or promoted by adding a phase separator.

Preferred phase separators are water and/or an organic solvent and/or fatty acid alkyl esters.

The combined preparation of acrolein and fatty acid alkyl esters can also be achieved in accordance with the invention by deliberately promoting the phase separation into a lipophilic phase A comprising tri-glyceride and fatty acid alkyl esters and into a water- and glycerol-containing hydrophilic phase B actually at the start of the transesterification, and by virtue of reactions a) and b) proceeding in parallel in the two different liquid phases (biphasic catalysis). This can be effected firstly by the addition of water or other solvents.

On the other hand, the excess alcohol used for the transesterification can be removed by distillation in order to accelerate the phase separation. This has the advantage that catalysts optimized in each case can be  
5 used for the transesterification reaction a) and for the dehydration reaction b). The two reactions additionally proceed separately in the particular phases without influencing one another.

10 Preference is therefore given to a process in which reaction a) is performed in the lipophilic phase A, which comprises triglyceride and fatty acid alkyl esters, and reaction b) in the hydrophilic phase B which comprises glycerol, water and acrolein.

15

The easy transfer of the acrolein from the lipophilic phase A comprising fatty acid alkyl esters to the aqueous hydrophilic phase B becomes clear in Example 1, in which acrolein is found predominantly in the aqueous  
20 phase.

The yield of the two target products can thus be enhanced overall by virtue of fewer unselective side reactions proceeding. It is also desired to bind  
25 residual moisture or added water exclusively in the glycerol phase, since it otherwise leads to an enhanced degree of undesired formation of free fatty acids.

The catalyst systems for the transesterification and  
30 for the dehydration are, in the case of biphasic catalysis, adjusted such that, in the case of use of homogeneous catalysts, the transesterification catalyst dissolves in the triglyceride phase and the dehydration catalyst in the glycerol-containing phase and not vice  
35 versa, so that a catalyst preferably soluble in the lipophilic phase A accelerates reaction a) there, and a catalyst preferably in the hydrophilic phase B accelerates reaction b) there.

In general, a homogeneous solution is advantageous for good mass transfer, but is not absolutely necessary here. This is even exploited deliberately by the principle of biphasic catalysis, where the acrolein product is readily soluble in the aqueous glycerol phase. Acrolein can thus be separated from the fatty acid alkyl ester in a simple manner by phase separation or additional extraction without complicated workup, and the overall process can thus be simplified. This also becomes clear in Example 1.

The ester cleavage is an equilibrium reaction which can be directed in one or another direction according to the reaction conditions. This is exploited deliberately in the embodiment of biphasic catalysis described by removing glycerol as the reaction product from the phase comprising triglyceride and fatty acid alkyl ester and hence from the equilibrium. Reaction a) is thus accelerated to an enhanced degree in the direction of fatty acid alkyl ester or biodiesel, and a back-reaction to triglycerides is minimized. As a result, reaction conditions which would otherwise not be optimal for the production of biodiesel can be established, or the range of suitable reaction conditions can be widened. For example, the excess of alcohol can be lowered.

Fatty acid alkyl esters of the formula I are preferably obtained from the lipophilic phase A and can be used as a fuel directly or optionally after further purification.

Acrolein is obtained from the hydrophilic phase B and can be used as a starting material for methionine products or acrylic acid directly or optionally after further purification.

A further embodiment of the invention is characterized in that the triglycerides used are converted catalytically to fatty acid alkyl esters and acrolein in the presence of alcohol  $R'OH$ , the trans-  
5 esterification reaction a) and the dehydration reaction b) being performed simultaneously or spatially separately using membranes (membrane separation). The membrane selectively retains the triglycerides and fatty acid alkyl esters (retentate), while glycerol  
10 formed passes into the permeate. As a result, the separation is effected without a separate workup step, which lowers the preparation costs.

For instance, glycerol can, in accordance with the  
15 invention, also be removed by membrane filtration from the reaction mixture of reaction a). Suitable membrane materials are especially organic or ceramic materials.

The dehydration reaction can also be effected by means  
20 of suitable catalysts immobilized on or in the membrane or by means of a separate catalyst addition into the permeate. The catalytically active components for the dehydration may also be an insoluble constituent of the membrane.

25 Suitable membranes are, for example, solubility membranes or diffusion membranes from micro- or ultra-filtration, which, owing to their functional groups, polarity or pore structure, retain the triglycerides,  
30 but are permeable to glycerol. Suitable membranes are especially formed from organic materials such as polyether sulphones (PES), cellulose esters, polyimides or polyether imides, poly(fatty acid amides) or polyacrylonitrile (PAN), or from ceramic materials such as  
35 aluminium oxide, titanium dioxide, silicon dioxide, zirconium dioxide (baddeleyite) and combinations thereof.

The advantages of the simultaneous preparation of biodiesel and acrolein described consist in increased productivity, addition of value and saving of time. At the same time, the transport and energy costs are reduced. Overall, the production of biodiesel and acrolein becomes more economically viable.

At the same time, relatively high-boiling by-products which are obtained in the acrolein synthesis can be added to the biodiesel as additional calorific value or, if appropriate, be left in the biodiesel. These may, for example, be dimers or trimers of acrolein or ethers of glycerol.

The invention also provides a mixture which comprises acrolein and has been prepared by the process according to the invention detailed here, and a mixture which comprises fatty acid alkyl esters of the formula I and has been prepared by the process according to the invention detailed here.

The examples which follow are intended to illustrate the invention described in detail, but in no way to have any restrictive effect.

## Examples

### Example 1:

5 50 g of biodiesel and 50 g of acrolein were mixed and  
formed a homogeneous mixture. In a separating funnel,  
this homogeneous mixture was admixed with 250 g of  
water, shaken and left to stand, in the course of which  
two phases formed. After the formation of the phase  
10 interface, the lower aqueous phase in the separating  
funnel was removed and analysed by means of gas  
chromatography to determine the acrolein content.  
Overall, 33.4 g of acrolein were obtained in the  
aqueous phase in this way. Even in the case of simple  
15 single-stage extraction with water, it was thus  
possible to remove a large portion of the acrolein from  
the biodiesel.

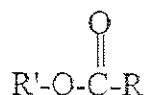
### Example 2:

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The flask of a rotary evaporator was initially charged  
with a mixture of 50 g of biodiesel and 50 g of  
acrolein and heated to 35°C in a water bath. By means  
of a water-jet pump, the mixture was placed under  
25 vacuum slowly. In the cooled distillation receiver,  
50 mg of hydroquinone were initially charged to  
stabilize the acrolein distilled. Within one hour, a  
distillate of 49.1 g of acrolein was obtained. The  
purity of the distillate was confirmed to be at least  
30 99.5% by means of gas chromatography. 50.6 g remained  
in the flask of the rotary evaporator.

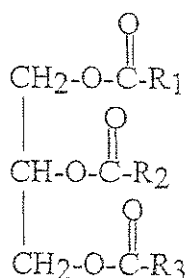
# Claims

1. Process for preparing fatty acid alkyl esters of the general formula I:



(I)

and acrolein by converting triglycerides of the general formula II:



(II)

characterized in that

a) the triglycerides are reacted by means of alcohols R'-OH in the presence of a suitable catalyst to give the fatty acid alkyl ester and glycerol and

b) the glycerol formed is dehydrated catalytically to acrolein,

where R is R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are all the same or some are the same or all are different and are each a straight-chain or branched and optionally mono- or poly-unsaturated C<sub>10</sub>-C<sub>30</sub>-alkyl radical, preferably C<sub>12</sub>-C<sub>20</sub>-alkyl radical, and R' is a C<sub>1</sub>-C<sub>10</sub>-alkyl radical, preferably C<sub>1</sub>-C<sub>6</sub>-alkyl radical, a C<sub>3</sub>-C<sub>6</sub>-cycloalkyl radical, preferably C<sub>6</sub>-cycloalkyl radical.

2. Process according to Claim 1, characterized in that

$R_1$ ,  $R_2$  and  $R_3$  =  $C_{12}$ - $C_{18}$ -alkyl radical.

3. Process according to Claim 1 or 2, characterized in that  
5  $R'$  = methyl or ethyl.
4. Process according to one of Claims 1 to 3, characterized in that reactions a) and b) are performed simultaneously in one step.
- 10 5. Process according to one of Claims 1 to 4, characterized in that a homogeneous or heterogeneous acidic catalyst and/or salts of mineral acids or a biocatalyst are used for reactions a) and b).
- 15 6. Process according to Claim 5, characterized in that a homogeneous catalyst with a  $pK_a$  of  $< 7$  is used.
- 20 7. Process according to Claim 6, characterized in that sulphuric acid, phosphoric acid, toluene-sulphonic acid or methanesulphonic acid is used.
- 25 8. Process according to Claim 5, characterized in that potassium sulphate, sodium sulphate or caesium sulphate, potassium hydrogensulphate, sodium hydrogensulphate or caesium hydrogensulphate, or mixtures of the hydrogensulphates and sulphates mentioned, lithium phosphate, iron  
30 phosphate, zinc sulphate, optionally in the presence of a solvent, are used as a catalyst.
9. Process according to Claim 5, characterized in that a heterogeneous catalyst with an  $H_0$  value of  
35  $< +2$  is used, preferably  $< -3$ .
10. Process according to Claim 9, characterized in that the zeolites, solid acids, mixed base metal

oxide catalysts or acidic ion exchange resins are used as the heterogeneous catalyst.

5 11. Process according to Claim 10, characterized in that

10 (i) natural or synthetic silicatic substances, especially mordenite, montmorillonite and acidic zeolites, especially HZSM-5, MCM-22 and zeolite beta,

15 (ii) support materials, especially oxidic or silicatic substances, preferably aluminium oxide, titanium dioxide, silicon dioxide, zirconium dioxide or mixtures thereof, coated with mono-, di- or polybasic inorganic acids, especially phosphoric acid, sulphuric acid or  
20 acidic salts of inorganic acids,

25 (iii) oxides and mixed oxides, especially aluminium oxides, zinc oxide-aluminium oxide mixtures or heteropolyacids, or

30 (iv) polystyrenesulphonic acid resins, especially Lewatit or Aberlite resins or perfluorinated polymeric sulphonic acid resins, especially Nafion, are used.

12. Process according to Claim 5, characterized in that lipases, esterases, hydratases and/or hydrolases are used as a biocatalyst.

35 13. Process according to one of Claims 1 to 12, characterized in that the reaction is performed in the presence of a solvent.

14. Process according to Claim 13, characterized in that the solvent used is methyl tert-butyl ether, ethyl tert-butyl ether, tetrahydrofuran, 1,4-dioxane, diglyme, toluene, methyl isobutyl ketone and/or the alcohol R'-OH utilized for the transesterification according to Claim 1.
15. Process according to one of Claims 1 to 14, characterized in that the acrolein formed in reaction b) is removed from the reaction mixture alone or optionally together with at least a portion of the solvent.
16. Process according to Claim 15, characterized in that the acrolein is removed from the reaction mixture by stripping, distillation, extraction, phase separation or use of membranes.
17. Process according to Claim 16, characterized in that the acrolein is removed from the reaction mixture by distillation actually during the reaction.
18. Process according to one of Claims 1 to 3, characterized in that reactions a) and b) are performed in separate steps.
19. Process according to Claim 18, characterized in that reaction a) is performed with the aid of an alkaline catalyst for which the pKa of the corresponding acid is  $> 13$ .
20. Process according to Claim 19, characterized in that the alkaline catalysts used are alkali metal alkoxides of the alcohol R'-OH used for the transesterification or alkali metal methoxides or ethoxides, preferably sodium methoxide.

21. Process according to Claim 18, characterized in that reaction a) is performed with the aid of a homogeneous or heterogeneous acidic catalyst.
- 5 22. Process according to Claim 21, characterized in that a homogeneous acidic catalyst with a pKa of < 7 is used.
- 10 23. Process according to Claim 21, characterized in that a heterogeneous catalyst with an  $H_0$  of < +2, preferably < -3, is used.
- 15 24. Process according to Claim 18, characterized in that reaction a) is performed with the aid of a biocatalyst.
- 20 25. Process according to Claim 24, characterized in that a lipase, esterase, hydratase or hydrolase is used as the biocatalyst.
- 25 26. Process according to one of Claims 18 - 25, characterized in that the glycerol formed as the primary product from the reaction mixture of reaction a) is removed completely or partly and is dehydrated catalytically to acrolein in reaction b).
- 30 27. Process according to Claim 26, characterized in that a homogeneous or heterogeneous acidic catalyst is used for the dehydration reaction b).
- 35 28. Process according to Claim 27, characterized in that a homogeneous catalyst with a pKa of < 7 is used.
29. Process according to Claim 28, characterized in that sulphuric acid, phosphoric acid, toluene-

sulphonic acid or methanesulphonic acid is used as the catalyst.

30. Process according to Claim 26, characterized in  
5 that salts of mineral acids are used as catalysts for the dehydration reaction b).
31. Process according to Claim 30, characterized in  
10 that potassium sulphate, sodium sulphate or caesium sulphate, potassium hydrogensulphate, sodium hydrogensulphate or caesium hydrogensulphate, or mixtures of the hydrogensulphates and sulphates mentioned, lithium phosphate, iron  
15 phosphate, zinc sulphate, optionally in the presence of a solvent, are used as a catalyst.
32. Process according to Claim 26, characterized in  
20 that a heterogeneous catalyst with an  $H_0$  of  $< +2$ , preferably  $< -3$ , is used for the dehydration reaction b).
33. Process according to Claim 32, characterized in  
25 that the zeolites, solid acids, mixed base metal oxide catalysts or acidic ion exchange resins are used as the heterogeneous catalyst.
34. Process according to Claim 33, characterized in  
that
- 30 (i) natural or synthetic silicatic substances, especially mordenite, montmorillonite and acidic zeolites, especially HZSM-5, MCM-22 and zeolite beta,
- 35 (ii) support materials, especially oxidic or silicatic substances, preferably aluminium oxide, titanium dioxide,

5 silicon dioxide, zirconium dioxide or mixtures thereof, coated with mono-, di- or polybasic inorganic acids, especially phosphoric acid, sulphuric acid or acidic salts of inorganic acids,

10 (iii) oxides and mixed oxides, especially aluminium oxides, zinc oxide-aluminium oxide mixtures or heteropolyacids, or

(iv) polystyrenesulphonic acid resins, especially Lewatit or Aberlite resins or perfluorinated polymeric sulphonic acid resins, especially Nafion, are used.

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35. Process according to Claim 26, characterized in that the dehydration reaction b) is performed with the aid of a biocatalyst.

20 36. Process according to Claim 35, characterized in that a dehydratase, hydratase or hydrolase is used as the biocatalyst.

25 37. Process according to one of Claims 26 to 36, characterized in that reaction b) is performed in the presence of a solvent.

30 38. Process according to Claim 37, characterized in that the solvent used is methyl tert-butyl ether, ethyl tert-butyl ether, tetrahydrofuran, 1,4-dioxane, diglyme, toluene, methyl isobutyl ketone and/or the alcohol R'-OH utilized for the transesterification according to Claim 1.

35 39. Process according to one of Claims 26 to 38, characterized in that glycerol is removed from the reaction mixture a) by distillation.

40. Process according to Claim 39, characterized in that glycerol is removed from the reaction solution by reactive distillation and, at the same time, is dehydrated to acrolein over the acidic catalyst present simultaneously.
41. Process according to one of Claims 26 to 38, characterized in that glycerol is removed from the reaction solution by membrane filtration.
42. Process according to Claim 41, characterized in that the membranes used are organic or ceramic materials.
43. Process according to one of Claims 26 to 38, characterized in that glycerol is removed from the reaction solution by phase separation after a lipophilic phase A comprising fatty acid alkyl esters and a glycerol-containing hydrophilic phase B have formed.
44. Process according to Claim 43, characterized in that the phase separation is enabled or promoted by addition of a phase separation agent.
45. Process according to Claim 44, characterized in that the phase separation agents used are water and/or an organic solvent and/or fatty acid alkyl esters.
46. Process according to one of Claims 18 or 21 to 38, characterized in that reactions a) and b) proceed in parallel in two different liquid phases.
47. Process according to Claim 46, characterized in that reaction a) is performed in a lipophilic phase A which comprises triglyceride and fatty acid alkyl esters.

48. Process according to Claim 47, characterized in  
that a catalyst which is preferably soluble in the  
lipophilic phase A accelerates the reaction a)  
5 there.
49. Process according to Claim 47, characterized in  
that reaction b) is performed in a hydrophilic  
phase B which comprises glycerol, water and  
10 acrolein.
50. Process according to Claim 49, characterized in  
that a catalyst which is preferably soluble in the  
hydrophilic phase B accelerates the reaction b)  
15 there.
51. Process according to one of Claims 46 - 50,  
characterized in that the fatty acid alkyl esters  
of the formula I are obtained from the phase A.  
20
52. Process according to one of Claims 46 - 50,  
characterized in that acrolein is obtained from  
the phase B.
- 25 53. Acrolein-comprising mixture prepared by a process  
according to one of Claims 1 - 52.
54. Mixture comprising fatty acid alkyl esters of the  
formula I, prepared by a process according to one  
30 of Claims 1 - 52.