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(56) Documents Cited:
**EP 2000522 A1** **EP 1580255 A1**
**WO 2010/053354 A2** **WO 2008/096187 A1**
**CN 101608131 A** **JP 2007277288 A**
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(54) Title of the Invention: **Biodiesel compositions**
Abstract Title: **Biodiesel compositions**

(57) The invention relates to multicomponent biodiesel compositions with advantageous properties such as low freezing point and the lack of a waste stream of glycerol, their use as fuels, and processes for their manufacture. The compositions contain: firstly an ester or esters $R^{l}$-C(O)O-R' having at least nine non-hydrogen atoms per molecule, wherein $R^{l}$ is H or an alkyl group containing one to seven carbon atoms, and $R^2$ is an alkyl group containing one to eight carbon atoms, wherein if $R^1$ is $C_1$-$C_2$ alkyl then $R^2$ is $C_5$-$C_8$; secondly a fatty ester or esters of formula $R^3$ -C(O)O-$R^4$ where $R^3$-C(O)- represents the acyl residue of $C_{10}$-$C_{24}$ fatty acids and -O-$R^4$ is the alkoxy group of an alcohol containing one to eight carbon atoms; and thirdly triesters of glycerol; wherein said alkyl groups $R^1$,$R^2$ and $R^4$ may optionally be linear branched or cyclic and may optionally contain one or more double bonds, and optionally one or more carbon atoms may replaced by oxygen atoms or bear on oxo substituent, wherein each of these three components is in a molar proportion of at least 5% of the mixture.

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# BIODIESEL COMPOSITIONS

## Field of the Invention

**[0001]** This invention relates to novel biodiesel compositions and processes for their manufacture from interesterification reactions between triglycerides such as vegetable oils, and an ester, or mixture of esters.

## Background to the Invention

**[0002]** Biodiesel is a term that is understood in the literature to refer to a fuel composition useful in diesel engines produced from processing of triglyceride oils. The triglyceride oils are typically vegetable oils obtainable from various plant species, but might also be obtained from other sources such as from algae or by microbial fermentation. They principally comprise triesters of glycerol with fatty acids of between 10 and 24 carbon atoms. Such fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, oleic, myristoleic, palmitoleic, sapienic, linoleic, linolenic, arachidonic and erucic acids. The triglyceride oils themselves are not well suited for use as fuels because their viscosities are too high. In the conventional process for the manufacture of biodiesel, the triglyceride is made to undergo a transesterification process with a lower alcohol, most usually methanol, and the biodiesel comprises the methyl esters of the fatty acid components from the triglycerides. These methyl esters have approximately one eighth the viscosity of the parent triglycerides and consequently are much more suited for use as a fuel. However there are several disadvantages associated with these fatty acid methyl esters and the processes to them:

(i) The process generates a waste stream of glycerol, which either must be disposed of, or some other use found for it. The glycerol is immiscible with the fatty acid ester so it cannot be combined in with the fuel as such. Handling of the waste glycerol is also hampered by its containing methanol and catalyst (typically alkali) from the transesterification reaction.

(ii) The glycerol component of the triglyceride represents about 5% of the available combustion energy, which is not passed on to the fuel with the conventional biodiesel.

(iii) The catalyst used for the transesterification is typically sodium hydroxide or sodium methoxide, and this must be completely removed

from the biodiesel before it can be used, else presumably incombustible sodium salts will otherwise remain and build up in the engine. Consequently an additional wash step (or steps) is needed for the biodiesel, which complicates the processing and makes the process more expensive to operate.

(iv) In order to drive the transesterification reaction sufficiently to completion, an excess of methanol (or other alcohol) must be used; typically use of around 6 equivalents of methanol is taught by the prior art for example in US Patent No.4164506 although stoichiometrically the reaction would only require 3 mole equivalents of methanol to break down one mole equivalent of triglyceride into three mole equivalents of fatty acid methyl ester. If insufficient methanol (or other alcohol) is used, for example 3 equivalents relative to the triglyceride, the equilibrium nature of the reaction means that there are partially cleaved glycerides remaining in the biodiesel, for example glycerol mono-fatty acid esters. These glycerol mono-fatty acid esters are liable to crystallise out from the biodiesel once it is cooled, clogging fuel lines and so making the composition unsuitable. Use of an excess of methanol (or other alcohol) means that the excess has to be removed before the biodiesel can be used. If methanol is left in the biodiesel, being highly volatile and flammable, it can result in the biodiesel having an unacceptable flash point. Removal of the excess methanol will typically require an extra processing step incurring additional expense, such a step would involve for example evaporation of the methanol by heating the biodiesel product under a partial vacuum.

(v) The conventional biodiesel compositions, especially the fatty acid methyl esters, are prone to freeze at low ambient temperatures, and this may limit their use in cold climates. For example a typical biodiesel composition might start to freeze around -5°C.

**[0003]** An alternative processing method to convert triglyceride oils into a biodiesel composition involves an interesterification reaction with a low molecular weight ester. Herein, the term interesterification is used to describe a reaction in which the alkoxy and acyl groups are interchanged between two or more reactants that have ester functionality. The interesterification reaction between a triglyceride and another ester molecule $R^1C(O)-OR^2$ is illustrated by the Scheme given below. It is already known that vegetable oils can be interesterified with low molecular weight esters. Thus in Y. Xu et al, *Biotechnol. Lett.*, **2003**,

*25*, 1239-41 it is shown that soybean oil with at least 6 equivalents, and at best 12 equivalents of methyl acetate and a 30wt% loading of a commercial enzyme Novozym 435 relative to the oil, gave a product they consider could be used as a biodiesel fuel. The same group in W. Du et al, *J. Mol. Catalysis B: Enzymatic*, **2004**, *30*, 125-129, comment that the enzyme could be reused 100 fold.

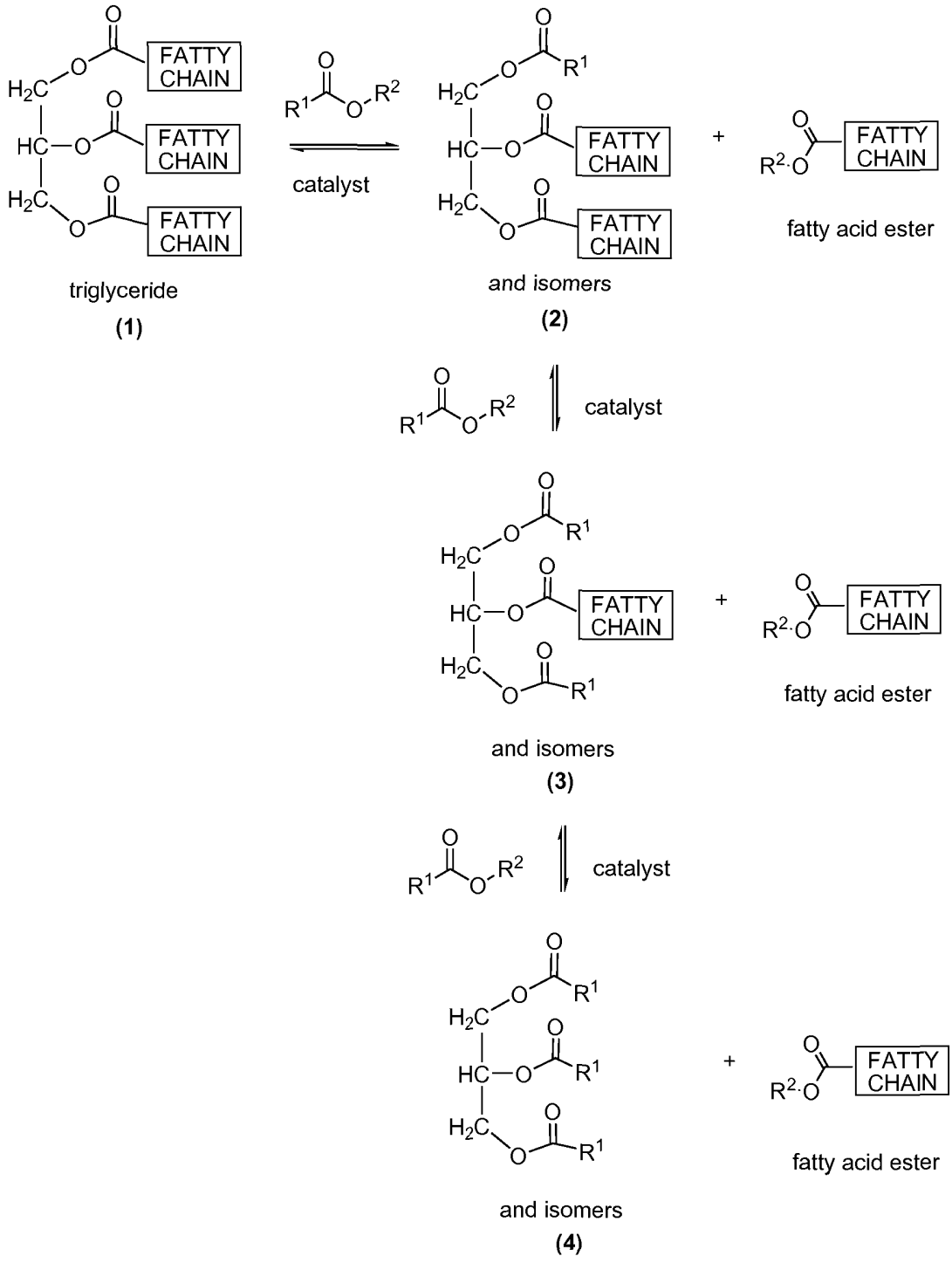
**[0004]** The interesterification reaction is an equilibrium between similar compounds, and in order to drive the reaction forward towards to the fatty acid methyl ester and triacetin (triacetylglycerol) in the case of using methyl acetate, a large excess amount of the low molecular weight ester is required. Thus a calculation would indicate that with 6 equivalents of methyl acetate, only two-thirds of the stoichiometric amount of fatty acid methyl ester might be formed. When using methyl acetate as an example of a low molecular weight ester, which is volatile and flammable, the excess must be removed from the biodiesel before it is used, for example by an evaporation step, in order for the resulting biodiesel composition to be safe to use. An alternative to the interesterification, for utilising the glycerol into the fuel, is to generate a similar resulting composition by mixing the fatty acid ester (i.e. conventional biodiesel) with a glycerol derivative. Thus in EP1331260, addition of triacetin to conventional transesterification is claimed to improve the low temperature properties. The same patent gives the example of a chemically catalysed reaction of sunflower oil with proportions that calculate as 11 equivalents of methanol and 5.9 equivalents of methyl acetate to provide a composition that incorporates glycerol into the composition.

**[0005]** Patent application EP 1580255 claims to describe biodiesel fuels from chemically acid-catalysed interesterification reactions between triglyceride oils and low molecular weight esters, particularly methyl acetate and ethyl acetate, in mole ratios in the range 3:1 to 9:1, with the excess low-molecular weight ester distilled off after the reaction.

**[0006]** In Du et al, US Patent 7473791, is described enzyme catalysed interesterification reactions between triglyceride oils and fats and low molecular weight esters in mole ratios ranging from 3:1 to 20:1 (preferably 4:1 to 14:1) and then cleavage of the obtained glycerol esters with an alcohol to regenerate the low molecular weight ester which is recycled. Preferred low molecular weight esters for this purpose are methyl acetate, ethyl acetate, methyl formate, ethyl formate, methyl propionate and combinations of those, and the examples include butyl propionate as the highest molecular weight ester tried.

**[0007]** In international patent application WO 2008/096187 are mixtures of glycerol esters with mixed short and fatty acyl chains together with fatty acid esters with short chain alcohols, obtained from interesterifications using a chemical catalyst. An example uses 2 equivalents of methyl acetate in the interesterification reaction, then distils the mixture under 5 mmHg vacuum to obtain a mixture of fatty acid methyl esters and diacetylated triglycerides having a kinematic viscosity at 40°C of 6.5 CSt. Their preferred esters are methyl and ethyl esters with carbon chains up to three carbon atoms in length.

**[0008]** It should be noted that whilst the prior art does not always describe the evaporation step of excess ester, the weight of biodiesel composition obtained means that such evaporation step (or other means to remove the excess ester) must have taken place. Such evaporation step will likely incur significant process complexity and cost. Then in order to facilitate such an evaporation step, it would be favourable to use a particularly volatile ester such as methyl acetate.




## Disclosure of the Invention

**[0009]** In this invention, the discovery is that through use of an interesterification reaction with an ester of medium molecular weight, a biodiesel composition useful as a fuel can be obtained with much simpler

processing than hitherto realised. The only processing necessary after the reaction is removal of the catalyst, although part of the excess ester can optionally be removed by evaporation. In this context the term "medium molecular weight ester" refers to an ester having a molecular weight of at least 126 grams per mole, which is the case if the ester has nine or more non-hydrogen atoms per molecule, to distinguish the esters used in this invention from the typically low molecular weight esters utilised in the prior art. With reference to the list given in the above Background of disadvantages associated with the conventional biodiesel synthesis, advantages of the biodiesel compositions of this invention are:

(i) There is no waste stream of glycerol; the glycerol is incorporated into the fuel composition, thereby all of the combustion energy available from the triglyceride oil is now transferred into the biodiesel composition.

(ii) An enzyme catalyst may optionally be used, which enables very simple removal from the biodiesel composition at the end of the interesterification reaction.

(iii) It is not necessary to use an excess of the ester relative to the fatty acids, indeed less than three equivalents of ester per equivalent of triglyceride molecules may optionally be used.

(iv) Through appropriate choice of ester, there is no need to remove unreacted ester at the conclusion of the interesterification reaction, indeed retaining the ester, or at least part of it, in the resulting biodiesel composition gives some advantageous properties.

(v) The resulting biodiesel compositions have lower freezing point than the conventional biodiesel (fatty acid methyl esters).

**[0010]** The principal embodiment of this invention concerns a biodiesel composition made from an interesterification reaction using a medium molecular weight ester, where all or some of the excess/unreacted ester is retained within the composition, so that this ester remains at a proportion of at least 5 mol% of the resulting composition. To our surprise the obtained biodiesel compositions possess favourable properties for use as diesel engine fuels, for example for automotive use. A particularly favourable property of the obtained composition is a low freezing point, lower than that of the corresponding fatty acid methyl ester, derived from the same triglyceride.

**[0011]** Within this principal embodiment, a preferred composition comprises 10-70 mol% of the medium molecular weight ester, 20-70 mol% of the fatty

acid esters resulting from the interesterification, and 10-60 mol% of glycerol triesters. A more preferred composition comprises 15-50 mol% of the medium molecular weight ester, 25-60 mol% of the fatty acid esters resulting from the interesterification, and 15-50 mol% of glycerol triesters. A still more preferred composition comprises 20-45 mol% of the medium molecular weight ester, 30-50 mol% of the fatty acid esters resulting from the interesterification, and 20-45 mol% of glycerol triesters.

**[0012]** Medium molecular weight esters applicable to the invention $R^1$-CO-O-$R^2$ have at least nine non-hydrogen atoms per molecule, and wherein $R^1$ is H or an alkyl group containing one to seven carbon atoms, and $R^2$ is an alkyl group containing one to eight carbon atoms, wherein the alkyl groups $R^1$ and $R^2$ may be linear, branched or cyclic, or a combination thereof, and in those alkyl groups there can optionally be one or more double bonds, and optionally one or more carbon atoms may be replaced by oxygen atoms or bear an oxo substituent. Especially suited to the invention are esters where the acyl group $R^1$-CO is selected from the group consisting of formyl, acetyl, propionyl, n-butyryl, isobutyryl, hexanoyl, 2-ethylhexanoyl, octanoyl, crotonyl, sorbyl, levulinyl and 2-tetrahydrofuryl, and where the alkyl group $R^2$ is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, 2-ethylhexyl, cyclohexyl, cyclohexylmethyl, crotyl and 2-tetrahydrofurfuryl.

**[0013]** Preferred esters for the purpose of this invention are ones that may be obtained from renewable resource materials. Thus n-butyric acid may be obtained by microbial fermentation and used to provide butyrate esters. Such alcohols as ethanol, n-butanol and isobutanol may likewise be obtained through fermentation methods and used to provide corresponding esters. n-Butanol can also be obtained by reduction of n-butyric acid obtained from fermentation methods, such as with hydrogen as described in US patent no. 199172, as can be the ester butyl butyrate directly, for example by the fermentation process with Chlostridium acetobutylicum as described in US patent no. 4487832. Likewise levulinic acid may be obtained from renewable source materials. Consequently, preferred esters for the purpose of this invention are esters of n-butyric acid and levulinic acid and in particular n-butyl n-butyrate and methyl or ethyl levulinate.

**[0014]** As an alternative to using a single ester, a mixture of esters may be used.

**[0015]** In a further embodiment of this invention, other compounds may be added in addition to the ester either before or after the interesterification reaction. Examples of such other compounds that may be added are alcohols for example as methanol, butanol or tetrahydrofurfuryl alcohol. In the case of adding an alcohol it is preferred that no more than 0.5 equivalents relative to the triglyceride oil is used. That is to limit the extent of formation of mono- or di-glycerides (glycerol mono-esters or di-esters) which might crystallise from the product if it is cooled. Other compounds added can include for example antioxidants or antimicrobial agents to improve stability, lubricants, or compounds to improve the low temperature flow properties.

**[0016]** In yet a further embodiment of this invention, an option is to use a greater excess of the medium molecular weight ester, and to evaporate off some but not all of the excess ester after the interesterification, so that there remains at least 5 mol% of that ester in the mixture. In doing so, one can combine the benefits to the composition retaining some content of medium molecular weight ester with the benefits of a greater extent of cleavage of the triglyceride, such as lower viscosity.

**[0017]** In yet a further embodiment of this invention, a composition equivalent to those produced by the interesterification reactions disclosed herein, may be generated by other means, such as by mixing together separately produced components being (i) one or more medium molecular weight ester, (ii) one or more fatty acid esters, and (iii) one or more glycerol triesters, or by mixing the third such component with a mixture that contains the other two. In particular a mixture of fatty acid esters and glycerol triesters produced by other means may be combined with a medium molecular weight ester such that the resulting composition contains at least 5 mol% of each of these three components. A preferred embodiment is to carry out an interesterification between a triglyceride oil and a low molecular weight ester such as methyl acetate with a catalyst, to remove the catalyst, to evaporate off the excess low molecular weight ester, and then to add one or more medium molecular weight esters so there is at least 5 mol% of the medium molecular weight ester within the resulting composition.

**[0018]** When an interesterification reaction is undertaken, it is generally made to take place using a catalyst. Any such catalysts known in the prior art for interesterification reactions may be used, for example a basic catalyst such as sodium methoxide or magnesium oxide, an acidic

catalyst such as an acidic ion exchange resin or para-toluenesulfonic acid, or an enzyme catalyst. For the purpose of this invention preferred catalysts are enzymes because they can be easily removed at the end of the interesterification, do not leave metal ions in the resulting composition, and will not affect the olefinic linkages in the fatty acid chains. Preferred enzymes for the purpose of this invention are either present in a microbial cell, isolated from the microbial cell, or immobilised on a support. Preferred enzymes for the purpose of this invention are those from the class of enzymes known as lipases. The interesterification is conducted so that a resulting composition can be obtained that has at least 5 mol% of a low or medium molecular weight ester, by means of any of the above embodiments of the invention. For this purpose it is preferred to use in the interesterification, a molar ratio of the low or medium molecular weight ester, to the triglyceride in the range of 1.0 - 12.0. More preferred is to use in the interesterification, a molar ratio of the low or medium molecular weight ester, to the triglyceride in the range of 1.5 - 6.0. Still more preferred is to use in the interesterification, a molar ratio of the low or medium molecular weight ester, to the triglyceride in the range of 2.0 - 4.0. The preferred molar ratio of the low or medium molecular weight ester, to the triglyceride will also depend upon the particular embodiment of this invention employed. Thus, when excess or unreacted ester is not removed after the interesterification reaction, it is preferred to use a molar ratio of less than or equal to 3.0. However, when any amount of ester is removed by evaporation after the interesterification it is preferred to use a molar ratio that is more than 3.0 in the interesterification, and then to remove excess ester to the extent that the resulting composition comprises a molar ratio of ester relative to the input triglyceride of less than or equal to 3.0.

## Practise of the Invention

**[0019]** The following examples illustrate aspects of the practise of the invention. In these examples a molecular weight of 885 was taken for the vegetable oils.

Example 1. Interesterification with 2 equivalents of butyl butyrate catalysed by an enzyme.

A mixture of rapeseed oil (food grade having a kinematic viscosity at 40°C of 39.5 CSt; 50 g, 56 mmol) and butyl butyrate (16.1 g, 112 mmol, 2 equivs) were mixed together and the kinematic viscosity at 40°C was measured as 11.5 CSt, and an open-cup flash point as 80°C, and a freezing

point at -9°C. Immobilised Candida antarctica lipase B (0.5g) was added, then the mixture was shaken in a closed bottle at 40°C. After 120 hours a sample had a kinematic viscosity at 40°C of 9.6 CSt, an open-cup flash point of 115°C, and freezing took place in the range of -10 to -17°C. The composition, estimated from gas chromatography analysis of the remaining butyl butyrate and formed fatty acid butyl ester, was 29 mol% butyl butyrate, 38 mol% fatty acid butyl ester and 33 mol% glycerol esters. In comparison fatty acid methyl ester prepared from the same rapeseed oil froze at -4°C.

Example 2. Interesterification with 2 equivalents of butyl butyrate catalysed by sodium methoxide.

A mixture of rapeseed oil (food grade; 147 g, 166 mmol) and butyl butyrate (47.9 g, 332 mmol, 2 equivs) was warmed and the mixture was shaken at intervals and portions of sodium methoxide totalling 1.06 g added during 4 hrs. After a day, the mixture was shaken with an aqueous solution of potassium dihydrogen phosphate, the phases allowed to separate, and the organic phase dried over anhydrous sodium sulfate and filtered to yield 186 g of a biodiesel with a kinematic viscosity at 40°C of 9.6 CSt and an open-cup flash point of 115°C was measured.

Example 3. Interesterification with 1.5 equivalents of butyl butyrate.

A mixture of rapeseed oil (food grade; 50 g, 56 mmol), butyl butyrate (12.1 g, 84 mmol, 1.5 equivs) and immobilised Candida antarctica lipase B (0.5g) was shaken in a closed bottle at 40°C. After 120 hours a sample had a kinematic viscosity at 40°C of 12.1 CSt.

Example 4. Interesterification with 2.5 equivalents of butyl butyrate.

Rapeseed oil (food grade; 50 g, 56 mmol) and butyl butyrate (20.1 g, 140 mmol, 2.5 equivs) were mixed together then immobilised Candida antarctica lipase B (0.5g) was added. The mixture was shaken in a closed bottle at 40°C. After 120 hours a sample had a kinematic viscosity at 40°C of 7.8 CSt.

Example 5. Interesterification with 3.0 equivalents of butyl butyrate.

Rapeseed oil (food grade; 25 g, 28 mmol) and butyl butyrate (12.1 g, 84 mmol, 3 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 44 hours a sample had a kinematic viscosity at 40°C of 6.9 CSt.

Example 6. Interesterification with 4.0 equivalents of butyl butyrate.

Rapeseed oil (food grade; 25 g, 28 mmol) and butyl butyrate (16.1 g, 112 mmol, 4 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 44 hours a sample had a kinematic viscosity at 40°C of 5.4 CSt.

Example 7. Interesterification with 6 equivalents of butyl butyrate catalysed by sodium methoxide and recovery of part of the butyl butyrate.

A mixture of rapeseed oil (food grade; 80 g, 90 mmol), butyl butyrate (78 g, 540 mmol, 6 equivs) and sodium methoxide (1.0 g) was warmed at 60°C and shaken at intervals. After 1h, further sodium methoxide (1.0 g) was added. After a further 1h, the mixture was shaken with an aqueous solution of potassium dihydrogen phosphate, the phases allowed to separate, and the organic phase dried over anhydrous sodium sulfate and filtered to yield 150g of a biodiesel with a kinematic viscosity at 40°C of 3.4 CSt, 144g of which was concentrated under reduced pressure at 70°C to give 33g of recovered butyl butyrate and 109g of a biodiesel with a kinematic viscosity at 40°C of 5.6 CSt and an open-cup flash point of 102°C was measured.

Example 8. Interesterification with 6 equivalents of methyl acetate, removal of unreacted methyl acetate and addition of butyl butyrate.

A mixture of rapeseed oil (food grade; 80 g, 90 mmol), methyl acetate (40.4 g, 545 mmol, 6 equivs) and sodium methoxide (2.0 g) was heated at reflux for 2 hours. Then the mixture was shaken with an aqueous solution of potassium dihydrogen phosphate, the phases allowed to separate, the organic phase dried over anhydrous sodium sulfate and concentrated under reduced pressure to obtain 83g of an oil of kinematic viscosity at 40°C of 7.8 CSt, and an estimated composition by weight by gas chromatography analysis of 67% fatty acid methyl esters and 2% triacetin, from which was

divided out four 15g portions. To these were mixed in butyl butyrate amounts of (a) 0.33g so as to represent 5mol% of the mixture giving a kinematic viscosity at 40°C of 6.9 CSt, (b) 0.70g so as to represent 10 mol% of the mixture giving a kinematic viscosity at 40°C of 6.45 CSt; (c) 1.58g so as to represent 20 mol% of the mixture giving a kinematic viscosity at 40°C of 5.87 CSt; (d) 2.71g so as to represent 30 mol% of the mixture giving a kinematic viscosity at 40°C of 5.00 CSt

Example 9. Interesterification of sunflower oil with 2 equivalents of butyl butyrate.

Sunflower oil (food grade; 25 g, 28 mmol) and butyl butyrate (8.06 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 113 hours a sample had a kinematic viscosity at 40°C of 8.9 CSt.

Example 10. Interesterification of soya bean oil with 2 equivalents of butyl butyrate.

Soya bean oil (food grade; 25 g, 28 mmol) and butyl butyrate (8.06 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 113.5 hours a sample had a kinematic viscosity at 40°C of 9.1 CSt.

Example 11. Interesterification of corn oil with 2 equivalents of butyl butyrate.

Corn oil (food grade; 25 g, 28 mmol) and butyl butyrate (8.06 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 113 hours a sample had a kinematic viscosity at 40°C of 9.0 CSt.

Example 12. Interesterification with butyl butyrate and tetrahydrofurfuryl alcohol.

Rapeseed oil (food grade; 25 g, 28 mmol), butyl butyrate (4.03 g, 28 mmol, 1 equiv) and tetrahydrofurfuryl alcohol (2.88g, 28 mmol, 1 equiv) were

mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 164 hours a sample was taken which was assayed and had a kinematic viscosity at 40°C of 9.6 CSt.

Example 13. Interesterification with butyl butyrate and methanol.

Rapeseed oil (food grade; 25 g, 28 mmol), butyl butyrate (8.06 g, 56 mmol, 2 equivs) and methanol (0.43g, 14 mmol, 0.5 equiv) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 22 hours a sample had a kinematic viscosity at 40°C of 9.0 CSt.

Example 14. Interesterification with butyl butyrate and tributyrin.

Rapeseed oil (food grade; 25 g, 28 mmol), butyl butyrate (8.06 g, 56 mmol, 2 equivs) and tributyrin (4.23g, 14 mmol, 0.5 equiv) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 22 hours a sample was had a kinematic viscosity at 40°C of 10.5 CSt.

Example 15. Interesterification with 2 equivalents butyl butyrate and 0.5 equivalents butanol.

Rapeseed oil (food grade; 25 g, 28 mmol), butyl butyrate (8.06 g, 56 mmol, 2 equivs) and n-butanol (1.04g, 14 mmol, 0.5 equiv) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 93 hours a sample had a kinematic viscosity at 40°C of 8.2 CSt.

Example 16. Interesterification with 1.5 equivalents butyl butyrate and 0.5 equivalents butanol.

Rapeseed oil (food grade; 25 g, 28 mmol), butyl butyrate (6.05 g, 42 mmol, 1.5 equivs) and n-butanol (1.04g, 14 mmol, 0.5 equiv) was mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 93 hours a sample had a kinematic viscosity at 40°C of 10.1 CSt.

Example 17. Interesterification with isobutyl isobutyrate.

Rapeseed oil (food grade; 25 g, 28 mmol) and isobutyl isobutyrate (8.06 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 69 hours a sample had a kinematic viscosity at 40°C of 10.5 CSt.

Example 18. Interesterification with 2-ethylhexyl butyrate.

Rapeseed oil (food grade; 25 g, 28 mmol) and 2-ethylhexyl butyrate (11.2 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 69 hours a sample had a kinematic viscosity at 40°C of 11.5 CSt.

Example 19. Interesterification with tetrahydrofurfuryl butyrate.

Rapeseed oil (food grade; 25 g, 28 mmol) and tetrahydrofurfuryl butyrate (9.63 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 69 hours a sample had a kinematic viscosity at 40°C of 13.4 CSt.

Example 20. Interesterification with ethyl levulinate.

Rapeseed oil (food grade; 25 g, 28 mmol) and ethyl levulinate (8.06 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 45 hours a sample had a kinematic viscosity at 40°C of 13.6 CSt.

Example 21. Interesterification with hexyl acetate.

Rapeseed oil (food grade; 25 g, 28 mmol) and hexyl acetate (8.06 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 114 hours a sample was taken which was assayed and had a kinematic viscosity at 40°C of 11.5 CSt.

Example 22. Interesterification with methyl 2-ethylhexanoate.

Rapeseed oil (food grade; 25 g, 28 mmol) and methyl 2-ethylhexanoate (8.79 g, 56 mmol, 2 equivs) were mixed together then immobilised Candida antarctica lipase B (0.25g) was added. The mixture was shaken in a closed bottle at 40°C. After 114 hours a sample was taken which was assayed and had a kinematic viscosity at 40°C of 12.6 CSt.

Example 23. Recycling of enzyme in the interesterification with butyl butyrate.

Rapeseed oil (food grade; 50 g, 56 mmol) and butyl butyrate (16.1 g, 112 mmol, 2 equivs) were mixed together. Immobilised Candida antarctica lipase B (0.5g) was added, then mixture was shaken in a closed bottle at 40°C. After 7 days a sample had a kinematic viscosity at 40°C of 10.1 CSt. The product was decanted from the immobilised enzyme, then 20ml fresh substrate added (substrate stock solution contained 250g of rapeseed oil and 81g butyl butyrate), and the mixture shaken at 40°C for 24 hours. This process was repeated for 11 cycles, decanting the product and replacing with 20ml fresh substrate. The kinematic viscosity after 2 enzyme cycles was 9.8, after 5 cycles was 9.9, after 8 cycles was 10.1 and after 11 cycles was 10.2.

## Claims

1. A composition comprising:

(i) one or more esters, which may be the same or different, of formula $R^1$-C(O)O-$R^2$

wherein

$R^1$ is H or $C_1$-$C_7$ alkyl,

$R^2$ is $C_1$-$C_8$ alkyl, and

$R^1$-C(O)O-$R^2$ represents at least nine non-hydrogen atoms;

with the proviso that if $R^1$ is H or $C_1$-$C_2$ alkyl, then $R^2$ is $C_5$-$C_8$ alkyl,

(ii) one or more fatty acid esters, which may be the same or different, of formula $R^3$-C(O)O-$R^4$

wherein

$R^3$C(O) represents the acyl residue of a $C_{10}$-$C_{24}$ fatty acid; and

$R^4$ is $C_1$-$C_8$ alkyl,

and

(iii) one or more triesters of glycerol, which may be the same or different of formula $CH_2$(O-C(O)$R^5$)-CH(O-C(O)$R^6$)-$CH_2$(O-C(O)$R^7$)

wherein $R^5$,$R^6$ and $R^7$ are each independently $R^1$ or $R^3$ as defined in (i) and (ii);

wherein

said alkyl groups are linear, branched or cyclic, or a combination thereof; and

optionally contain one or more double bonds;

and optionally, one or more carbon atoms may be replaced by oxygen atoms or bear an oxo substituent; and

components (i), (ii) and (iii) each total a molar proportion of at least 5% of the mixture.

2. A composition according to claim 1 wherein ester component(s)(i)represent 10 to 70 mole % of the mixture, the fatty acid ester components (ii)

represent 20 to 70 mol% of the mixture, and the glycerol triester components (iii) represent 10 to 60 mol% of the mixture.

**3.** A composition according to claim 2 wherein ester component(s) (i) represent 15 to 50 mole % of the mixture, the fatty acid ester components (ii) represent 25 to 60 mol% of the mixture, and the glycerol triester components (iii) represent 15 to 50 mol% of the mixture.

**4.** A composition according to claim 3 wherein ester component(s) (i) represent 20 to 45 mole % of the mixture, the fatty acid ester components (ii) represent 30 to 50 mol% of the mixture, and the glycerol triester components (iii) represent 20 to 45 mol% of the mixture.

**5.** A composition according to any one of Claims 1-4 wherein $R^1$-CO is selected from the group consisting of formyl, acetyl, propionyl, n-butyryl, isobutyryl, pentanoyl, hexanoyl, 2-ethylhexanoyl, octanoyl, crotonyl, sorbyl, levulinyl, and 2-tetrahydrofuroyl.

**6.** A composition according to claim 5 wherein $R^1$-CO- is n-butyryl.

**7.** A composition according to Claim 6 wherein $R^1$-CO-O-$R^2$ is n-butyl n-butyrate.

**8.** A composition according to claims 5 wherein $R^1$-CO- is levulinyl.

**9.** A composition according to claim 8 wherein $R^1$-CO-O-$R^2$ is methyl levulinate or ethyl levulinate.

**10.** A composition according to any of Claims 1-6 or 8 where $R^2$ and $R^4$ are each independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, 2-ethylhexyl, cyclohexyl, cyclohexylmethyl, crotyl and 2-tetrahydrofurfuryl.

**11.** A composition according to any one of Claims 1-10 wherein $R^2$ and $R^4$ are the same.

**12.** A composition according to any of the above claims where the triesters of glycerol comprise (a) esters of glycerol having three fatty acyl residues, (b) esters of glycerol having two fatty acyl residues and one shorter chain acyl residue, (c) esters or glycerol having one fatty acyl residue and two shorter chain acyl residues, and optionally (d) esters of glycerol having three shorter chain acyl residues.

**13.** A composition according to any of the above claims that additionally comprises any of (i) an alcohol having up to 8 carbon atoms in a molar amount that is not more than half of the amount of triglyceride used, (ii) an antioxidant, (iii) a lubricant, or (iv) a cold flow additive.

**14.** A composition according to any of the above claims that additionally contains a catalyst for ester exchange reactions.

**15.** A composition according to Claim 14 where that catalyst is an enzyme.

**16.** A composition according to any of Claims 1-15 that is an automotive fuel composition.

**17.** A diesel fuel composition comprising:

(i) one or more esters, which may be the same or different, of formula $R^1$-C(O)O-$R^2$

wherein

$R^1$ is H or $C_1$-$C_7$ alkyl, and

$R^2$ is $C_1$-$C_8$ alkyl,

(ii) one or more fatty acid esters, which may be the same or different, of formula $R^3$-C(O)O-$R^4$

wherein

$R^3$C(O) represents the acyl residue of a $C_{10}$-$C_{24}$ fatty acid; and

$R^4$ is $C_1$-$C_8$ alkyl,

and

(iii) one or more triesters of glycerol, which may be the same or different of formula $CH_2$(O-C(O)$R^5$)-CH(O-C(O)$R^6$)-$CH_2$(O-C(O)$R^7$)

wherein $R^5$,$R^6$ and $R^7$ are each independently $R^1$ or $R^3$ as defined in (i) and (ii);

wherein

said alkyl groups are linear, branched or cyclic, or a combination thereof; and

optionally contain one or more double bonds;

and optionally, one or more carbon atoms may be replaced by oxygen atoms or bear an oxo substituent; and

components (i), (ii) and (iii) each total a molar proportion of at least 5% of the mixture.

**18.** A diesel fuel composition according to Claim 17 wherein the formula of the ester $R^1$-C(O)-O$R^2$ represents at least nine non-hydrogen atoms.

**19.** A diesel fuel composition according to Claim 18 wherein if $R^1$ is H or $C_1$-$C_2$ alkyl, then $R^2$ is $C_5$-$C_8$ alkyl.

**20.** A diesel fuel composition according to any of Claims 17-19 wherein ester components (i) represent 10 to 70 mole % of the mixture, the fatty acid ester components (ii) represent 20 to 70 mol% of the mixture, and the glycerol triester components (iii) represent 10 to 60 mol% of the mixture.

**21.** A diesel fuel composition according to any of Claims 17-19 wherein ester components (i) represent 15 to 50 mole % of the mixture, the fatty acid ester components (ii) represent 25 to 60 mol% of the mixture, and the glycerol triester components (iii) represent 15 to 50 mol% of the mixture.

**22.** A diesel fuel composition according to any of Claims 17-19 wherein ester components (i) represent 20 to 45 mole % of the mixture, the fatty acid ester components (ii) represent 30 to 50 mol% of the mixture, and the glycerol triester components (iii) represent 20 to 45 mol% of the mixture.

**23.** A composition according to any of the above claims where the triglyceride is or has been obtained from plant seeds or other parts of plants, algae, or a microbial fermentation.

**24.** Use of a composition according to any of Claims 1-16 or 23 as a fuel.

**25.** Use of a composition according to any of Claims 1-23 in a diesel engine for an automotive or electricity generation purpose.

**26.** A process for the manufacture of a composition according to any of claims 1-23 wherein a mixture of a triglyceride oil composed of esters between glycerol and fatty acids of between 10 and 24 carbon atoms, and one or more esters of formula $R^1$-CO(O)-$R^2$, wherein $R^1$ is H or an alkyl group containing one to seven carbon atoms, and $R^2$ is an alkyl group containing one to eight carbon atoms, wherein the alkyl groups $R^1$ and $R^2$ may be linear, branched or cyclic and optionally contain one or more double bonds; and optionally, one or more carbon atoms may be replaced by oxygen atoms or bear on oxo substituent;
is made to undergo an ester exchange reaction by means of an added catalyst, then either (i) any excess ester $R^1$-CO(O)-$R^2$ is not removed from the mixture, or (ii) some excess ester $R^1$-CO(O)-$R^2$ is removed so that the resulting composition still comprises at least 5 mol% of one or more of such esters, or (iii) some or all of the excess ester $R^1$-CO(O)-$R^2$ is removed from the mixture but is replaced by adding one or more esters $R^1$-CO(O)-$R^2$ so that the resulting composition comprises at least 5 mol% of one or more of such esters.

**27.** A process according to Claim 26, which further comprises the addition of one or more components selected from (i) an alcohol having up to 8 carbon atoms in a molar amount that is not more than half of the amount of triglyceride used, (ii) an antioxidant, (iii) a lubricant, or (iv) a cold flow additive.

**28.** A process according to any of Claims 26-27 where the molar ratio of the ester $R^1$-CO-O-$R^2$ used to the triglyceride in the ester exchange reaction is in the range of 1.0 - 12.0.

**29.** A process according to Claim 28 where the molar ratio of the ester $R^1$-CO-O-$R^2$ used to the triglyceride in the ester exchange reaction is in the range of 1.5 - 6.0.

**30.** A process according to Claim 29 where the molar ratio of the ester $R^1$-CO-O-$R^2$ used to the triglyceride in the ester exchange reaction is in the range of 2.0 - 4.0.

**31.** A process according to any of Claims 28-30 wherein the molar ratio of the ester $R^1$-CO-O-$R^2$ used to the triglyceride in the ester exchange reaction is less than or equal to 3.0 and excess ester is not removed afterwards.

**32.** A process according to any of Claims 28-30 where the molar ratio of the ester $R^1$-CO-O-$R^2$ used to the triglyceride in the ester exchange reaction is more than 3.0 but some of the excess ester is removed by an evaporation step such that the elements of the ester incorporated into the resulting composition represent a molar ratio of less than or equal to 3.0 relative to the input triglyceride

**33.** A process according to any of claims 26-32 where ester $R^1$-C(O)-O$R^2$ remains present at least at 10mol% of the resulting composition.

**34.** A process according to any of Claims 26-33 where $R^1$-CO- is n-butyryl.

**35.** A process according to Claim 34 where the ester is n-butyl n-butyrate.

**36.** A process according to any of claims 26-35 where the catalyst is an enzyme.

**37.** A process according to Claim 36 where the enzyme is of the class known as a lipase.

**38.** A process according to Claim 36 or 37 where the enzyme is present in a microbial cell, is isolated from the microbial cell, or is immobilised on a support.

**39.** A process for the manufacture of a composition of Claim 1 where components of:

(i) one or more esters of formula $R^1$-CO-O-$R^2$ as defined in Claim 1;

(ii) one or more fatty esters of formula $R^3$-CO-O-$R^4$ as defined in Claim 1; and

(iii) one or more triesters of glycerol of formula $CH_2$(O-C(O)$R^5$)-CH(O-C(O)$R^6$)-$CH_2$(O-C(O)$R^7$)as defined in Claim 1,

are mixed together, or the third such component is added to a mixture containing the other two, wherein components (i),(ii) and (iii) are each to become in the proportions of 5-90 mol% of the resulting mixture.

**40.** A process according to Claim 39 where the components (i),(ii) and (iii) are to become in the proportions of 10-70 mol%, 20-70 mol% and 10-60 mol% of the resulting mixture respectively.

**41.** A process according to Claim 40 where the components (i),(ii) and (iii) are to become in the proportions of 15-50 mol%, 25-60 mol% and 15-50 mol% of the resulting mixture respectively.

**42.** A process according to Claim 41 where the components (i),(ii) and (iii) are to become in the proportions of 20-45 mol%, 30-50 mol% and 20-45 mol% of the resulting mixture respectively.

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|---|---|---|---|
| **Application No:** | GB1003203.5 | **Examiner:** | Mr Martin Price |
| **Claims searched:** | 1-42 | **Date of search:** | 24 June 2010 |

## Patents Act 1977: Search Report under Section 17

**Documents considered to be relevant:**

| Category | Relevant to claims | Identity of document and passage or figure of particular relevance |
|---|---|---|
| X | 1 at least | WO 2008/096187 A1<br>Thesz - see e.g. claim 1, examples 1-7 and page 6 |
| X | 1 at least | US 2006/0257986 A1<br>Du - see e.g. claim 1 and the examples, especially examples 9, 19, 20 |
| X | 1 at least | EP 1580255 A1<br>Instytut Chemii - see e.g. claim 1 and the examples |
| X | 1 at least | EP 2000522 A1<br>Petrobras - see e.g. example 2 |
| X,E | 1 at least | WO 2010/053354 A2<br>Criss Cross - see e.g. example 4 |
| X | 1 at least | CN 101608131 A<br>Univ East China - see WPI abstract number 2010-A27170 |
| X | 1 at least | JP 2007277288 A<br>Nippon BDF - see WPI abstract number 2008-A89347 |

Categories:

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| X | Document indicating lack of novelty or inventive step | A | Document indicating technological background and/or state of the art. |
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| & | Member of the same patent family | E | Patent document published on or after, but with priority date earlier than, the filing date of this application. |

**Field of Search:**

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC$^{X}$ :

Worldwide search of patent documents classified in the following areas of the IPC

C10L; C11C

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI

**International Classification:**

| Subclass | Subgroup | Valid From |
|---|---|---|
| C11C | 0003/10 | 01/01/2006 |
| C10L | 0001/02 | 01/01/2006 |