

ACID COMPOSITION FOR TREATING FATTY ACIDS

Field of the invention

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The invention relates to the treatment of fatty acids, and more particularly the esterification of fatty acids. The fatty acid esters obtained can thus be used as starting materials in various fields, such as cosmetics or biofuel production. In particular, the invention relates to a composition of acids that can in particular be used as a catalyst in fatty acid esterification processes.

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Prior art

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During fatty acid esterification, it is often necessary to use a catalyst, for example an acid catalyst.

Among the acid catalysts used, the use of para-toluenesulphonic acid is in particular known.

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For example, Patent WO 2007/05003 provides a process for producing alkyl fatty acid esters from tall oil containing sulphur-comprising compounds in the presence of a strong acid catalyst such as, in particular, para-toluenesulphonic acid.

More generally, Patent US 4 652 406 describes the use of aromatic sulphonic acids as a catalyst for esterifying free fatty acids in oils.

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However, since para-toluenesulphonic acid is less soluble in an aqueous medium, the phase separation is made more difficult.

The use of alkane-sulphonic acid as an acid catalyst of fatty acid esterification reactions is also known.

Thus, documents WO 2006/081644 and WO 2015/134495 describe the use of methanesulphonic acid in fatty acid esterification processes.

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However, since alkane-sulphonic acids are relatively expensive compounds, it is sought to optimize the use thereof. Furthermore, it may be useful to be able to further improve the efficiency of esterification catalysts.

It is therefore advisable to find an acid catalyst that is more efficient, both in terms of the conversion of fatty acids and from the point of view of the esterification

kinetics, and that is not very expensive. For this, the applicant has demonstrated that a catalyst comprising at least one particular acid composition makes it possible, *inter alia*, to overcome these drawbacks.

5 Summary of the invention

In a first aspect, the present invention relates to a composition comprising:

- at least one alkane-sulphonic acid of formula $R-SO_3H$ in which R represents a linear or branched, saturated hydrocarbon-based chain comprising from 1 to 4 carbon atoms which may or may not be substituted with at least one halogen atom ;
- at least one aryl-sulphonic acid;
- and, optionally, at least one solvent;

in which:

- the proportion by weight of alkane-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 5% and 85%, preferably between 8% and 65%;
- the proportion by weight of aryl-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 15% and 95%, preferably between 35% and 92%.

The solvent may be of any type known to those skilled in the art and, for example, water, an organic solvent for a mixture of organic solvents or else a mixture of water and one or more organic solvents.

In one embodiment of the invention, the solvent is chosen from water, an alcohol and an ether, preferably water and a C_1 to C_3 alcohol, and more particularly water and methanol, taken alone or in combination.

The proportion by weight of solvent relative to the total weight of the composition is generally between 0% and 50%, preferably between 5% and 35%.

When the hydrocarbon-based chain of group R defined above is substituted with at least one halogen atom, the said halogen atom is chosen from fluorine, chlorine and bromine, preferably fluorine.

The alkane-sulphonic acid, of formula $R-SO_3H$ defined above, that can be used in the context of the present invention, is advantageously chosen from

methanesulphonic acid, ethanesulphonic acid, n-propanesulphonic acid, *iso*-propanesulphonic acid, n-butanesulphonic acid, *iso*-butanesulphonic acid, *sec*-butanesulphonic acid, *tert*-butanesulphonic acid, trifluoromethanesulphonic acid (also known as triflic acid), and mixtures of two or more thereof in any proportions, and, most particularly preferably, methanesulphonic acid.

The aryl-sulphonic acid is chosen from benzenesulphonic acid, para-toluenesulphonic acid, naphthalenesulphonic acid, phenanthrenesulphonic acid, anthracenesulphonic acid, xylenesulphonic acid, alkyl-benzenesulphonic acid, cumenesulphonic acid, and most particularly preferably, para-toluenesulphonic acid.

In addition, the acid composition according to the present invention may comprise one or more additive(s) and/or filler(s), well known to those skilled in the art, such as those chosen, for example, from corrosion inhibitors, fragrances, odorous agents, and the like.

The present invention also relates to the use of said composition as an esterification catalyst, and more particularly a catalyst for esterification of fatty acid(s).

Finally, the invention relates to a process for producing alkyl fatty acid esters, comprising the steps of:

- a/ introducing at least one fatty acid into a reactor;
- b/ adding at least one alcohol;
- c/ heating the reaction medium;
- d/ introducing an acid composition as defined above, as catalyst;
- e/ optionally, eliminating the water formed during esterification process ;
- f/ recovering the fatty acid esters;

step d possibly being carried out at the same time as step a and/or b, preferably at the same time as steps a and b.

Step e/ can be carried out by heating with or without vacuum, or by decanting the water/alcohol phase with respect to the fatty acid ester phase.

In said process, the catalyst/fatty acid molar ratio may be between 0.001 and 0.5 and more particularly between 0.01 and 0.2.

Detailed description of the invention

The invention will be understood more clearly from the viewpoint of the description, the figures and the examples which follow, but is in no way limited to said figures and examples.

Figure 1 represents the percentage of residual fatty acids (y-axis) in the organic phase after esterification reaction as a function of the nature of the used acid catalyst.

Figure 2 represents the kinetics of conversion of the residual fatty acids during the esterification step as a function of the nature of the used acid catalyst.

In said Figures 1 and 2:

- 100 MSA signifies that the catalyst used contains 70% of pure methanesulphonic acid and 30% of water.
- 70 MSA/30 PTSA signifies that the catalyst used is the catalyst according to the invention and that it comprises:
 - o 49% by weight of pure methanesulphonic acid relative to the total weight of the mixture,
 - o 26.7% by weight of pure para-toluenesulphonic acid relative to the total weight of the mixture, and
 - o 24.3% of water.
- 100 PTSA signifies that the catalyst used comprises 89% of pure para-toluenesulphonic acid and 11% of water.

The MSA (denoted AMS in the figures) used is an MSA diluted to 70% by weight in water and the para-toluenesulphonic acid used is an acid diluted to 89% by weight in water.

More specifically, the invention relates to a composition comprising:

- at least one alkane-sulphonic acid of formula $R-SO_3H$ in which R represents a linear or branched, saturated hydrocarbon-based chain comprising from 1 to 4 carbon atoms which may or may not be substituted with at least one halogen atom ;

- at least one aryl-sulphonic acid.

The term "aryl" is intended to mean all aromatic radicals, such as, for example, phenyl, naphthyl, phenanthryl and anthryl radicals, preferably those comprising from 1 to 3 rings; said radicals possibly being substituted with at least one alkyl comprising from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as, for example, a methyl, an ethyl, a propyl or a butyl, preferably a methyl. In the case where the aromatic radical is a radical substituted with at least one alkyl, it may for example be a tolyl, a xylyl, an ethylphenyl or a cumenyl.

These acids can be used alone or as a mixture.

In the composition according to the invention:

- the proportion by weight of pure alkane-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 5% and 85%;
- the proportion by weight of pure aryl-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 15% and 95%.

Preferably:

- the proportion by weight of pure alkane-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 8% and 65%;
- the proportion by weight of pure aryl-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 35% and 92%.

The term "pure" is intended to mean a compound not diluted in water or a solvent.

By virtue of the composition according to the invention, the applicant has demonstrated surprising results, such as those cited in examples in the present application.

It should be noted that said composition may also comprise one or more solvents, and optionally one or more additives.

The term "solvent" is intended to mean aqueous, organic or water-soluble products. Preferably, the solvent may be water, an alcohol or an ether, taken alone or in combination. Preferably, the solvent is water and/or a C₁ to C₃ alcohol. In addition, more particularly, the solvent is water, methanol or a water/methanol

mixture. The content by weight of solvent relative to the total weight of the composition is between 0 and 50%, and preferably between 5% and 35%.

When the hydrocarbon-based chain of group R defined above is substituted with at least one halogen atom, the said halogen atom is chosen from fluorine, chlorine and bromine, preferably fluorine.

Preferably, the alkane-sulphonic acid included in the composition according to the invention is chosen from methanesulphonic acid, ethanesulphonic acid, n-propanesulphonic acid, *iso*-propanesulphonic acid, n-butanesulphonic acid, *iso*-butanesulphonic acid, *sec*-butanesulphonic acid, *tert*-butanesulphonic acid and trifluoromethanesulphonic acid (also known as triflic acid), and mixtures of two or more thereof in any proportions. Preferably, the alkane-sulphonic acid is methanesulphonic acid.

Said alkane-sulphonic acid can be used as it is, or in combination with one or more other components, i.e. in formulation. Any type of formulation comprising at least one alkane-sulphonic acid may be suitable. As a general rule, the formulation comprises from 0.01% to 100% by weight of alkane-sulphonic acid, more generally from 0.05% to 90% by weight, in particular from 0.5% to 75% by weight, limits included, of alkane-sulphonic acid(s), relative to the total weight of said alkane-sulphonic acid formulation.

The formulation is, for example, an aqueous, organic or else aqueous-organic formulation. The formulation can be prepared in the form of a concentrated mixture, it being possible for said concentrated mixture to be diluted before use. Finally, for the purposes of the present invention, the formulation may be a pure alkane-sulphonic acid, or else a mixture of pure alkane-sulphonic acids, i.e. the formulation may contain only one or more alkane-sulphonic acid(s), without other formulation additive or other solvent or diluent.

For example, according to one embodiment of the invention, the alkane-sulphonic acid can be diluted to 70% in a solvent, preferably in water. Preferably, the alkane-sulphonic acid is methanesulphonic acid diluted to 70%, such as that found commercially. Use may, for example, be made of anhydrous methanesulphonic acid or AMSA or else of methanesulphonic acid in aqueous solution, for example a solution of methanesulphonic acid at 70% by weight in water and sold by the

company Arkema under the name Scaleva[®]. Use may also be made of the methanesulphonic acid sold by the company Arkema under the name MSA LC.

Use may also be made of methanesulphonic acid in aqueous solution, as sold by B.A.S.F under the name Lutropur[®]MSA, ready to use or diluted in water for example, in the proportions indicated above.

Preferably, the aryl-sulphonic acid is chosen from benzenesulphonic acid, para-toluenesulphonic acid, naphthalene sulphonic acid, phenanthrenesulphonic acid, anthracenesulphonic acid, xylenesulphonic acid and cumenesulphonic acid, and quite particularly preferably para-toluenesulphonic acid.

The aryl-sulphonic acid included in the composition may be used alone or in combination with one or more other components, i.e. in a formulation.

Any type of formulation comprising at least one aryl-sulphonic acid may be suitable. As a general rule, the formulation comprises from 0.01% to 100% by weight of aryl-sulphonic acid, more generally from 0.05% to 95% by weight, in particular from 74% to 89% by weight, limits included, of aryl-sulphonic acid, relative to the total weight of said formulation.

The formulation is, for example, an aqueous, organic or else aqueous-organic formulation. The formulation can be a concentrated mixture. As a variant, the formulation can also be a ready-to-use formulation, i.e. a formulation which does not need to be diluted. Finally, in another embodiment of the invention, the formulation may be pure aryl-sulphonic acid without other formulation additive or other solvent or diluent.

According to one embodiment of the invention, the aryl-sulphonic acid is para-toluenesulphonic acid, which is undiluted or diluted, between 60% and 100% by weight in water, such as that sold by the company Huntsman for example. According to another embodiment of the invention, the para-toluenesulphonic acid is diluted to 89% by weight in water, such as that sold by the company Sigma-Aldrich.

According to one preferred embodiment, the composition according to the invention is used as an acid catalyst for esterification, and preferably an acid catalyst for fatty acid esterification.

The present invention also relates to an acid catalyst for esterification, preferably for fatty acid esterification, comprising, and preferably consisting of, the acid composition as defined above.

5 The composition according to the invention is of most particularly advantageous use as a catalyst, for example a catalyst for esterification of pure fatty acids or fatty acids as a mixture in oils or fats, which are then referred to as "free fatty acids", as opposed to the fatty acids present in the form of mono-, di- and/or triglycerides present in said oils and/or fats.

10 The fatty acid esterification reaction makes it possible, on the basis of the condensation of an alcohol with a fatty carboxylic acid, to obtain an ester and a molecule of water. The term "fatty acid" is intended to mean a carboxylic acid comprising an aliphatic chain, which is in particular C₄-C₃₆. Natural fatty acids have a saturated or unsaturated, linear or branched carbon-based chain comprising
15 from 4 to 36 carbon atom(s).

According to the invention, the fatty acids can preferably be fatty acids present in oils. In this case, the esterification reaction can be followed by a transesterification reaction in the presence of a light alcohol (1 to 4 carbon atoms) in order to obtain fatty acid esters and glycerol, it being possible for said fatty acid esters to then be
20 used as fuel ("biodiesel"). Typically, during the preparation of biodiesel, if the content of residual fatty acids present in the oil or the fat is greater than 1%, there is a risk of saponification of said residual fatty acids by reaction with the transesterification catalysts. This can in particular be a drawback during the production of biodiesel, since the soaps formed create an emulsion and make the
25 separation of the biodiesel and the glycerol difficult or even impossible.

The applicant has thus demonstrated that, compared with an alkane-sulphonic acid used alone as catalyst or compared with an aryl-sulphonic acid used alone as catalyst, the mixture of at least one alkane-sulphonic acid with an aryl-sulphonic acid in the proportions claimed makes it possible, at the end of an esterification
30 step, to reduce the content of residual fatty acids in the organic phase below 1.1% by weight, preferably 1% by weight, and more particularly 0.95%; this is very difficult to do with an alkane-sulphonic acid used alone or an aryl-sulphonic acid used alone. The low content of residual fatty acids provides in particular an

advantage with regard to the final purity of the ester or during the transesterification step, often carried out subsequently, since the latter will consume less catalyst, generally basic catalyst, which is often expensive, and will limit the formation of soaps that disrupt the reaction.

5 It has also been demonstrated that the use of the acid composition according to the invention as esterification catalyst makes it possible to obtain a lower amount of residual catalyst in the organic phase than that obtained with the alkane-sulphonic acid catalyst alone. This makes it possible to reduce the consumption of basic catalyst during an optional subsequent transesterification step for the
10 purpose of preparing, for example, biodiesel.

Surprisingly, it has also been demonstrated that the use of the composition according to the invention makes it possible to improve the fatty acid conversion kinetics compared with the use of an alkane-sulphonic acid used alone or an aryl-sulphonic acid used alone.

15 According to one embodiment of the invention, the composition according to the invention is an esterification and transesterification catalyst thus making it possible to carry out in a single step the esterification and the transesterification of free fatty acids and of fatty acids present in the form of mono-, di- and/or triglycerides.

20 Optionally, the composition according to the invention may comprise one or more additives well known to those skilled in the art, such as those chosen from:

- corrosion inhibitors;
- fragrances, odorous agents;

and other additives well known to those skilled in the art.

25 According to one preferred embodiment, the composition according to the invention comprises at least one corrosion inhibitor.

According to another preferred embodiment, the composition comprises at least one fragrance and/or one odorous agent.

30 The composition according to the invention can be prepared according to any method known to those skilled in the art, such as, for example, the process described hereinafter, said process not being limiting.

The alkane-sulphonic acid is introduced into a container, at ambient temperature. The aryl-sulphonic acid is then added in solid form and the mixture is then heated at approximately 40°C until complete dissolution. In the case where a solvent and optional additives are used, it is preferable to pre-mix them with the alkane-sulphonic acid before slowly adding the aryl-sulphonic acid.

The present application also relates to a process for producing fatty acid esters, in which the fatty acids are esterified in the presence of the composition according to the invention.

The esterification process consists in introducing a fatty acid or a mixture of fatty acids into a reactor. The alcohol is subsequently added, then the medium is heated to a temperature generally of between 50°C and 200°C, more generally between 60°C and 120°C, preferably between 60°C and 80°C. The composition according to the invention is preferentially introduced at the esterification temperature. According to another embodiment of the invention, said composition can be added before the heating. According to yet another embodiment of the invention, the alcohol and the said composition can be added continuously, together or separately, when the medium has reached the esterification temperature. According to one embodiment of the invention, the said composition can be added with the fatty acid or the mixture of fatty acids. According to one preferred embodiment of the invention, the fatty acid or the mixture of fatty acids, the alcohol and said composition are added together before the heating. The esterification reaction is then carried out in the temperature range as indicated previously.

During this esterification process, the composition according to the invention acts as catalyst.

The fatty acids may be of any type chosen from the fatty acids and the mixtures of fatty acids known to those skilled in the art, among which are fatty acids from the plant or animal kingdom, including algae, and more generally from the plant kingdom. These said acids generally and advantageously comprise at least one olefinic unsaturation.

These said acids are usually present in vegetable oils extracted from various oleaginous plants such as, in a non-limiting manner, peanut plant, sunflower,

rapeseed, the castor oil plant, bladderpod, olive, soya, oil palm, avocado, walnut, hazelnut, almond, sesame, sea buckthorn and meadowfoam, including algae. They can also be from the terrestrial or marine animal world, and in the latter case, they may be derived from fish fats or from mammalian fats, such as, for example
5 and in a non-limiting manner, fats from cattle, from cod, from whales or from seals. Finally, said acids may come from recycled used oils such as, in a non-limiting manner, used cooking oil.

As described above, the acids present in these oils are placed in the presence of
10 an alcohol. The alcohol can be an alcohol of any type known to those skilled in the art, such as mono-alcohol, diols, triols, tetrols, and others, used alone or in combination. Preferably, the used alcohol has a molar mass of between 30 and 200 g.mol⁻¹. According to one embodiment of the invention is an alcohol of R¹-OH type, where R¹ is a linear or branched, saturated or unsaturated, alkyl or aromatic
15 chain comprising from 1 to 20 carbon atoms. Preferably, R¹ is an alkyl chain containing from 1 to 10 carbon atoms and in particular from 1 to 4. According to another embodiment of the invention, the alcohol has more than one -OH function and, for example, the alcohol can be glycerol (propane-1,2,3-triol).

20 In one embodiment of the invention in which the acid composition is used as a catalyst for esterification reaction of fatty acids, and in particular of free fatty acids present in oils, the catalyst according to the invention/fatty acid molar ratio is between 0.001 and 0.5 and more particularly between 0.01 and 0.2. The number of moles of fatty acids is measured by acid-base titration by potentiometry and is
25 expressed in moles per gramme of fatty acids present in the starting product. This value is then multiplied by the catalyst/fatty acid molar ratio, to determine the amount of catalyst to be added.

According to one embodiment of the esterification process according to the invention, the alcohol/fatty acid molar ratio is between 1 and 20, preferably
30 between 4 and 10.

According to one embodiment of the invention, the fatty acid esterification reaction can be carried out at any temperature, but preferably at temperatures of between

50°C and 200°C, more generally at temperatures of between 60°C and 120°C, preferably between 60°C and 80°C.

According to one embodiment of the invention, the fatty acid esterification reaction can be carried out at any pressure, but preferably at a pressure of between 10^4 Pa (0.1 bar absolute) and $2 \cdot 10^6$ Pa (20 bar absolute), more generally between atmospheric pressure and 10^6 Pa (10 bar absolute) and most particularly preferably at atmospheric pressure.

The reaction time for the fatty acid esterification can vary to large extents and is generally between a few minutes and a few hours, for example between 10 minutes and 6 hours, typically between 30 minutes and 180 minutes.

The esterification reaction can be carried out batchwise or continuously. The catalyst according to the invention is added to the mixture or separately into the reaction medium. It can be added alone or in a co-feed with the fatty acid source (oil, animal fat, etc.) and/or the alcohol. The reaction can be carried out in one or more reactors, between 2 and 15, more generally 2 to 10 reactors, even more generally from 2 to 5 reactors, arranged in parallel or in cascade. According to one particular mode, the batchwise process with several reactors arranged in cascade is preferred. It may be advantageous to perform organic and aqueous phase separations between two reactors. In order to improve the reaction yield, the water formed is eliminated according to any method well known to those skilled in the art, for example as it forms, and for example by heating. According to one embodiment of the invention, the elimination of water can lead the elimination of all or part of the solvent, in particular when the solvent is an alcohol.

According to one embodiment of the invention, the free fatty acids used come from an oil of plant origin in order to obtain biofuel, in particular biodiesel. In that case, the biodiesel is obtained after a transesterification step, as described above. If a step for neutralization of this biodiesel is required, it is possible to use the acid phase obtained at the end of the free fatty acid esterification reaction, this being after elimination of the alcohol.

The fatty acid esterification reaction according to the invention also makes it possible to obtain products that can be used in various fields, such as the

cosmetics industry, lubricants, agrochemistry, the pharmaceutical industry, cleaning, etc.

Examples

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The examples which follow make it possible to illustrate the present invention, but are in no way limiting.

Method for preparing a composition according to the invention:

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A composition comprising the following is prepared:

- 70% by weight of methanesulphonic acid diluted to 70% in water (i.e. 49% by weight of pure methanesulphonic acid);
- 30% by weight of para-toluenesulphonic acid (PTSA) diluted to 89% in water (i.e. 27% by weight of pure para-toluenesulphonic acid).

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The above composition is prepared from an aqueous solution containing 70% by weight of MSA LC from the company Arkema, introduced into a jacketed reactor. The para-toluenesulphonic acid at 89% by weight is a solid which is added in one step at ambient temperature, then the medium with stirring is heated to approximately 40°C until the para-toluenesulphonic acid has dissolved.

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The composition thus obtained contains, per 100 g of composition, 0.667 mol of catalyst ($49/96 + 27/172$ (with 96 being the molar mass of MSA and 172 being the molar mass of PTSA)), i.e. a molar mass of the formulation of = 149.9 g/mol (= $100/0.667$).

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The composition thus prepared is used as esterification catalyst in the example below.

Example of esterification of an oil:

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An industrial mixture comprising an oil comprising triglycerides and 94% by weight of free fatty acids (FFAs) with an average molecular weight of the fatty acids at 268 ± 1 g/mol is used.

The methanol/FFA molar ratio is equal to 8.

The catalyst/FFA molar ratio is equal to 0.175.

471 g of an industrial mixture comprising triglycerides and FFAs at 94% by weight of FFAs, i.e. 1.652 mol of fatty acid, are introduced into a jacketed reactor preheated to 50°C and equipped with a mechanical stirrer, with a temperature probe and with a condenser. The amount of methanol introduced is determined as follows:

$1.652 \times 8 \times 32 = 423$ g of methanol (8 molar equivalents/FFA).

The reaction mixture is heated to 70°C and the catalyst prepared above is then introduced. The amount of catalyst to be added is calculated as follows:

$1.652 \times 0.175 \times 149.9 = 43.3$ g of composition.

The reaction medium is stirred for 2 hours at 70°C, then decanted and left overnight at 70°C.

The aqueous and organic phases are analyzed according to the methods described below.

Methods of analysis:

The FFAs and the catalyst, in the organic phase, are titrated by potentiometry in the following way: approximately 1.5 g of organic phase are introduced into a beaker, then the volume is made up to 50 mL with a toluene/isopropanol/water mixture in the proportions 500/495/5 by volume.

The potentiometer titration is carried out with KOH at 0.1 mol/l in ethanol with a DG113-SC No. 2 electrode and a T50 titrator, both from Mettler Toledo.

The titration makes it possible to be able to accurately determine, on the one hand, the amount of residual catalyst in the organic phase in moles per gramme and, on the other hand, the content of residual fatty acids in the organic phase in % by weight.

The acid-base titration makes it possible to obtain 2 potential jumps: the first jump corresponds to the catalyst and the second jump corresponds to the residual fatty acids.

Results:

a/ The titrations described above make it possible to measure the percentage of residual FFAs in the organic phase which will then undergo transesterification.

These results are represented in Figure 1.

The results show that the percentage by weight of residual FFAs is:

- 1.2 with the MSA (denoted AMS in the figures) alone
- 1.02 with the PTSA alone
- 0.87 with the composition according to the invention.

5 By virtue of the composition according to the invention, a percentage of residual FFAs that is lower than that obtained with the MSA alone or the PTSA alone is thus obtained.

b/ The FFA conversion kinetics are improved compared with the use of each acid alone, as represented in Figure 2. Indeed, with the composition according to the
10 invention, faster kinetics for conversion into ester are noted.

CLAIMS

1. Composition comprising:

- 5 - at least one alkane-sulphonic acid of formula $R-SO_3H$ in which R represents a linear or branched, saturated hydrocarbon-based chain comprising from 1 to 4 carbon atoms which may or may not be substituted with at least one halogen atom ;
- at least one aryl-sulphonic acid;
- 10 - and, optionally, at least one solvent;

in which:

- the proportion by weight of alkane-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 5% and 85%, preferably between 8% and 65%;
- 15 - the proportion by weight of aryl-sulphonic acid relative to the total weight of alkane-sulphonic acid and of aryl-sulphonic acid is between 15% and 95%, preferably between 35% and 92%.

2. Composition according to Claim 1, in which the solvent is chosen from water, an alcohol and an ether, taken alone or in combination.

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3. Composition according to one of the preceding claims, in which the solvent is water or a C_1 to C_3 alcohol, taken alone or in combination.

25 4. Composition according to one of the preceding claims, in which the solvent is water or methanol, taken alone or in combination.

5. Composition according to one of the preceding claims, in which the proportion by weight of solvent relative to the total weight of the composition is between 0% and 50%, preferably between 5% and 35%.

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6. Composition according to one of the preceding claims, in which the alkane-sulphonic acid is chosen from methanesulphonic acid, ethanesulphonic acid, n-propanesulphonic acid, *iso*-propanesulphonic acid, n-butanesulphonic acid,

iso-butanesulphonic acid, *sec*-butanesulphonic acid, *tert*-butanesulphonic acid and trifluoromethanesulphonic acid, and mixtures of two or more thereof in any proportions.

- 5 7. Composition according to one of the preceding claims, in which the alkane-sulphonic acid is methanesulphonic acid.
8. Composition according to one of the preceding claims, in which the aryl-sulphonic acid is para-toluenesulphonic acid.
- 10 9. Composition according to one of the preceding claims, comprising at least one corrosion inhibitor.
10. Composition according to one of the preceding claims, comprising at least one
15 fragrance or one odorous agent, taken alone or in combination.
11. Use of the composition according to Claims 1 to 10, as an esterification catalyst, preferably a catalyst for esterification of fatty acid.
- 20 12. Process for producing esters of fatty acids, comprising the steps of:
- a/ introducing at least one fatty acid into a reactor;
 - b/ adding at least one alcohol;
 - c/ heating the reaction medium;
 - d/ introducing a composition according to any one of Claims 1 to 10, as
25 catalyst;
 - e/ optionally, eliminating the water formed during esterification process;
 - f/ recovering the fatty acid esters;
- step d possibly being carried out at the same time as step a and/or b, preferably at the same time as steps a and b.
- 30 13. Process according to Claim 12, in which the catalyst/fatty acid molar ratio is between 0.001 and 0.5 and more particularly between 0.01 and 0.2.