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(54) Title: PROCESS FOR THE PRODUCTION OF TRIACETIN, ALKYL ESTERS OF FATTY ACIDS

(57) Abstract: The present invention relates to a process for the production of triacetin and alkyl esters of fatty acids, wherein said process comprise the following steps: (i) mixing an alkanolic potassium alkoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes; (ii) reacting said vegetable oil and/or animal fat with an alkyl acetate in the presence of said alkanolic potassium alkoxide catalyst, wherein (a) the molar ratio of vegetable oil and/or animal fat to alkyl acetate is from 1:10 to 1:500; (b) the molar ratio of vegetable oil and/or animal fat to potassium alkoxide is from 1:0.01 to 1:1; and wherein the vegetable oil and/or animal fat, alkyl acetate and alkanolic potassium alkoxide catalyst comprise less than 1000 ppm water; and (iii) separating triacetin and alkyl esters of fatty acids from the resulting reaction mixture.

WO 2016/180498 A1

Process for the production of triacetin, alkyl esters of fatty acids

Field of the Invention

The present invention relates to a process for the production of triacetin and alkyl esters of fatty acids. Furthermore, the present invention also discloses a process for the production of a biodiesel composition comprising triacetin and alkyl esters of fatty acids.

Background to the Invention

Triacetin (1,2,3-triacetoxypropane) is a triester which finds application in the field of fuel additives, in particular because it not only serves as an antiknock agent which can reduce engine knocking in gasoline (*i.e.* prevent explosion outside the normal combustion front in response to improper initiation of combustion upon ignition), but also because it improves the performance (in particular, viscosity) of diesel at low temperatures.

Typically, triacetin is produced by reacting glycerol (glycerine) with acetic acid, or with methyl or ethyl acetates, whereby the glycerol is a by-product from the transesterification of triglycerides with alkyl alcohols to produce alkyl esters of fatty acids for use as biodiesel (*cf.* US Patent 7,637,969). Triacetin may also be produced by inter-esterification of triglycerides with alkyl acetates. However, each of these processes tends to optimize the production of a single product (usually alkyl esters of fatty acids suitable for use as biodiesel) and to generate by-products in high amounts. Moreover, the demand for triacetin as a diesel additive is seasonal (with demand peaking in the colder months), such that it is necessary to develop a process that it capable of not only producing alkyl esters of fatty acids suitable for use as biodiesel, but also of producing triacetin, preferably in improved yields with reduced amounts of by-products, wherein the ratio of triacetin:alkyl esters of fatty acids may be varied according to seasonal demand.

Thus, it is a problem of the present invention to provide an process for the improved production of triacetin and alkyl esters of fatty acids, wherein the ratio of triacetin:alkyl esters of the fatty acids produced by said process may be increased or decreased according to demand.

In addition it is a problem of the present invention to provide an improved process for the high-yield production of triacetin and alkyl esters of fatty acids, wherein the yield of by-products is minimised.

Brief Description of the Invention

The present invention relates to a process for the production of triacetin and alkyl esters of fatty acids, wherein said process comprises the following steps:

(i) mixing an alkanolic potassium alkoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes;

(ii) reacting said vegetable oil and/or animal fat with an alkyl acetate in the presence of said alkanolic potassium alkoxide catalyst, wherein

(a) the molar ratio of vegetable oil and/or animal fat to alkyl acetate is from 1:10 to 1:500;

(b) the molar ratio of vegetable oil and/or animal fat to alkanolic potassium alkoxide catalyst is from 1:0.01 to 1:1; and

wherein the vegetable oil and/or animal fat, alkyl acetate and alkanolic potassium alkoxide catalyst comprise less than 1000 ppm water; and

(iii) separating triacetin and alkyl esters of fatty acids from the resulting reaction mixture.

Moreover, the present invention relates to a process for the production of triacetin and C_{1-6}-alkyl esters of C_{10-26}-fatty acids which comprises the following steps:

(i) mixing a C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 30 and 60 °C;

(ii) reacting said vegetable oil and/or animal fat with a C_{1-6}-alkyl acetate in the presence of said C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst for between 5 and 120 minutes at between 20 and 70 °C, wherein

(a) the molar ratio of vegetable oil and/or animal fat to C_{1-6}-alkyl acetate is from 1:20 to 1:50;

(b) the molar ratio of vegetable oil and/or animal fat to C_{1-6}-alkanolic potassium

C_{1-6}-alkoxide catalyst is from 1:0.05 to 1:0.2; and

wherein the vegetable oil and/or animal fat, C_{1-6}-alkyl acetate and C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst comprise less than 500 ppm water; and

(iii) separating triacetin and C_{1-6}-alkyl esters of C_{10-26}-fatty acids from the resulting reaction mixture by distillation under a vacuum.

Furthermore, the present invention relates to a process for the production of triacetin and methyl esters of fatty acids which comprises the following steps:

(i) mixing a methanolic potassium methoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 30 and 60 °C;

(ii) reacting said vegetable oil and/or animal fat with methyl acetate in the presence of said methanolic potassium methoxide catalyst for between 5 and 60 minutes at between 30 and 60 °C, wherein

(a) the molar ratio of vegetable oil and/or animal fat to methyl acetate is from 1:20 to 1:50;

(b) the molar ratio of vegetable oil and/or animal fat to methanolic potassium methoxide catalyst is from 1:0.05 to 1:0.2; and

wherein the vegetable oil and/or animal fat, methyl acetate and methanolic potassium methoxide catalyst comprise less than 500 ppm water; and

(iii) treating the reaction mixture obtained after step (ii) with an acid and filtering out the resulting solids, wherein the acid is selected from phosphoric acid, sulfuric acid, citric acid or acetic acid; and

separating triacetin and methyl esters of fatty acids from the resulting treated and filtered reaction mixture by distillation at between 130 and 195 °C under a vacuum at a pressure of between 1 and 1500 Pa.

In addition, the present invention relates to a process for the production of a biodiesel composition comprising triacetin and alkyl esters of fatty acids, wherein said process comprises the process disclosed herein, followed by mixing the triacetin and alkyl esters of fatty acids, thus separated, in a weight ratio of from 1:200 to 1:4.

Moreover, the present invention relates to a process for the production of a biodiesel composition comprising triacetin and methyl esters of fatty acids, wherein said process comprises:

(i) mixing a methanolic potassium methoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 30 and 60 °C;

(ii) reacting said vegetable oil and/or animal fat with methyl acetate in the presence of said methanolic potassium methoxide catalyst for between 5 and 60 minutes at between 30 and 60 °C, wherein

(a) the molar ratio of vegetable oil and/or animal fat to methyl acetate is from 1:20 to 1:50;

(b) the molar ratio of vegetable oil and/or animal fat to methanolic potassium methoxide catalyst is from 1:0.05 to 1:0.2; and wherein the vegetable oil and/or animal fat, methyl acetate and methanolic potassium methoxide catalyst comprise less than 500 ppm water; and

(iii) treating the reaction mixture obtained after step (ii) with an acid and filtering out the resulting solids, wherein the acid is selected from phosphoric acid, sulfuric acid, citric acid or acetic acid; and

separating triacetin and methyl esters of fatty acids from the resulting treated and filtered reaction mixture by distillation at between 130 and 195 °C under a vacuum at a pressure of between 1 and 1500 Pa; and

(iv) mixing the triacetin and alkyl esters of fatty acids, thus separated, in a weight ratio of from 1:100 to 1:5.

Brief Description of the Figures

Figure 1. A. is diagram showing the general reaction scheme, wherein a vegetable oil and/or animal fat [*i.e.* a triglyceride (TG) of fatty acids (where R^1 is alkyl, preferably $C_{8\text{-}36}$ alkyl)] is reversibly reacted with an alkyl acetate (where R^2 is alkyl, preferably $C_{1\text{-}6}$ alkyl) in the presence of an alkanolic potassium alkoxide catalyst (preferably a $C_{1\text{-}6}$ alkanolic potassium $C_{1\text{-}6}$ alkoxide catalyst) to form triacetin (TA) and an alkyl alkanoate (preferably a $C_{1\text{-}6}$ alkyl ester of a $C_{8\text{-}36}$ fatty acid), and **B.** Mechanism of reaction exemplified using methyl acetate as the alkyl acetate, showing successive reversible reactions with methyl acetate of a vegetable oil and/or animal fat [*i.e.* a triglyceride (TG)] to form a monoacetyl diglyceride (MADG), of MADG to form a diacetyl monoglyceride (DAMG), and of DAMG to form triacetin (TA), accompanied by formation of one equivalent of a fatty acid methyl ester at each step. Respective rate constants are indicated for the forward (K_1, K_3 and K_5) and reverse (K_2, K_4 and K_6) reactions.

Figure 2. Graph of the equilibrium content of products produced in the interesterification of triglycerides with methyl acetate at different molar ratios of triglyceride to methyl acetate.

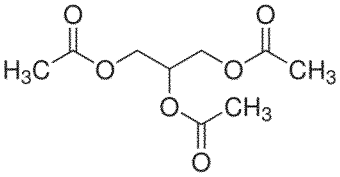
Figure 3. Graph of the effect of the presence of water as an impurity on the content of products produced in the interesterification of triglycerides with methyl acetate at different molar ratios of triglyceride to potassium methoxide.

Figure 4. Graph of the variation in content (weight percent) of components over time (minutes) for the reaction of vegetable oil (*i.e.* triglyceride, TG) with methyl acetate at 50 °C, to form triacetin (TA), methyl esters of fatty acids (*i.e.* biodiesel, EM), monoacetyl diglyceride (MADG), and diacetyl monoglyceride (DAMG), wherein the

molar ratio of triglyceride to methyl acetate is 1:12 and the molar ratio of triglyceride to catalyst is 1:0.2, **A.** in the presence of activated solid potassium methoxide catalyst, and **B.** in the presence of methanolic potassium methoxide catalyst.

Detailed Description of the Invention

The present invention relates to a process for the production of triacetin and alkyl esters of fatty acids. Triacetin, also known as 1,3-diacetyloxypropan-2-yl acetate or glycerin triacetate, is the triester of glycerol and acetic acid and has the following formula:



Triacetin

Alkyl esters of fatty acids are derived from esterification of at least one fatty acid with at least one alkyl alcohol. A fatty acid is a saturated or unsaturated carboxylic acid and an alkyl alcohol is an alkanol. In a preferred embodiment, the fatty acid has from 8 to 36 carbon atoms, more preferably from 10 to 26 carbon atoms, furthermore preferably from 12 to 24 carbon atoms. In another preferred embodiment, the alkyl alcohol has from 1 to 6 carbon atoms, more preferably 1 or 2 carbon atoms (*i.e.* methanol or ethanol), more preferably 1 carbon atom (*i.e.* methanol). Thus, the alkyl esters of fatty acids of the present invention are preferably C_{1-6}-alkyl esters of C_{8-36}-fatty acids, C_{10-26}-fatty acids or C_{12-24}-fatty acids, more preferably methyl or ethyl esters of C_{8-36}-fatty acids, C_{10-26}-fatty acids or C_{12-24}-fatty acids, furthermore preferably methyl esters of C_{8-36}-fatty acids, C_{10-26}-fatty acids or C_{12-24}-fatty acids, yet more preferably methyl esters of C_{12-24}-fatty acids.

Said process comprises three steps. The first of these steps, (i), comprises mixing an alkanolic potassium alkoxide catalyst with vegetable oil and/or animal fat.

The alkanolic potassium alkoxide catalyst comprises a potassium alkoxide in alkyl alcohol. Preferably the potassium alkoxide and the alkyl alcohol have from 1 to 6 carbon atoms, more preferably 1 or 2 carbon atoms (*i.e.* methanolic potassium methoxide or ethanolic potassium ethoxide), more preferably 1 carbon atom (*i.e.* methanolic potassium methoxide). In an embodiment of the present invention, the alkanolic potassium alkoxide catalyst comprises a potassium alkoxide, preferably a potassium C_{1-6}-alkoxide, in an alcohol, preferably a C_{1-6}-alkyl alcohol, in between 20 and 60 wt.%, more preferably between 25 and 50 wt.%, as measured before being mixed in step (i) of the process of the invention. Optionally, said alkanolic potassium alkoxide catalyst comprises a phase transfer agent, preferably a polyethylene glycol such as PEG200, in a ratio of potassium alkoxide:PEG of 1:1.

The vegetable oil is an oil obtained from at least one plant, while the animal fat is a fat obtained from at least one animal. Vegetable oils may be selected from rapeseed oil, colza oil, soybean oil, palm oil, sunflower oil, safflower oil, algal oil, castor oil, coconut oil, copaiba oil, corn oil, cottonseed oil, dammar oil, olive oil, false flax oil, grapeseed oil, hemp oil, *Jatropha* oil, linseed oil, milk bush oil, mustard oil, nahor oil, paradise oil, peanut oil, perilla seed oil, petroleum nut oil, *Pongamia* oil, poppyseed oil, radish oil, ramtil oil, rice bran oil, salicornia oil, sesame oil, tigernut oil or tung oil, or mixtures thereof, while animal fats may be selected from milk fat, butter fat, beef fat, dripping, tallow or suet, pig fat, dripping or lard, sheep (mutton) fat or tallow, goat (mutton) fat or tallow, deer fat, chicken fat or schmaltz, turkey fat, duck fat, goose fat or schmaltz or fish oil, or mixtures thereof. In a preferred embodiment of the present invention, the vegetable oil is selected from rapeseed oil, colza oil, soybean oil, palm oil, sunflower oil, safflower oil, algal oil, castor oil, coconut oil, corn oil, cottonseed oil, olive oil, false flax oil, grapeseed oil, hemp oil, *Jatropha* oil, linseed oil, mustard oil, peanut oil, *Pongamia* oil, poppyseed oil, radish oil, rice bran oil, salicornia oil, sesame oil, tigernut oil or tung oil, or mixtures thereof. More preferably, the vegetable oils may be selected from rapeseed oil, colza oil, soybean oil, palm oil, sunflower oil, safflower oil, algal oil, castor oil, coconut oil, corn oil, cottonseed oil, olive oil, false flax oil, hemp oil, *Jatropha* oil, *Pongamia* oil, rice bran oil, salicornia oil or sesame oil, or mixtures thereof, while animal fats may be selected from milk fat, beef fat, pig fat, sheep fat, chicken fat, turkey fat, duck fat, goose fat or fish oil, or mixtures thereof. Furthermore preferably, the vegetable oils may be selected from rapeseed oil, colza oil, soybean oil, palm oil, sunflower oil, safflower oil, castor oil, coconut oil, cottonseed oil, false flax oil, *Jatropha* oil or *Pongamia* oil, or mixtures thereof, while animal fats may be selected from milk fat, beef fat, pig fat, chicken fat or duck fat, or mixtures thereof.

In said step (i) of mixing, said alkanolic potassium alkoxide catalyst is mixed with the vegetable oil and/or animal fat for between 1 and 5 minutes. Preferably, alkanolic potassium alkoxide catalyst is mixed with the vegetable oil and/or animal fat for between 1 and 5 minutes at between 10 and 80 °C, more preferably for between 2 and 4 minutes at between 30 and 60 °C. The homogeneity of said reaction mixture may be increased by physical means comprising laminar and/or turbulent flow, such as stirring. In a preferred embodiment, the step (i) of mixing is also accompanied by preactivation of the alkanolic potassium alkoxide catalyst with the vegetable oil and/or animal fat. Said step of mixing therefore accelerates the interesterification reaction by (a) providing elevated amounts of potassium alkoxide in solution and, (b) preactivation of the catalyst.

The second of these steps, (ii), comprises reacting said vegetable oil and/or animal fat with an alkyl acetate in the presence of said alkanolic potassium alkoxide catalyst. The alkyl acetate is derived from esterification of acetic acid with at least one alkyl alcohol. In a preferred embodiment, each alkyl alcohol has from 1 to 6 carbon atoms, more preferably 1 or 2 carbon atoms (*i.e.* methanol or ethanol), more preferably 1 carbon atom (*i.e.* methanol). Thus, the alkyl acetate is preferably at least one C_{1-6}-alkyl ester of acetic acid, more preferably a methyl and/or ethyl ester of acetic acid, furthermore preferably a methyl ester of acetic acid. Consequently, in one preferred embodiment of the present invention, the alkyl ester is the methyl ester, the alkyl acetate is methyl acetate and the alkanolic potassium alkoxide catalyst is methanolic potassium methoxide.

In said step (ii) of reacting, (a) the molar ratio of vegetable oil and/or animal fat to alkyl acetate is from 1:10 to 1:500, more preferably from 1:15 to 1:100, furthermore preferably from 1:20 to 1:50. Moreover, in said step (ii) of reacting, (b) the molar ratio of vegetable oil and/or animal fat to alkanolic potassium alkoxide catalyst is from 1:0.01 to 1:1, more preferably from 1:0.02 to 1:0.5, furthermore preferably from 1:0.05 to 1:0.2. Furthermore, in said step (ii) of reacting, the vegetable oil and/or animal fat, alkyl acetate and alkanolic potassium alkoxide catalyst comprise less than 1000 ppm water, more preferably less than 500 ppm water, furthermore preferably less than 200 ppm water. In a preferred embodiment of the present invention, the molar ratio of vegetable oil and/or animal fat to methyl acetate is from 1:20 to 1:50, and the molar ratio of vegetable oil and/or animal fat to methanolic potassium methoxide is from 1:0.05 to 1:0.2. Note that for the purposes of the present invention, the triglyceride (*i.e.* the vegetable oil and/or animal fat) is taken to be a triglyceride of C_{18}-saturated fatty acids [on the assumption that the predominant (*i.e.* average) triglyceride present in nature is a triglyceride of C_{18}-saturated fatty acids]. Consequently, said triglyceride would have a molecular weight of approximately 891.5 g/mol, such that, for example, a mixture comprising equal weights of triglyceride (*i.e.* the vegetable oil and/or animal fat) and an alkyl acetate is considered to have a molar ratio of triglyceride to alkyl acetate (*i.e.* a molar ratio of vegetable oil and/or animal fat to alkyl acetate) of 1:12.

In a preferred embodiment of the present invention, said step (i) of reacting, said vegetable oil and/or animal fat is reacted with an alkyl acetate in the presence of said alkanolic potassium alkoxide catalyst for between 5 and 720 minutes (12 hours) at between 10 and 80 °C. Preferably, said vegetable oil and/or animal fat may be reacted with an alkyl acetate in the presence of said alkanolic potassium alkoxide catalyst for between 5 and 120 minutes at between 20 and 70 °C, more preferably for between 10 and 60 minutes at between 30 and 60 °C. The homogeneity of said reaction mixture may be increased by physical means comprising laminar and/or turbulent flow, such as stirring.

The process of the invention minimizes production of glycerol (glycerine), preferably to less than 1 wt.%, more preferably to less than 0.1 wt.%, furthermore preferably to less than 0.05 wt.%, still more preferably to less than 0.02 wt.%, of the total content of the components comprised in the reaction mixture resulting from step (ii) of said process.

As can be seen from Tables 2 and 3 and Figures 2 and 3, the amount of glycerol-triacetin by-products is minimized by (i) increasing the amount of methyl acetate and (ii) reducing the amount of catalyst present in the reaction mixture. Moreover, when said increased amounts of methyl acetate and said reduced amounts of catalyst are used, the reaction outcome may be directed by the addition of water, so as to obtain crude biodiesel mixtures which are either comprised principally of methyl esters of fatty acids or comprised principally of mixtures of said methyl esters of fatty acids and triacetin. Consequently, it is possible to use the process of the invention to provide high-purity crude biodiesel mixtures having different proportions of triacetin and, thus, different properties, by controlling the amounts of methyl acetate, catalyst (including methanol) and water present in the reaction mixture. Thus, the proportion of products produced by the process of the invention may be customised by controlling the amounts of methyl acetate, catalyst (including methanol) and water present in the reaction mixture, relative to the amounts of triglyceride, depending on demand for triacetin or methyl esters of fatty acids. In particular, in one embodiment of the invention, the process of the invention may be switched between (i) a process involving a decreased amount of alkyl acetate and increased amounts of catalyst (and, hence, alcohol) and water relative to the vegetable oil and/or animal fat and (ii) a process involving an increased amount of alkyl acetate and decreased amounts of catalyst (and, hence, alcohol) and water relative to the vegetable oil and/or animal fat, depending on the demand for biodiesel (i) having a higher ratio of alkyl esters of fatty acids to triacetin (*i.e.* lowered proportion of triacetin relative to the alkyl esters of fatty acids) or (ii) having a lower ratio of alkyl esters of fatty acids to triacetin, respectively.

Consequently, the third of these steps, (iii), comprises separating triacetin and alkyl esters of fatty acids from the resulting reaction mixture. In a preferred embodiment of the invention, said step (iii) comprises separating triacetin and alkyl esters of fatty acids from the resulting reaction mixture by distillation under a vacuum. In a more preferred embodiment of the invention, distillation is carried out at a temperature of no greater than 210 °C. Yet more preferably the distillation is performed by heating the distilland to between 120 and 210 °C at a pressure of between 0.1 and 7000 Pa, still more preferably between 130 and 200 °C at a pressure of between 1 and 2500 Pa, furthermore preferably between 135 and 195 °C at a pressure of between 100 and 1500 Pa.

Optionally, the alkanolic potassium alkoxide catalyst is removed from the reaction mixture prior to step (iii). In one preferred embodiment of the present invention, prior to step (iii) the reaction mixture is (a) treated with an acid and the resulting solids are filtered, and/or (b) centrifuged. In a more preferred embodiment of the present invention, the reaction mixture obtained after step (ii) is treated with an acid and the resulting solids are filtered, wherein the acid is selected from phosphoric acid, sulfuric acid, citric acid or acetic acid.

Thus, in one embodiment, said process comprises three steps, as follows:

(i) mixing an C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 20 and 80 °C;

(ii) reacting said vegetable oil and/or animal fat with a C_{1-6}-alkyl acetate in the presence of said C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst, wherein

(a) the molar ratio of vegetable oil and/or animal fat to C_{1-6}-alkyl acetate is from 1:10 to 1:500;

(b) the molar ratio of vegetable oil and/or animal fat to C_{1-6}-alkanolic potassium

C_{1-6}-alkoxide catalyst is from 1:0.01 to 1:1; and

wherein the vegetable oil and/or animal fat, C_{1-6}-alkyl acetate and C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst comprise less than 500 ppm water; and

(iii) separating triacetin and C_{1-6}-alkyl esters of fatty acids from the resulting reaction mixture by distillation under a vacuum.

In a more preferred embodiment, said process is a process for the production of triacetin and C_{1-6}-alkyl esters of C_{10-26}-fatty acids and comprises the following steps:

(i) mixing a C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 30 and 60 °C;

(ii) reacting said vegetable oil and/or animal fat with a C_{1-6}-alkyl acetate in the presence of said C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst for between 5 and 120 minutes at between 20 and 70 °C, wherein

(a) the molar ratio of vegetable oil and/or animal fat to C_{1-6}-alkyl acetate is from 1:20 to 1:50;

(b) the molar ratio of vegetable oil and/or animal fat to C_{1-6}-alkanolic potassium

C_{1-6}-alkoxide catalyst is from 1:0.05 to 1:0.2; and

wherein the vegetable oil and/or animal fat, C_{1-6}-alkyl acetate and C_{1-6}-alkanolic potassium C_{1-6}-alkoxide catalyst comprise less than 500 ppm water; and

(iii) separating triacetin and C_{1-6}-alkyl esters of C_{10-26}-fatty acids from the resulting reaction mixture by distillation at between 130 and 200 °C under a vacuum at a pressure of between 1 and 2500 Pa.

In a yet more preferred embodiment, said process is a process for the production of triacetin and methyl esters of fatty acids and comprises the following steps:

(i) mixing a methanolic potassium methoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 30 and 60 °C;

(ii) reacting said vegetable oil and/or animal fat with methyl acetate in the presence of said methanolic potassium methoxide catalyst for between 5 and 60 minutes at between 30 and 60 °C, wherein

(a) the molar ratio of vegetable oil and/or animal fat to methyl acetate is from 1:20 to 1:50;

(b) the molar ratio of vegetable oil and/or animal fat to methanolic potassium methoxide catalyst is from 1:0.05 to 1:0.2; and

wherein the vegetable oil and/or animal fat, methyl acetate and methanolic potassium methoxide catalyst comprise less than 500 ppm water; and

(iii) treating the reaction mixture obtained after step (ii) with an acid and filtering out the resulting solids, wherein the acid is selected from phosphoric acid, sulfuric acid, citric acid or acetic acid; and

separating triacetin and methyl esters of fatty acids from the resulting treated and filtered reaction mixture by distillation at between 130 and 195 °C under a vacuum at a pressure of between 1 and 1500 Pa.

In addition, the present invention also relates to a process for the production of a biodiesel composition, wherein said biodiesel composition comprises triacetin and alkyl esters of fatty acids. The process for the production of a biodiesel composition comprises (i) the process for the production of triacetin and alkyl esters of fatty acids according to any of the foregoing, followed by (ii) mixing the triacetin and alkyl esters of fatty acids, thus separated.

The triacetin and alkyl esters of fatty acids are mixed in a weight ratio of from 1:200 to 1:4. Preferably the triacetin and alkyl esters of fatty acids are mixed in a weight ratio of from 1:100 to 1:5. In a preferred embodiment of the present invention, the triacetin and alkyl esters of fatty acids are mixed in a weight ratio of from 1:50 to 1:10. The homogeneity of said biodiesel composition may be increased by physical means of mixing, comprising laminar and/or turbulent flow, such as stirring.

Thus, a preferred embodiment relates to a process for the production of a biodiesel composition comprising triacetin and methyl esters of fatty acids, wherein said process comprises:

(i) mixing a methanolic potassium methoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes at between 30 and 60 °C;

(ii) reacting said vegetable oil and/or animal fat with methyl acetate in the presence of said methanolic potassium methoxide catalyst for between 5 and 60 minutes at between 30 and 60 °C, wherein

  (a) the molar ratio of vegetable oil and/or animal fat to methyl acetate is from 1:20 to 1:50;

  (b) the molar ratio of vegetable oil and/or animal fat to methanolic potassium methoxide catalyst is from 1:0.05 to 1:0.2; and

  wherein the vegetable oil and/or animal fat, methyl acetate and methanolic potassium methoxide catalyst comprise less than 500 ppm water; and

(iii) treating the reaction mixture obtained after step (ii) with an acid and filtering out the resulting solids, wherein the acid is selected from phosphoric acid, sulfuric acid, citric acid or acetic acid; and

  separating triacetin and methyl esters of fatty acids from the resulting treated and filtered reaction mixture by distillation at between 130 and 195 °C under a vacuum at a pressure of between 1 and 1500 Pa; and

(iv) mixing the triacetin and alkyl esters of fatty acids, thus separated, in a weight ratio of from 1:100 to 1:5.

Examples

(I) Methods and materials:

General procedure

With reference to Figure 1A, vegetable oil and/or animal fat (triglyceride, TG) was treated with alkanolic potassium alkoxide (catalyst) in a 50 L reactor at 50 °C and agitated at 600 rpm using a mechanical stirrer for 3 minutes. Subsequently, alkyl acetate was added to the resulting mixture and reacted at 50 °C for a further 30 minutes, before separately distilling triacetin (TA) and alkyl esters of fatty acids (alkyl alkanoate, *i.e.* biodiesel) from the resulting reaction mixture at 180 °C under an oxygen-free atmosphere by varying the vacuum applied thereto.

Production of alkanolic potassium alkoxide catalyst

Potassium alkoxide was mixed with an alkyl alcohol and stirred for 1 minute at 20 °C to form a 32 wt.% solution of potassium alkoxide in alkyl alcohol.

Materials

In the following examples, the vegetable oil and/or animal fat is a vegetable oil selected from sunflower seed oil or palm oil, the alkanolic potassium alkoxide catalyst is methanolic potassium methoxide made from potassium methoxide in methanol, the alkyl acetate is methyl acetate and the products produced are triacetin and methyl esters of fatty acids (biodiesel). Said vegetable oils, methyl acetate and methanol were dried using molecular sieves, resulting in vegetable oils having contents of between 60 and 500 ppm of water, methyl acetate having content of between 20 and 500 ppm of water, and methanol having a content of between 20 and 500 ppm of water. Said potassium methoxide was dried under a vacuum of less than 100 Pascals at 20 °C.

(II) Working examples

Example 1: Effect of varying the vegetable oil and/or animal fat to methyl acetate ratio

The aforementioned general procedure was performed using two vegetable oils, namely sunflower seed oil and palm oil, wherein the molar ratio of vegetable oil:methyl acetate was varied between 1:12 to 1:100, wherein the molar ratio of the vegetable oil:potassium methoxide is 1:0.5.

As can be seen from Table 1 (relating to the procedure using sunflower seed oil) and Figure 2 (relating to the procedure using palm oil), the vegetable oil (*i.e.* triglyceride, TG) and monoacetin diglycerides (MADG, *cf.* Figure 1B) are consumed once the vegetable oil:methyl acetate molar ratios is less than 1:50, yet small amounts of diacetin monoglycerides (DAMG, *cf.* Figure 1B) remain even at smaller ratios of 1:100. Consequently, it is possible to use the process of the invention to provide biodiesels having different proportions of triacetin and, thus, different properties, by controlling the amount of methyl acetate present in the reaction mixture relative to the triglyceride. Thus, the process of the invention may be customised by controlling the amount of alkyl acetate present in the reaction mixture relative to the triglyceride, depending on demand for triacetin or methyl esters of fatty acids.

Table 1

Vegetable oil: methyl acetate molar ratio	**TA (wt.%)**	**EM (wt.%)**	**DAMG (wt.%)**	**MADG (wt.%)**	**TG (wt.%)**
1:12	13.07	72.85	9.75	3.84	0.40
1:18	15.37	73.34	9.17	2.58	0.02
1:24	15.23	76.54	6.42	1.19	0.02
1:32	16.59	80.48	5.72	0.88	0.03
1:50	19.97	78.39	3.53	0.00	0.00
1:75	20.37	79.69	2.62	0.00	0.00
1:100	23.09	79.56	1.80	0.00	0.00

TA = triacetin, EM = methyl esters of fatty acids, DAMG = diacetin monoglycerides, MADG = monoacetin diglycerides, TG = triglycerides (*i.e.* vegetable oil).

Example 2: Effect of the amount of catalyst and presence of water

The aforementioned general procedure was performed using two vegetable oils, namely sunflower seed oil and palm oil, wherein the molar ratio of vegetable oil:methyl acetate was 1:32, and the molar ratio of vegetable oil:potassium methoxide was 1:0.5, 1:0.2 and 1:0.1. Moreover, the reactants and catalyst were either dehydrated as disclosed above, or employed without prior dehydration.

As can be seen from Table 2 (relating to the procedure using sunflower seed oil) and Figure 2 (relating to the procedure using palm oil), a reduction in the amount of catalyst results in a reduction in the amounts of by-products which are produced. In addition, when said reduced amounts of catalyst are used, the reaction outcome may be controlled by the addition of water, such that it is possible to biodiesels which are either comprised of methyl esters of fatty acids or comprised of mixtures of said methyl esters of fatty acids and triacetin.

Table 2

Reagents	**Vegetable oil: $KOCH_3$ molar ratio**	**G (wt.%)**	**DA + MA (wt.%)**	**TA (wt.%)**	**EM (wt.%)**	**DAMG (wt.%)**	**MADG (wt.%)**	**TG (wt.%)**
Anhydrous	1:0.5	0.07	10.23	6.01	80.75	5.13	0.27	0.00
Not dried	1:0.5	0.09	9.07	7.52	80.48	5.72	0.88	0.03
Anhydrous	1:0.2	0.02	3.05	12.50	74.30	5.97	0.81	0.00
Not dried	1:0.2	0.04	9.71	7.76	77.91	6.16	0.98	0.03
Anhydrous	1:0.1	0.01	1.12	13.67	72.28	6.21	0.83	0.00
Not dried	1:0.1	0.01	0.59	0.33	21.06	4.86	18.34	43.91

G = glycerol, DA = diacetin, MA = monoacetin, TA = triacetin, EM = methyl esters of fatty acids, DAMG = diacetin monoglycerides, MADG = monoacetin diglycerides, TG = triglycerides (*i.e.* vegetable oil).

Consequently, it is possible to use the process of the invention to provide biodiesels having different proportions of triacetin and, thus, different properties, by controlling the amount of catalyst and amount of water present in the reaction mixture, relative to the triglyceride. Thus, the process of the invention may be customised by controlling the amount of catalyst and amount of water present in the reaction mixture relative to the triglyceride, depending on demand for triacetin or methyl esters of fatty acids.

Example 3: Effect of the addition of methanol/methanolic potassium alkoxide

The aforementioned general procedure was performed using sunflower seed oil:methyl acetate in a molar ratio of 1:12, and sunflower seed oil:potassium methoxide of 1:0.2.

As can be seen from Figures 4A and 4B, the use of a methanolic solution of potassium methoxide accelerates the reaction and does not require activation or dissolution of the methanolic potassium methoxide catalytic species. Moreover, the presence of methanol in the reaction mixture permits a reduction in the quantity of monoacetin diglycerides (MADG) and diacetin monoglycerides (DAMG), however also reduces the amount of triacetin present in the resulting biodiesel mixture. In fact, when methanol is added in amounts such that the ratio of sunflower seed oil:methanol drops below 1:6 (*i.e.* at greater molar amounts of methanol), the amount of triacetin produced drops to zero. This may be offset by increasing the amount of methyl acetate relative to the triglyceride, as per Example 1. Consequently, it is possible to use the process of the invention to provide biodiesels having different proportions of triacetin and, thus, different properties, by controlling the amount of methanol present in the reaction mixture, relative to the triglyceride. Thus, the process of the invention may be customised by controlling the amount of methanol present in the reaction mixture relative to the triglyceride, depending on demand for triacetin or methyl esters of fatty acids.

CLAIMS

1. Process for the production of triacetin and alkyl esters of fatty acids, wherein said process comprises the following steps:
   (i) mixing an alkanolic potassium alkoxide catalyst with vegetable oil and/or animal fat for between 1 and 5 minutes;
   (ii) reacting said vegetable oil and/or animal fat with an alkyl acetate in the presence of said alkanolic potassium alkoxide catalyst, wherein
      (a) the molar ratio of vegetable oil and/or animal fat to alkyl acetate is from 1:10 to 1:500;
      (b) the molar ratio of vegetable oil and/or animal fat to alkanolic potassium alkoxide catalyst is from 1:0.01 to 1:1; and

      wherein the vegetable oil and/or animal fat, alkyl acetate and alkanolic potassium alkoxide catalyst comprise less than 1000 ppm water; and
   (iii) separating triacetin and alkyl esters of fatty acids from the resulting reaction mixture.

2. The process according to claim 1, wherein the alkanolic potassium alkoxide catalyst comprises a potassium alkoxide in an alkyl alcohol in between 20 and 60 wt.%.

3. The process according to any of the preceding claims, wherein the alkyl ester is the methyl ester, the alkyl acetate is methyl acetate and the alkanolic potassium alkoxide catalyst is methanolic potassium methoxide.

4. The process according to claim 3, wherein the molar ratio of vegetable oil and/or animal fat to methyl acetate is from 1:20 to 1:50, and the molar ratio of vegetable oil and/or animal fat to methanolic potassium methoxide is from 1:0.05 to 1:0.2.

5. The process according to any of the preceding claims, wherein the reaction of step (ii) is carried out at between 20 and 70 °C for between 5 minutes and 12 hours.

6. The process according to any of the preceding claims, wherein the vegetable oil and/or animal fat is a vegetable oil selected from rapeseed oil, colza oil,

soybean oil, palm oil, sunflower oil, safflower oil, algal oil, castor oil, coconut oil, corn oil, cottonseed oil, olive oil, false flax oil, grapeseed oil, hemp oil, *Jatropha* oil, linseed oil, mustard oil, peanut oil, *Pongamia* oil, poppyseed oil, radish oil, rice bran oil, salicornia oil, sesame oil, tigernut oil or tung oil, or mixtures thereof.

7. The process according to any of the preceding claims, wherein prior to step (iii) the reaction mixture is (a) treated with an acid and the resulting solids are filtered, and/or (b) centrifuged.

8. The process according to claim 7, wherein the reaction mixture obtained after step (ii) is treated with an acid and the resulting solids are filtered, wherein the acid is selected from phosphoric acid, sulfuric acid, citric acid or acetic acid.

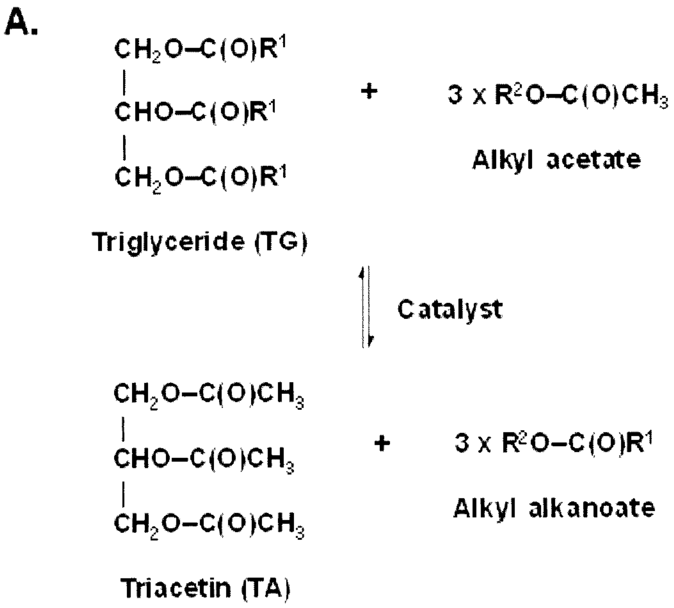
9. The process according to any of the preceding claims, wherein step (iii) is carried out by distillation under vacuum.

10. The process according to claim 9, wherein distillation is carried out at a temperature of no greater than 210 °C.

11. Process for the production of a biodiesel composition comprising triacetin and alkyl esters of fatty acids, wherein said process comprises the process according to claims 1 to 10, followed by mixing the triacetin and alkyl esters of fatty acids, thus separated, in a weight ratio of from 1:200 to 1:4.

12. The process according to claim 11, wherein the triacetin and alkyl esters of fatty acids are mixed in a weight ratio of from 1:50 to 1:10.

Figure 1



R^1 = alkyl, preferably $C_{8\text{-}36}$ alkyl
R^2 = alkyl, preferably $C_{1\text{-}6}$ alkyl

B.

$$TG + CH_3COOCH_3 \underset{K_2}{\overset{K_1}{\longleftrightarrow}} RCOOCH_3 + MADG$$

$$MADG + CH_3COOCH_3 \underset{K_4}{\overset{K_3}{\longleftrightarrow}} RCOOCH_3 + DAMG$$

$$DAMG + CH_3COOCH_3 \underset{K_6}{\overset{K_5}{\longleftrightarrow}} RCOOCH_3 + TA$$

Figure 2

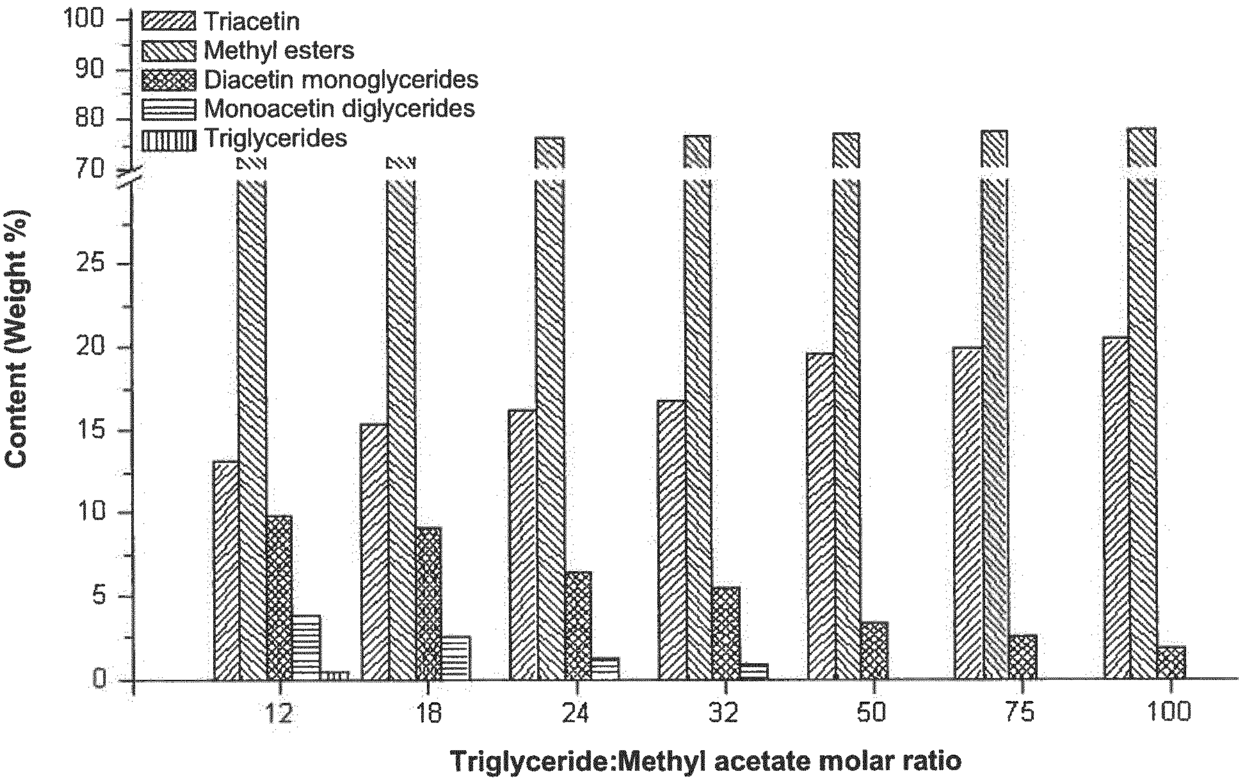


Figure 3

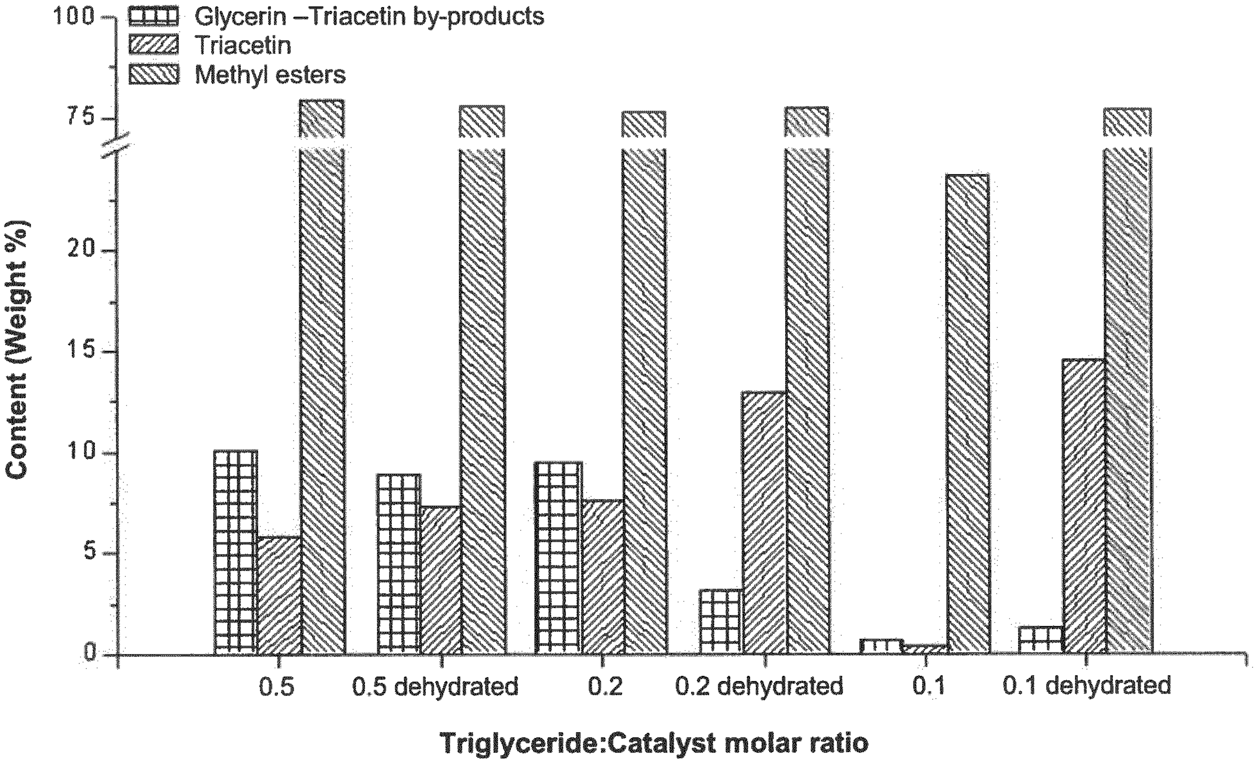
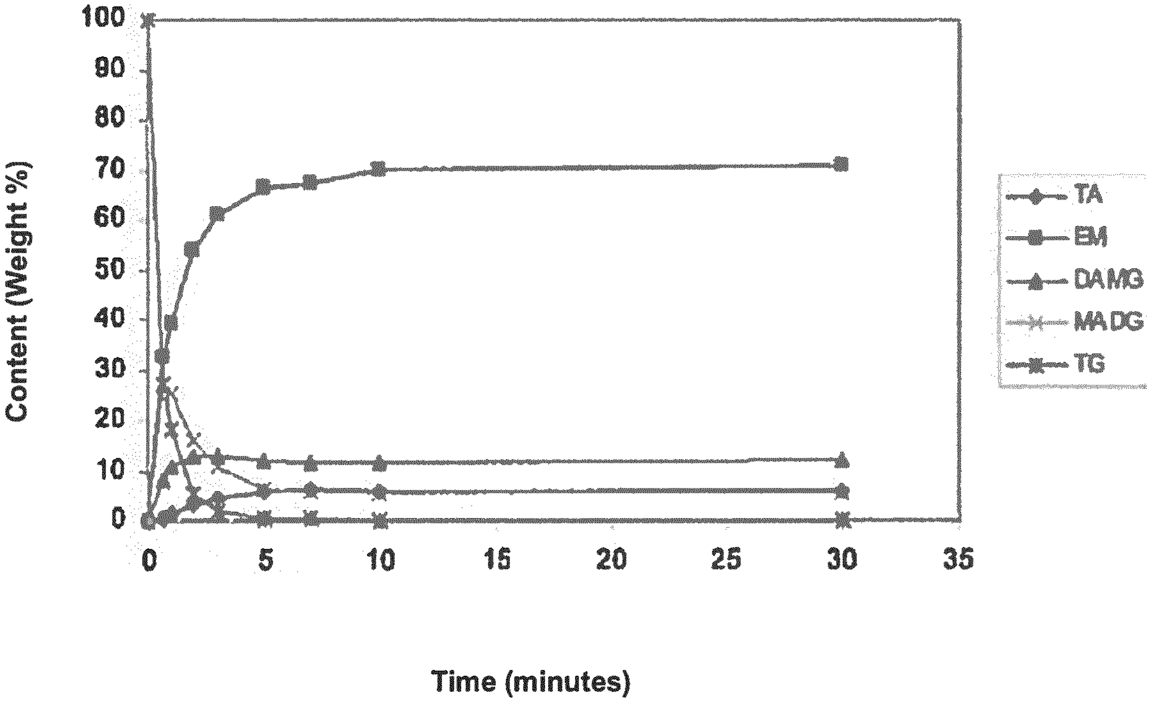


Figure 4

A.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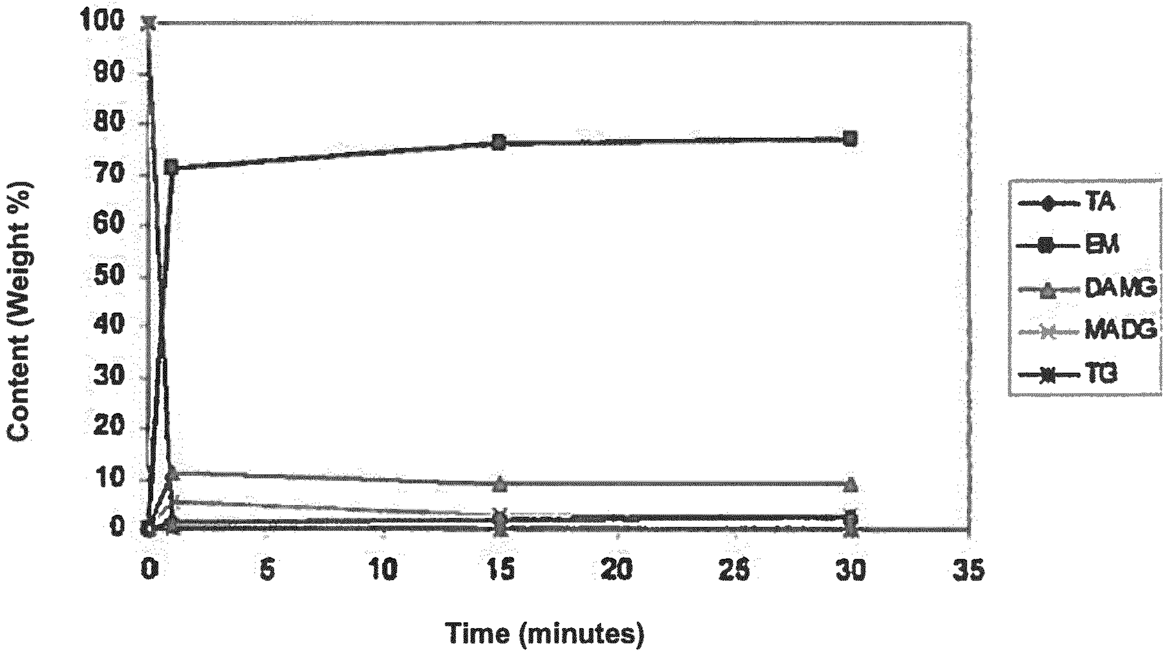
DAMG
MADG
TG

B.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Time (minutes)
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DAMG
MADG
TG

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/060720

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11C3/04 C11C3/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, BIOSIS, COMPENDEX, FSTA, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ABRAHAM CASAS ET AL: "Kinetics of chemical interesterification of sunflower oil with methyl acetate for biodiesel and triacetin production", CHEMICAL ENGINEERING JOURNAL, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 171, no. 3, 14 May 2011 (2011-05-14), pages 1324-1332, XP028098403, ISSN: 1385-8947, DOI: 10.1016/J.CEJ.2011.05.037 [retrieved on 2011-05-19] paragraphs [0001], [02.3], [02.4], [03.1]; figures 2-4 ----- -/--	1-12

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 6 January 2016	Date of mailing of the international search report 14/01/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Saettel, Damien

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/060720

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ABRAHAM CASAS ET AL: "Product Separation after Chemical Interesterification of Vegetable Oils with Methyl Acetate. Part I: Vapor-Liquid Equilibrium", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH., vol. 51, no. 23, 13 June 2012 (2012-06-13), pages 8087-8094, XP055238896, US ISSN: 0888-5885, DOI: 10.1021/ie3007903 paragraphs [02.2], [02.4] & Abraham Casas ET AL: "Effects of Triacetin on Biodiesel Quality", ENERGY & FUELS., vol. 24, no. 8, 19 August 2010 (2010-08-19), pages 4481-4489, XP055239000, WASHINGTON, DC, US. ISSN: 0887-0624, DOI: 10.1021/ef100406b paragraph [02.3] -----	1-12
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A	US 2010/223842 A1 (THESZ JANOS [HU] ET AL) 9 September 2010 (2010-09-09) paragraph [0046]; claims 13,15,18,20; example 6 -----	1-12
A	EP 2 862 915 A1 (UNIV RIGAS TEHNISKA [LV]) 22 April 2015 (2015-04-22) claims; examples -----	1-12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/060720

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