(19) NL Octrooicentrum (11) 1036154

(12)C OCTROOI

(21) Aanvraagnummer: **1036154**

(22) Aanvraag ingediend: **05.11.2008**

(51) Int.Cl.:
C07C 41/14 (2006.01) ***C07C 67/02*** (2006.01)
C07C 67/03 (2006.01) ***C10L 1/02*** (2006.01)
C10L 1/185 (2006.01) ***C10L 1/19*** (2006.01)
C10L 10/02 (2006.01) ***C10L 10/10*** (2006.01)
C11C 3/00 (2006.01) ***C11C 3/10*** (2006.01)

(43) Aanvraag gepubliceerd:
-

(47) Octrooi verleend:
06.05.2010

(45) Octrooischrift uitgegeven:
12.05.2010

(73) Octrooihouder(s):
Criss Cross Technology B.V. te Haarzuilens.

(72) Uitvinder(s):
Hendrik Adriaan Cornelis Groeneveld te Haarzuilens.

(74) Gemachtigde:
Drs. O. Griebling te Tilburg.

(54) **A motor fuel additive with enhanced properties, and processes for the production thereof.**

(57) The invention relates to motor fuel additives with enhanced properties. More specifically, the present additives improve the total fuel efficiency, and reduce the soot reduction of a motor fuel. The additives are based on at least partially esterified and/or partially etherified di- or polyhydroxy hydrocarbon compounds. In a gasoline/ethanol mixture, the addive acts as a co-solvent. Further, the present additives act as octane number improving composition. Processes for the production of the present additives are also described.

NL C 1036154

Title: A motor fuel additive with enhanced properties, and processes for the production thereof.

Background

The use of biofuel components as such or as admixture in fossil fuels is an ongoing hot topic.

A recent snapshot is that the classic routes using renewable resources at the cost of edible crops production will cause delays in developing the biodiesel potential. At the same time the efficiency of reducing CO_2-emissions is doubted and feedstock like rapeseed oil, palm oil etc. are derogatorily treated as first generation options without a clear definition of what is meant and how to improve on the overall efficiency, ecology and economy of the production and application chain.

Used vegetable oils and fats are also being considered as very attractive feedstocks for the production of biodiesel due to their lower market value compared to virgin oils and their fact of being recycled materials from other industrial sectors. The processing of the oil often requires a reduction of the high FFA content via acid catalysed esterification before the actual raw material can be transesterified to biodiesel (see R. Luque et al, Energy Environ. Sci.,, 2008, Biofuels: a technological perspective (DOI: 10.1039/b807094f)).

To meet the present new clean air standards, a high quality diesel fuel is required, which can improve the overall fuel efficiency, and reduces the soot generation.

Reduction of particulate matter by means of, for example, ether derivatives of glycerol, is claimed in US 5.308.365.

The production of biodiesel fuels with improved properties at low temperature is known from EP-A-1.331.260. This reference discloses, more specifically, a freezing point

lowering effect of a mixture of methyl esters of fatty acids, such as sunflower oil and soya oil, and glycerine (di- or tri)acetate (also called diacetin and triacetin respectively) in mixtures with diesel fuels of fossil origin. It is further suggested that methyl acetate possibly reacts with fatty acid triglyceride esters, to produce glycerol acetyl esters and fatty acid esters according to a transesterification reaction, at a higher rate than methanol to generate glycerine acetate and methyl esters of the fatty acids. The production process is, according to this reference, effected with a large excess of methanol and of methyl acetate.

EP 1.331.260 thus relates to mixtures of biodiesel and diesel fuel compositions based on fossil components, to which said glycerine triacetate has been added.

It has, nevertheless, been found by applicant that the biodiesel component in such mixtures is necessary to obviate the phase separation observed between triacetin and diesel of fossil origin, and must be present in quite large amounts; the biodiesel component thus acts in such mixtures as a compatabilizer.

Applicant now found an additive which, when used in small amounts in a diesel fuel of fossil origin, acts as a plasticizer, and therefore obviates the necessary presence of biodiesel, as disclosed in EP 1.331.260.

Although applicant does not want to be bound by any theory, it is assumed that the additive according to the invention has the effect that the intramolecular distance of the different fuel components is enlarged. Such an effect could explain the remarkable fuel efficiency improvement, seen when added to different diesel formulations, also when the additive was added in a small proportion.

The additive according to the invention has a further benificial effect, in that it also reduces the soot generation of diesel fuel, while the produced soot particles it-self are larger than the soot particles produced in the absence of the

additive according to the invention. It thus reduces the amount of fine dust, produced along with the combustion of diesel fuel, considerably.

The additive according to the invention is further based on the use of oils of vegetable or animal origin, including waste materials consisting of such oils. The invention is nevertheless not restricted to such oils.

Description of the invention.

Whilst businesswise we saw ample scope in using waste materials (used cooking oils etc.) we also did find out that there are ample opportunities to improve on conversion processes (i.e. routes to convert the oils into biodiesel components) and the use of products in a way that the product characteristics are tuned to achieve enhanced fuels based on reducing CO_2-emissions, soot repression and fuel economy as well as compatibility with other (fossil) fuels.

This approach brought us novel ideas and novel combinations in this field, dealing with the best use of the oil in terms of overall yield and performance based on a combination of properties. In this context fossil fuels are not treated as the adversary, but as a useful partner for mixed fuels in the gradual transition to a more sustainable future.

It is in this context that fossil ethers and esters as reactive components with the oils, the use of novel catalysts for process intensification, reactive destillation/extraction principles and product mixture optimization were put to work. As a result we have achieved much enhanced efficiency, much lower costs, better logistics and improved contributions to fuel efficiency and soot suppression.

Whilst the political debate goes on with regard to the introduction of biofuels, air quality standards etc. we are confident that the novel feedstock/process/application

combinations we set out below can make a considerable contribution by providing feasible options.

Although most of the benefits of oxygenated compounds to be added to diesel fuel mixtures are known, we have discovered that some classes of these compounds show a most remarkable fuel efficiency improvement even in those cases where the components were added in a small proportion, either in combination with Biodiesel (FAME type of products) or added to diesel formulations purely based on fossil components.

The invention thus relates, in a first aspect, to an additive for a motor fuel for the improvement of the total combustion efficiency of the motor fuel, selected from oxygenated compounds, obtainable by the at least partial esterification and/or etherification of di- and poly-hydroxy hydrocarbon compounds. The additive contains preferably a mixture of such esters and/or ethers.

It is observed that said hydrocarbon compounds comprise biogenic as well as fossil compounds, which are preferably derived from waste or used materials, such as vegetable oils or animal fats.

It has been found that oxygenated compounds derived from di- and polyhydroxy compounds, being esterified or etherified (at least partially) to their corresponding esters and/or ethers have the effect of improving the overall fuel efficiency as tested under realistic conditions by a value of some 10%. Thus a 2% addition of an additive according to the invention, with a lower energy content than the fuel itself, does improve energy to this level of 10%, which is based on an average of 7 - 13%.

The invention relates, in a second aspect, to an additive for a motor fuel for the reduction of soot emission at combustion, selected from oxygenated compounds, obtainable by the at least partial etherification and/or esterification of di- and polyhydroxy hydrocarbon compounds. The additive could contain a mixture of such esters and/or ethers. It is

observed, that for reduction of the soot emission, the oxygenated compounds will, preferably, not contain any non-derivatised OH-groups.

It has been found that the present esters, or ethers, of said oxygenated compounds reduce soot generation by more than 25%, whilst the amount of the smaller soot particles (the so-called fine dust particles) was reduced by 80% or more. As the latter exhibits a very high health risk, and the larger particles can easily be removed by relatively simple filters, a very realistic solution is provided for air pollution problems related to all kinds of car engines.

The di- or polyhydroxy hydrocarbon compound, which is part of the present additive, is preferably selected from ethylene glycol, diethylene glycol, glycerol, diglycerol, pentaerythritol, sugars such as tetroses, pentoses, hexoses, for example glucose, fructose, xylose, mannose; sorbitol, and mannitol, and the like. Said di- or polyhydroxy hydrocarbon compound can, of course, be obtained from a "green", renewable, feedstock.

The additive according to the invention consists preferably of a di- or polyhydroxy hydrocarbon compound, which is at least partially esterified with a straight or branched C_1 - C_5 alkyl carboxylic acid. Said carboxylic acid is preferably selected from formic acid, acetic acid, propionic acid, and (iso-)butyric acid. This list must nevertheless not deemed to be exhaustive; other carboxylic acids can be used as well.

The additive according to the invention is preferably selected from the group, consisting of the mono-, di-, and triacetylesters of glycerol, the acetyl esters of sorbitol, and of diethylene glycol, and any mixture of these compounds, preferably diacetin, triacetin, mono-acetyl isosorbide and diacetyl isosorbide, or any mixture of these compounds.

Testing these isosorbide esters as fuel additives confirmed our observations as made with the glycerol esters.

An energy efficiency improvement of 10%, and a soot emission reduction of over 25% were achieved.

We have also found that ethers from glycerol have similar properties, although the fuel efficiency is not so much improved. Therefore, combinations of ether and ester functionality still have a good fuel performance. This was confirmed in engine tests. The additive according to the invention thus also consists of a di- or polyhydroxy hydrocarbon compound, which is at least partially etherified with tert.butyl- or tert.amyl groups.

The motor fuel composition utilized in the present invention, generally consists of hydrocarbons which fall within the diesel fuel boiling range, typically from about 160^0 C to about 370^0 C. These fuels are often referred to as middle distillate fuels since they comprise the fractions which distill after gasoline.

In another embodiment of the invention, the motor fuel composition consists of a gasoline/ethanol mixture. The additive of the invention, which will still contain remaining OH-functionality, will, when used in a gasoline/ethanol mixture, improve the fuel efficiency of such a mixture, if added in a certain amount. Such a motor fuel composition contains an ethanol phase, which may contain from 1 to 7% of water, for example 4% of water, which will allow the use of an ethanol/water azeotropic mixture in gasoline. It is assumed that the presence of the additive according to the invention has a favourable influence on the mutual miscibility of the gasoline phase and the ethanol phase. It is well known that, upon contact with humid air, a gasoline/ethanol mixture usually takes up more water, resulting into undesirable phase separation. Because the additive according to the invention acts as a co-solvent, phase separation of a gasoline/ethanol mixture due to the presence of water can be prevented, or reduced.

The amount of the additive added to a gasoline formulation is generally from about 1 to 10 vol.%, preferably from about 2 to 3 vol.%.

It has also been found that the additives of the invention are octane number improving agents.

The invention further relates to a process for the preparation of an additive, as mentioned above, wherein a fatty acid triglyceride having formula $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, wherein R_1, R_2, and R_3 each independently represent a straight or branched, $C_5 - C_{30}$ alkyl carboxylic group, is reacted with a stoichiometric excess of a lower alkyl ester of a lower carboxylic acid, preferably a $C_1 - C_5$ alkyl acetate, more preferably methyl acetate or ethyl acetate, in the presence of a catalyst, to obtain said additive as a mixture of glyceryl carboxylic esters, preferably glyceryl acetate esters, and $C_1 - C_5$ alkyl esters of $C_5 - C_{30}$ fatty acids, preferably methyl or ethyl esters of $C_5 - C_{30}$ fatty acids.

A special embodiment of such a mixture consists of FAME (fatty acid methyl esters) and triacetin, which mixture can for example be produced starting from some used vegetable oil. We found that the production of FAME and triacetin can be combined into one step, whithout the intermediate glycerol formation. To that extent, e.g. methyl acetate, is reacted with the triglyceride oil, using a basic catalyst such as potassium methanolate, or a solid or liquid acid catalyst such as PTSA or H_2SO_4. The solid acid catalyst is preferably selected from the group, consisting of a zeolite, preferably H-ZSM-5, Y and Beta; and a mixed metal oxide, preferably sulphated zirconia. An enzymatic catalyst can also be used in this reaction. The reaction rates appeared to be higher than normal due to the solvency of the excess of methyl acetate. Also a heterogeneous catalyst such as an acid ion exchanger, such as Amberlyst-15, does result in good conversions, yielding a product that, depending on the excess of methyl

acetate, approaches the composition of a diesel plus mix, which can also be produced according to the two-step process to be discussed hereafter.

The above-mentioned reaction is preferably executed with a molar ratio of 1 - 10 moles of C_1 - C_5 alkyl acetate, preferably methyl acetate, to 1 mole of fatty acid triglyceride, preferably from 4 - 8 moles of methyl acetate to 1 mole of fatty acid triglyceride; we found more particularly that using a molar ratio of from about 6 moles of methyl acetate to 1 mole of triglycerides yields a product that will meet the requirements set for additives for a diesel fuel.

When preparing biodiesel, a typical route for transesterification is one that is catalysed by, for example, potassium methanolate, in a 2-step process.

More specifically relates the invention, in such an embodiment, to a process for the preparation of an additive, as disclosed above, wherein a fatty acid triglyceride of formula $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, wherein R_1, R_2, and R_3 each independently represent a straight or branched C_5 - C_{30} alkyl carboxylic group, is reacted with a C_1 - C_5 alkanol, preferably methanol, in the presence of a catalyst, preferably potassium methanolate, to obtain a 2-phase mixture, consisting of a glycerol containing, aqueous phase, and a C_1 - C_5 alkyl esters of C_5 - C_{30} fatty acids containing phase; the 2-phase mixture is, if desired, dried; and the glycerol containing phase is reacted with a C_1 - C_5 alkyl acetate, preferably methyl acetate or ethyl acetate, to produce a glycerol acetyl esters containing phase and an alkanol, preferably ethanol, containing phase, which, if desired, is subjected to phase separation; the phases thus obtained are purified according to a process known as such; to obtain an additive for a motor fuel composition.

In a preferred embodiment, said reaction is executed with a stoichiometrically insufficient amount of C_1 - C_5 alkanol,

preferably methanol. Said mixture is expediently dried by azeotropic distillation.

It is observed that it is known from EP 1.331.260 to prepare a mixture of glycerin acetate an and methyl esters of sunflower, by heating a mixture of sunflower oil, methanol and methyl acetate, in the presence of NaOH. More specifically, large excesses of methanol and of methyl acetate are used in this known process, to obtain a completely esterified product, i.e. the methyl esters of sunflower oil.

According to the process of the invention, nevertheless, a criss-cross reaction is effected with only an ester, and some (small amount of) methanol, which results in a mixture of products, which will dissolve better in a diesel fuel composition of fossil origin, than the mixture according to EP 1.331.260.

Similar to the above, etherification can be made part of the process of the invention: in that case, a catalyst switch will be necessary (neutralising KOH, etc.) and preferably an acid catalyst, e.g. Amberlyst-15, is applied in order to obtain glycerol ethers and glycerol ethers/esters.

Similar to the above, a criss-cross etherification can be carried out using MTBE (methyl tert.butyl ether) or methyl tert.amylether as agent, to produce a product mix that will contain GTBE (glyceryl tert.butyl ether)-type or GTAE (glyceryl tert.amyl ether)-type of components, along with FAME and intermediate products.

In a preferred embodiment of the invention, it is thus possible to convert the glycerol moiety of the natural (waste) oils into a mixture of glycerol ethers, by using ethers (such as MTBE, or ETBE, but not limited to these) instead of alkanols. The use of MTBE (which is amply available and more easily to handle than isobutylene as etherifying component) obviates the production of glycerol as a low-priced unpure bulk product, but produces an additional mass a suitable diesel components.

Such an embodiment comprises that a fatty acid triglyceride of formula $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, wherein R_1, R_2, and R_3 each independently, represent a straight or branched, $C_5 - C_{30}$ alkyl carboxylic group, is reacted with a stoichiometric insufficient amount of a $C_1 - C_5$ alkyl ether, preferably MTBE or ETBE, in the presence of a catalyst, to obtain an additive as a mixture of glyceryl ethers and $C_1 - C_5$ alkyl esters of $C_5 - C_{30}$ fatty acids. This reaction is expediently executed in the presence of a heterogeneous catalyst, such as an acid ion exchanger, preferably Amberlyst-15.

The above embodiment is a one-step process. It is nevertheless also possible to effect the aimed process in two steps. In that case, the additive according to the invention is prepared in that a fatty acid triglyceride of formula $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, wherein R_1, R_2, and R_3 each independently represent a branched or straight, $C_5 - C_{30}$ alkyl carboxylic group, is reacted with a lower alkanol, preferably a $C_1 - C_5$ alkanol, especially methanol, in the presence of a catalyst, preferably a basic catalyst, especially KOH, to obtain a 2-phasic mixture, consisting of a glycerol and alkali containing phase, on the one hand; and a $C_1 - C_5$ alkyl esters of $C_5 - C_{30}$ fatty acids containing phase, on the other hand. The 2 phases are thereafter separated and, if desired, dried. The glycerol containing phase is neutralised, and is thereafter reacted with a $C_1 - C_5$ alkyl ether, preferably methyl tert.butyl ether (MTBE), or methyl tert. amyl ether (MTAE), in the presence of an acid catalyst, such as an acid ion exchanger, preferably Amberlyst-15, to obtain an alkyl ether containing fraction, preferably a glyceryl tert.butyl ether or glyceryl tert.amyl ether containing fraction. The thus obtained phases are, if desired, purified according to a process known as such, and, if desired, mixed together, to obtain the additive of the invention as a mixture of $C_1 - C_5$ alkyl esters of $C_5 - C_{30}$ fatty acids and $C_1 - C_5$ alkyl ethers of

glycerol. The mixture will preferably contain glyceryl t.butyl ethers(GTBE) and glyceryl t.amyl ethers(GTAE).

As indicated above, GTBE and GTAE also act as plastizisers in a motor fuel composition of fossil origin, but in a lesser degree than the abovementioned esters, and thus also effect the improvement of the fuel efficiency. The present ether derivatives can, in fact, be regarded as pour points depressants when used in a motor fuel composition.

It will be obvious that glycerol, being a polyhydroxy hydrocarbon compound, can be replaced by other polyhydroxy compounds, such as diethylene glycol, ethylene glycol, diglycerol, pentaerythritol, and sugars such as tetroses, pentoses, hexoses, preferably glucose, fructose, xylose, sorbitol, and mannitol, to mention some from a non-exhaustive list, which will show the same favourable final result.

It is observed that the use of esters, like methylacetate, ethylacetate etc., and ethers like MTBE and MTAE do provide various options for azeotropic drying, and thus improve phase separation, enhancing the rate of reaction, reactive distillation, etc.

These types of process variants, as they are related to the product classes claimed in this invention, are part of the invention.

The invention is further explained in the following example.

Example 1.

A testrun was executed with a standard diesel engine. The fuel savings were measured at an electronically controlled constant load in a testrun in the stationary phase.
In this motor test, 4% (v/v)normal biodiesel fuel (EN14214) and 1% (v/v) GTAE were added to normal standard fossil diesel fuel.

This mixture gave a soot reduction of about 25%, compared with the standard diesel fuel, without the additives.
The fuel savings were 13,8% and 9,7%.
Almost the same results were obtained when the normal biodiesel fuel was not added.

Example 2.

The same standard diesel engine, as used in example 1, was used for effecting a testrun for the determination of the effect on the soot production of a standard fossil diesel fuel composition, to which 2% (v/v) diacetin was added.
This mixture also gave a soot reduction of about 25%, while the amount of fine dust particles was reduced by 85%.

CONCLUSIES

1. Additief voor een motorbrandstof voor het verbeteren van het totale verbrandingsrendement van de motorbrandstof, gekozen uit geoxygeneerde verbindingen, verkrijgbaar door gedeeltelijke verestering en/of verethering van di- of polyhydroxy koolwaterstofverbindingen.

2. Additief voor een motorbrandstof voor het verminderen van de roetuitstoot bij verbranding, gekozen uit geoxygeneerde verbindingen, verkrijgbaar door tenminste gedeeltelijke verethering en/of verestering van di- of polyhydroxy koolwaterstofverbindingen.

3. Additief volgens conclusie 1 of 2, waarbij de di- of polyhydroxy koolwaterstofverbinding is gekozen uit de groep, bestaande uit ethyleenglycol, diethyleenglycol, glycerol, diglycerol, pentaerythritol, suikers, zoals tetrosen, pentosen, hexosen, bijvoorbeeld glucose, fructose, xylose, mannose, sorbitol en mannitol.

4. Additief volgens een of meer der conclusies 1 tot 3, bestaande uit met tenminste een, recht of vertakt, C_1-C_5 alkylcarbonzuur, tenminste gedeeltelijk veresterde, di- of polyhydroxy koolwaterstofverbinding.

5. Additief volgens conclusie 4, waarbij het C_1-C_5 alkylcarbonzuur is gekozen uit mierenzuur, azijnzuur, en propionzuur.

6. Additief volgens een of meer der conclusies 1 tot 3, bestaande uit een met tert.butyl- of tert.amylgroepen, tenminste gedeeltelijk veretherde di- of polyhydroxy koolwaterstofverbinding.

7. Additief volgens een of meer der conclusies 1 tot 5, gekozen uit de groep, bestaande uit de mono-, di-, en triacetylesters van glycerol, de acetylesters van sorbitol, en van diethyleenglycol, en enig mengsel van deze verbindingen, bij voorkeur diacetin, triacetin, mono-acetyl isosorbide, en diacetyl isosorbide.

8. Additief volgens een of meer der conclusies 1 tot 7, waarbij de motorbrandstof een brandstofsamenstelling is, bestaande uit koolwaterstoffen die koken in het dieselbrandstoftraject bij ongeveer 160^0 C tot ongeveer 370^0 C.

9. Motorbrandstofsamenstelling, bestaande uit koolwaterstoffen die koken in het dieselbrandstof kooktraject van ongeveer 160^0 C tot ongeveer 370^0 C, die een roetuitstoot verminderende of verbrandingsrendement verbeterende hoeveelheid bevat van een additief volgens een of meer der conclusies 1 tot 7.

10. Benzinebrandstofsamenstelling, bestaande uit een benzine/ethanol mengsel, die een verbrandingsrendement verbeterende hoeveelheid bevat van een additief volgens een of meer der conclusies 1 tot 7, waarbij het additief resterende OH-functionaliteit bezit.

11. Benzinebrandstofsamenstelling volgens conclusie 10, waarbij de ethanolfase 1% tot 7% water bevat, bij voorkeur 4% water.

12. Brandstofsamenstelling volgens een of meer der conclusies 9 tot 11, waarbij de samenstelling 1 - 10 vol.%, bij voorkeur 2 - 3 vol.%, van een additief volgens een of meer der conclusies 1 tot 7 bevat.

13. Co-solvent voor een brandstofsamenstelling op basis van een benzine/ethanol mengsel, bestaande uit een additief volgens een of meer der conclusies 1 tot 7.

14. Toepassing van een additief volgens een of meer der conclusies 1 tot 7 als octaangetal verhogend middel voor een brandstofsamenstelling.

15. Werkwijze voor de bereiding van een additief volgens conclusie 7, waarbij men een vetzuurtriglyceride met formule $(CH_2\text{-}OR_1)(CH_2\text{-}OR_2)(CH_2\text{-}OR_3)$, waarin R_1, R_2, en R_3, elk onafhankelijk, een rechte of vertakte, C_5 - C_{30} alkylcarboxylgroep voorstellen, laat reageren met een stoechiometrische overmaat van een lagere alkylester van een lager carbonzuur, bij voorkeur een C_1 - C_5 alkylacetaat, meer bij voorkeur methylacetaat of ethylacetaat, in aanwezigheid van een katalysator, ter verkrijging van het additief als een mengsel van glycerylcarboxylesters, bij voorkeur glycerylacetylesters, en C_1 - C_5 alkylesters van C_5 - C_{30} vetzuren, bij voorkeur methyl- of ethylesters van C_5 - C_{30} vetzuren.

16. Werkwijze volgens conclusie 15, waarbij de katalysator is gekozen uit de groep, bestaande uit een basische katalysator, bij voorkeur kalium methanolaat; een vaste of vloeibare zure katalysator, bij voorkeur zwavelzuur; een heterogene katalysator, bij voorkeur Amberlyst-15; of een enzymatische katalysator.

17. Werkwijze volgens conclusie 16, waarbij de vaste zure katalysator is gekozen uit de groep, bestaande uit een zeoliet, bij voorkeur H-ZSM-5, Y en Beta; en een gemengd metaaloxide, bij voorkeur gesulfateerd zirkoonoxide.

18. Werkwijze volgens een of meer der conclusies 15 tot 17, waarbij men de reactie uitvoert met een molaire verhouding van 1 - 10 mol C_1 - C_5 alkylacetaat, bij voorkeur methylacetaat, tot 1 mol vetzuurtriglyceride, bij voorkeur van 4 - 8 mol methylacetaat tot 1 mol vetzuurtriglyceride, in het bijzonder 6 mol methylacetaat tot 1 mol vetzuurtriglyceride.

19. Werkwijze voor de bereiding van een additief volgens conclusie 7, waarbij men een vetzuurtriglyceride met formule $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, waarin R_1, R_2, en R_3, elk onafhankelijk, een rechte of vertakte, C_5 - C_{30} alkylcarboxylgroep voorstellen, laat reageren met lagere alkanol, bij voorkeur een C_1 - C_5 alkanol, meer bij voorkeur methanol, in aanwezigheid van een katalysator, bij voorkeur kalium methanolaat, ter verkrijging van een 2-fasen mengsel, bestaande uit een glycerol bevattende, waterige fase, en een C_1 - C_5 alkylesters van C_5 - C_{30} vetzuren bevattende fase; het 2-fasen mengsel desgewenst droogt; en de glycerolbevattende fase laat reageren met C_1 - C_5 alkyl acetaat, bij voorkeur methylacetaat of ethylacetaat, ter vorming van een glycerolacetylesters bevattende fase en een alkanol, bij voorkeur methanol, bevattende fase, die men desgewenst onderwerpt aan fasenscheiding; de aldus verkregen fasen desgewenst zuivert volgens op zichzelf bekende wijze, ter verkrijging van een additief voor een motorbrandstofsamenstelling.

20. Werkwijze volgens conclusie 19, waarbij men de reactie uitvoert met een stoechiometrische ondermaat aan C_1 - C_5 alkanol, bij voorkeur methanol.

21. Werkwijze volgens conclusie 19 of 20, waarbij men het 2-fasen-mengsel droogt door azeotropische destillatie.

22. Werkwijze voor de bereiding van een additief volgens conclusie 6, waarbij men een vetzuurtriglyceride met formule $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, waarin R_1, R_2, en R_3, elk onafhankelijk, een rechte of vertakte, $C_5 - C_{30}$ alkylcarboxylgroep voorstellen, laat reageren met een stoechiometrische overmaat $C_1 - C_5$ alkylether, bij voorkeur MTBE of ETBE, in aanwezigheid van een katalysator, ter verkrijging van een additief als een mengsel van glycerolethers en $C_1 - C_5$ alkyl esters van $C_5 - C_{30}$ vetzuren.

23. Werkwijze volgens conclusie 22, waarbij men de reactie uitvoert in aanwezigheid van een heterogene katalysator, bij voorkeur een zure ionenwisselaar, in het bijzonder Amberlyst-15.

24. Werkwijze voor de bereiding van een additief volgens conclusie 6, waarbij men een vetzuurtriglyceride met formule $(CH_2 - OR_1)(CH_2 - OR_2)(CH_2 - OR_3)$, waarin R_1, R_2, en R_3, elk onafhankelijk, een rechte of vertakte, $C_5 - C_{30}$ alkylcarboxylgroep voorstellen, laat reageren met een lagere alkanol, bij voorkeur een $C_1 - C_5$ alkanol, meer bij voorkeur methanol, in aanwezigheid van een katalysator, bij voorkeur een basische katalysator, in het bijzonder KOH, ter verkrijging van een 2-fasen mengsel, bestaande uit enerzijds een glycerol en loog bevattende fase; en anderzijds een $C_1 - C_5$ alkylesters van $C_5 - C_{30}$ vetzuren bevattende fase; de 2 fasen scheidt en desgewenst droogt; de katalysator neutraliseert, en een zure katalysator toevoegt, en de glycerolbevattende fase, in aanwezigheid van een zure katalysator, bij voorkeur een zure ionenwisselaar, zoals Amberlyst-15, laat reageren met een $C_1 - C_5$ alkylether, bij voorkeur methyl tert.butylether (MTBE), of methyl tert.amylether (MTAE), ter verkrijging van een alkyletherbevattende fractie, bij voorkeur een glyceryl tert.butylether of glyceryl tert.amylether bevattende fractie; de aldus verkregen fasen desgewenst zuivert volgens een op

zichzelf bekende wijze; de fasen desgewenst bij elkaar voegt ter verkrijging van een additief voor een motorbrandstofsamenstelling in de vorm van een mengsel van C_1 - C_5 alkyl esters van C_5 - C_{30} vetzuren, en C_1 - C_5 alkylethers van glycerol, bij voorkeur glyceryl t.butylethers en glyceryl t.amylethers.

25. Werkwijze volgens een of meer der conclusies 15 tot 24, waarbij men het vetzuurtriglyceride vervangt door een overeenkomende ester van een di- of polyhydroxy koolwaterstofverbinding, gekozen uit de groep, bestaande uit diethyleenglycol, ethyleenglycol, glycerol, diglycerol, pentaerythritol, en suikers zoals tetrosen, pentosen, hexosen, bij voorkeur glucose, fructose, xylose, sorbitol, en mannitol.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE
	P2008 NL 038
Nederlands aanvraag nr. **1036154**	Indieningsdatum **05-11-2008**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **Criss Cross Technology B.V.**	
Datum van het verzoek voor een onderzoek van internationaal type **29-12-2008**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN 51427**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

C07C67/02 **C07C67/03**
C10L1/19 **C10L1/185** **C10L10/02** **C10L10/10**
C11C3/00 **C11C3/10** **C10L1/02** **C07C41/14**

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen		
IPC 8	**C10L**	**C11C**	**C07C**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III. ☐ **GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES** (opmerkingen op aanvullingsblad)

IV. ☐ **GEBREK AAN EENHEID VAN UITVINDING** (opmerkingen op aanvullingsblad)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 1036154

A. CLASSIFICATIE VAN HET ONDERWERP
INV. C10L1/18 C10L1/19 C10L1/185 C10L10/02 C10L10/10
C11C3/00 C11C3/10 C10L1/02 C07C41/14 C07C67/02
C07C67/03

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte miminum documentatie (classificatie gevolgd door classificatiesymbolen)
C10L C11C C07C

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)
EPO-Internal

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X Y	EP 1 580 255 A (INST CHEMII PRZEMYSLOWE IM PRO [PL]) 28 september 2005 (2005-09-28) alineas [0015] - [0017], [0020]; conclusies 1-12; voorbeelden I-X	1-5,7-9, 13,15-18 25
X Y	GB 791 165 A (EASTMAN KODAK CO) 26 februari 1958 (1958-02-26) bladzijde 2, regel 7 - regel 42; conclusies 1-5,8,12,13	2,3 25

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[X] Verdere documenten worden vermeld in het vervolg van vak C.

[X] Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid	Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type
8 Juli 2009	

Naam en adres van de instantie	De bevoegde ambtenaar
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	de La Morinerie, B

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ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 1036154

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	WO 2007/061903 A (CPS BIOFUELS INC [US]; BRADIN DAVID [US]; GRUNE GUERRY L [US]; TRIVETT) 31 mei 2007 (2007-05-31) bladzijde 6, regel 9 - regel 13; conclusies 1-6,11-19,23-25,28-30,32-34 bladzijde 7, regel 13 - regel 25 bladzijde 15, regel 28 - regel 33 bladzijde 19, regel 25 - bladzijde 20, regel 9 bladzijde 21, regel 5 - regel 14	1-3,6, 8-14
X	EP 1 331 260 A (IND MAN S A [ES]) 30 juli 2003 (2003-07-30) in de aanvraag genoemd	2-5,7-9, 13,19-21
A	alineas [0011], [0012]; conclusies 1,8,10; voorbeelden 3,4; tabel 2	15,16
X	US 6 174 501 B1 (NOUREDDINI HOSSEIN [US]) 16 januari 2001 (2001-01-16)	1-3,6,13
Y	kolom 5, regel 5 - kolom 7, regel 60; figuur 1a; voorbeeld 1 kolom 10, regel 20 - kolom 11, regel 67	24
X	US 5 731 476 A (SHAWL EDWARD T [US] ET AL) 24 maart 1998 (1998-03-24)	1-3,6,8, 13
Y	kolom 3, regel 35 - regel 37; conclusies 1,5,6; voorbeelden 2,3	24
A		22,23
X	EP 0 198 243 A (HUELS CHEMISCHE WERKE AG [DE]) 22 oktober 1986 (1986-10-22)	1-3,8,9, 13
A	kolom 1, regel 49 - kolom 2, regel 11; conclusies 1,2,11-13; voorbeelden 1,43-47 bladzijde 18	22,23
X	DU WEI ET AL: "Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors" JOURNAL OF MOLECULAR CATALYSIS. B, ENZYMATIC, ELSEVIER, AMSTERDAM, NL, deel 30, nr. 3-4, 16 augustus 2004 (2004-08-16), bladzijden 125-129, XP002481979 ISSN: 1381-1177 bladzijde 126 alinea [0004]	2-5,7, 13,15,16

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ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 1036154

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	WO 2005/093015 A (INST FRANCAIS DU PETROLE [FR]; HILLION GERARD [FR]; DELFORT BRUNO [FR]) 6 oktober 2005 (2005-10-06) bladzijde 2, regel 4 - bladzijde 3, regel 11; conclusies 1-14; voorbeelden 1-5; tabel 1 bladzijde 6, regel 24 - bladzijde 7, regel 20	1-3,6,8, 9,12
X	WESSENDORF R: "GLYCERINDERIVATE ALS KRAFTSTOFFKOMPONENTEN" ERDOEL ERDGAS KOHLE, URBAN VERLAG, HAMBURG, DE, deel 48, nr. 3, 1 maart 1995 (1995-03-01), bladzijden 138-143, XP000501434 ISSN: 0179-3187 bladzijde 138; tabellen I,VI-VIII alineas [02.3], [0003]	1-8,13, 14
X	EP 0 718 270 A (WESSENDORF RICHARD DR [DE]) 26 juni 1996 (1996-06-26) bladzijde 2, regel 28 - regel 49; conclusies 1,7-12; voorbeelden 1-10; tabellen 1,2 bladzijde 3, regel 13 - regel 41 bladzijde 4, regel 7 - regel 10	1-3,6,8, 13,14
X	WO 2007/058556 A (INST CHEMII PRZEMYSLOWEJ [PL]; LIPKOWSKI ANDRZEJ [PL]; KIJENSKI JACEK) 24 mei 2007 (2007-05-24) conclusies 1-12; voorbeelden 1-3	2-5,7,8, 13,15,16
X	EP 0 641 854 A (ARCO CHEM TECH [US]) 8 maart 1995 (1995-03-08) in de aanvraag genoemd bladzijde 2, regel 5 - regel 8; conclusies 1-16; voorbeelden 1,2 bladzijde 3, regel 50 - regel 55 bladzijde 4, regel 29 - regel 37 bladzijde 6, regel 7 - regel 37	1-3,6,8, 9,12,13
X	US 3 222 146 A (CASE EVERETT N ET AL) 7 december 1965 (1965-12-07) conclusies 1-3,5; tabel 1	2-5,7,8, 13,14
X	WO 98/11177 A (EXXON RESEARCH ENGINEERING CO [US]) 19 maart 1998 (1998-03-19) bladzijde 3, alinea 2; conclusies 1,7-11 bladzijde 9, alinea 2	1-5,7,8, 10,12,13
X	WO 98/11178 A (EXXON RESEARCH ENGINEERING CO [US]) 19 maart 1998 (1998-03-19) bladzijde 3, alinea 2; conclusies 1,7-10,12	1-5,7-9, 12,13

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ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 1036154

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	JP 57 055993 A (TAGUCHI CHOBEE) 3 april 1982 (1982-04-03) samenvatting -----	1-5,8,13

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek: NL 1036154

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
EP 1580255 A	28-09-2005	GEEN	
GB 791165 A	26-02-1958	GEEN	
WO 2007061903 A	31-05-2007	EP 1948767 A1	30-07-2008
		US 2009013591 A1	15-01-2009
EP 1331260 A	30-07-2003	AT 394461 T	15-05-2008
		EP 1985684 A1	29-10-2008
		ES 2305192 T3	01-11-2008
		ES 2201894 A1	16-03-2004
		US 2003167681 A1	11-09-2003
US 6174501 B1	16-01-2001	US 6015440 A	18-01-2000
US 5731476 A	24-03-1998	US 5476971 A	19-12-1995
EP 0198243 A	22-10-1986	BR 8601563 A	09-12-1986
		DE 3512497 A1	09-10-1986
		ES 8703134 A1	16-04-1987
		JP 61236749 A	22-10-1986
		PH 21986 A	02-05-1988
		ZA 8602502 A	30-12-1986
WO 2005093015 A	06-10-2005	BR PI0507963 A	17-07-2007
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		US 2007283619 A1	13-12-2007
EP 0718270 A	26-06-1996	DE 4445635 A1	27-06-1996
		DE 19544413 A1	05-06-1997
WO 2007058556 A	24-05-2007	GEEN	
EP 0641854 A	08-03-1995	DE 69415617 D1	11-02-1999
		DE 69415617 T2	20-05-1999
		JP 7082576 A	28-03-1995
		US 5308365 A	03-05-1994
US 3222146 A	07-12-1965	GEEN	
WO 9811177 A	19-03-1998	AU 734585 B2	14-06-2001
		AU 4416697 A	02-04-1998
		BR 9711783 A	24-08-1999
		CA 2264707 A1	19-03-1998
		CN 1230210 A	29-09-1999
		EP 0948586 A1	13-10-1999
		JP 2001501231 T	30-01-2001
WO 9811178 A	19-03-1998	AU 4416897 A	02-04-1998
		BR 9711780 A	24-08-1999
		CA 2264712 A1	19-03-1998
		CN 1230209 A	29-09-1999
		EP 0946682 A1	06-10-1999
		JP 2001501992 T	13-02-2001
		US 5993498 A	30-11-1999
JP 57055993 A	03-04-1982	JP 1479208 C	10-02-1989
		JP 63012919 B	23-03-1988

OCTROOICENTRUM NEDERLAND

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
SN51427	05.11.2008		NL1036154

International Patent Classification (IPC)

INV. C10L1/18 C10L1/19 C10L1/185 C10L10/02 C10L10/10 C11C3/00 C11C3/10 C10L1/02 C07C41/14 C07C67/02 C07C67/03

Applicant

Criss Cross Technology B.V. te Haarlem

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☒ Box No. VIII Certain observations on the application

	Examiner
	de La Morinerie, B

Application number

WRITTEN OPINION

NL1036154

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	17, 20-25
	No:	Claims	1-16, 18, 19
Inventive step	Yes:	Claims	22, 23
	No:	Claims	1-21, 24, 25
Industrial applicability	Yes:	Claims	1-25
	No:	Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Box No. VIII Certain observations on the application

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1: EP-A-1 580 255 (INST CHEMII PRZEMYSLOWE IM PRO [PL]) 28 september 2005 (2005-09-28)

D2: GB 791 165 A (EASTMAN KODAK CO) 26 februari 1958 (1958-02-26)

D3: WO 2007/061903 A (CPS BIOFUELS INC [US]; BRADIN DAVID [US]; GRUNE GUERRY L [US]; TRIVETT) 31 mei 2007 (2007-05-31)

D4: EP-A-1 331 260 (IND MAN S A [ES]) 30 juli 2003 (2003-07-30) in de aanvraag genoemd

D5: US-B1-6 174 501 (NOUREDDINI HOSSEIN [US]) 16 januari 2001 (2001-01-16)

D6: US-A-5 731 476 (SHAWL EDWARD T [US] ET AL) 24 maart 1998 (1998-03-24)

D7: EP-A-0 198 243 (HUELS CHEMISCHE WERKE AG [DE]) 22 oktober 1986 (1986-10-22)

D8: DU WEI ET AL: "Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors" JOURNAL OF MOLECULAR CATALYSIS. B, ENZYMATIC, ELSEVIER, AMSTERDAM, NL, deel 30, nr. 3-4, 16 augustus 2004 (2004-08-16), bladzijden 125-129, XP002481979 ISSN: 1381-1177

D9: WO 2005/093015 A (INST FRANCAIS DU PETROLE [FR]; HILLION GERARD [FR]; DELFORT BRUNO [FR]) 6 oktober 2005 (2005-10-06)

D10: WESSENDORF R: "GLYCERINDERIVATE ALS KRAFTSTOFFKOMPONENTEN" ERDOEL ERDGAS KOHLE, URBAN VERLAG, HAMBURG, DE, deel 48, nr. 3, 1 maart 1995 (1995-03-01), bladzijden 138-143, XP000501434 ISSN: 0179-3187

D11: EP-A-0 718 270 (WESSENDORF RICHARD DR [DE]) 26 juni 1996 (1996-06-26)

D12: WO 2007/058556 A (INST CHEMII PRZEMYSLOWEJ [PL]; LIPKOWSKIANDRZEJ [PL]; KIJENSKI JACEK) 24 mei 2007 (2007-05-24)

D13: EP-A-0 641 854 (ARCO CHEM TECH [US]) 8 maart 1995 (1995-03-08) in de aanvraag genoemd

D14: US-A-3 222 146 (CASE EVERETT N ET AL) 7 december 1965 (1965-12-07)

D15: WO 98/11177 A (EXXON RESEARCH ENGINEERING CO [US]) 19 maart 1998 (1998-03-19)
D16: WO 98/11178 A (EXXON RESEARCH ENGINEERING CO [US]) 19 maart 1998 (1998-03-19)
D17: JP 57 055993 A (TAGUCHI CHOBEE) 3 april 1982 (1982-04-03)

2. The lack of clarity mentioned under item VIII of the present communication notwithstanding, the subject-matter of **claim 1 and independent claims 2, 14, 15 and 19** is not new, and therefore the criteria of patentability are not met.

2.1 All the documents D1-D17 disclose (See the references applying to these documents in the search report) partially or fully etherefied or esterified polyols, mainly etherified or esterified glycerol: Glycerol acetates are disclosed for example in D1, D4, D8, D10, D12, D14; Glyceryl tertiary butyl ethers or glyceryl tertiary amyl ethers are disclosed for example in D3, D5, D6, D9, D10, D11, D13; Diesel fuel compositions comprising these esters or ethers are disclosed in D1, D3, D4, D7, D9, D13, D16, and gasoline fuel compositions comprising gasoline, ethanol and these esters or ethers are disclosed in D3 and D5; The use of these esters or ethers to raise the octane number of a fuel composition is disclosed in D3, D10, D11, D14; D1, D8, D12 disclose the preparation process of glycerol esters, wherein a triglyceride of fatty acids is reacted with a molar stoichiometric excess of an ester of a C1-C7 carboxylic acid with a C1-C6 monoalcohol in the presence of a catalyst; The prepared glycerol esters can contain a partially esterified glycerol in the case of D1; D4 discloses a preparation process wherein a fatty acid triglyceride is reacted with methanol or ethanol in presence of a catalyst, two phases are obtained, a glycerol phase and a methyl esters of fatty acids phase, the two phases are separated, and the glycerine phase is reacted with methyl acetate to prepare glycerine triacetate; The triglycerides used in D1, D4, D8 and D12 can be made of a major amount of saturated fatty acids, depending on their origines.
Thus the subject-matter of claims 1, 2, 14, 15 and 19 is not new.

3. The lack of clarity mentioned under item VIII of the present communication notwithstanding, the subject-matter of **independent claims 24 and 25** does not involve an inventive step, thus the present application does not meet the criteria of patentability.

Claim 24:

3.1 The document D5 is regarded as being the closest prior art to the subject-matter of **claim 24**, and discloses (See the references applying to this document in the search report) a process wherein a fatty acid triglyceride is reacted with methanol in presence of a basic catalyst, two phases are obtained and separated, one phase containing the transesterified glycerides: methyl esters of the fatty acids, and the other phase containing glycerol and base from the catalyst, this glycerol stream is caused to pass through a desionisation unit where anions(Na+, K+...) are removed and neutralized, this desionisation unit could be replaced by a strongly acidic hydrogen form macromolecule cationic exchange resins (For example Amberlyst-15), then the glycerol phase is reacted with isobutylene or isoamylene in the presence of an acid catalyst to produce glycerol ethers; The triglyceride used in D5 could be made of saturated fatty acids.

3.2 The subject-matter of claim 24 therefore differs from this known D5 in that in claim 24, C1-C5 alkylether is used, in this case methyl tertiary buty ether (MTBE) or methyl tertiary amyl ether (MTAE), instead of isobutylene or isoamylene, in the second step of the two stepped process of preparing glyceryl ethers starting from a fatty acid triglyceride.

3.3 The description of the present application mentions (Page 9, lines 27-32) that it is possible to convert the glycerol moiety into a mixture of glycerol ethers, by using ethers such as MTBE or ETBE, but not limited to these, instead of alkanols; The description mentions that MTBE which is amply available and easier to handle than isobutylene as etherifying component can be used.

3.4 The problem to be solved by the present invention may therefore be regarded as improving the preparation process of tertiary butyl glycerol ethers (GTBE) and tertiary amyl glycerol ethers (GTAE) starting from a fatty acid triglyceride.

3.5 D6 discloses (See the references applying to this document in the search report) a process for the preparation of a polyether by reaction of a polyhydric compound having at least 3 hydroxyl groups per molecule with a C5-C10 tertiary olefin or a C4-C10 tertiary alkanol or ether, or by reaction of isobutylene with a polyhydric compound having more than 3 hydroxyl groups per molecule in the presence of an acid catalyst; A process of preparation of di-t-amyl glycerine by reaction of tertiary amylene with glycerine in the presence of an acid catalyst is disclosed.

3.6 In view of D6, the skilled person would regard it a normal option to replace the isobutylene or isoamylene by an ether in the second step of the process described in D5; An ether able to give the final glyceryl ether must be used: MTBE and MTAE are the most simple ethers which can be used for obtaining GTBE or GTAE in the process described in D5.
Thus the solution proposed in claim 24 of the present application cannot be considered as involving an inventive step.

Claim 25:

3.7 The document D1 is regarded as being the closest prior art to the subject-matter of **claim 25**, and discloses (See the references applying to this document in the search report) a process wherein a fatty acid triglyceride is reacted with an ester of a C1-C7 carboxylic acid with a C1-C6 alcohol in the presence of a catalyst, wherein esters of the C1-C6 alcohol with the triglyceride fatty acids and esters of glycerol with the C1-C7 carboxylic acid are obtained.

3.8 In view of D2 disclosing (See the references applying to this document in the search report) a method of effecting interesterification comprising heating a mixture of substantially completely esterified fatty acid esters in the presence of a catalyst, the mixture of fatty acid esters being able to include a fatty acid ester of a polyhydric alcohol, a fatty acid ester of a monohydric alcohol, a mixture of triglycerides, or the mixture being a mixture of fatty acid triglyceride and a fatty acid ester of a monohydric alcohol, or the mixture being a mixture of esters of two diferent polyhydric alcohols having dissimilar fatty acid radicals, the skilled person would regard it a normal option to replace the fatty acid triglyceride in the process of D1 by an ester of an other polyol, such as ethylene glycol, sorbitol, mannitol, pentaerythritol, or glycerol.
Thus the subject-matter of claim 25 of the present application cannot be considered as involving an inventive step.

4. If the problems of the objections mentioned under item VIII of the present communication were solved, the subject-matter of **independent claim 22** could be considered as involving an inventive step.

4.1 The document D7 is regarded as being the closest prior art to the subject-matter of **claim 22**, and discloses (See the references applying to this document in the search report) a process to prepare fatty acid alkyl esters and ethers of glycerine

with C1-4-alcohols, by heterogen catalytic reaction of triglycerides with an excess of C1-4-alcohols; The triglycerides used can be saturated; D7 discloses the use of the obtained fatty acid alkyl esters and glycerine ethers, eventually with other diesel substitutes or with conventional fuels to operate diesel engines.

4.2 The difference between the subject-matter of claim 22 and D7, is that in claim 22 a C1-C5 alkyl ether is used instead of the C1-4 alcohol.

4.3 Thus if the problems of the objections under item VIII were solved, the subject-matter of claim 22 could be considered as new.

4.4 The description of the present application mentions (Page 9, lines 21-31) that ethers, such as MTBE, ETBE, MTAE, but not limited to these, can be used instead of alkanol, in a process of criss-cross etherification of a fatty acid triglyceride, wherein a product mix which can contain GTBE or GTAE along with fatty acid methyl esters, can be obtained, But no special effect originating from using a C1-C5 alkyl ether instead of a C1-C4 alcohol appears to have been shown in the present application.

4.5 The problem to be solved by the present invention may therefore be regarded as finding an alternative preparation process of a mixture of glycerol ethers and C1-C5 alkyl esters of fatty acids, starting from a saturated fatty acid triglyceride.

4.6 D6 discloses (See paragraph 3.5 of the present communication) the possible preparation of a polyol ether by reaction of a polyol with an ether or an alkanol, the polyol can be a glycerol, but starting from a glyceride instead of a glycerol is not mentioned. No document has been found which would suggest reacting a fatty acid glyceride with an ether to obtain a mixture of glycerol ethers and alkyl esters of fatty acids.
Thus if the problem of the objections under item VIII were solved, the subject-matter of claim 22 of the present application could be considered as involving an inventive step.

5. **Dependent claims 3-13, 16-18, 20, 21** do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of novelty and/or inventive step, because these features are known from at least one of D1-D17 (See the corresponding passages cited in the search report) and/or no special effect originating from these features appears to have

been shown in the present application.

6. **Claim 23** is dependent on claim 22, and as such could also meet the requirements of novelty and inventive step, if the problems of the objections under item VIII were solved.

Re Item VIII
Certain observations on the application

1. **Claim 1, independent claim 2 and dependent claim 6** are product-by-process claims: Their subject-matter is a product obtainable by esterification or etherification of polyhydroxy hydrocarbon compounds: A claim defining a product in terms of a process is to be construed as a claim to the product as such; The products defined in terms of a process of manufacture are not allowable if the products as such having the features induced by this specific preparation process do not fulfill the requirements for patentability, i.e. inter alia that they are neither new nor inventive.

2. Claims 1 and 2 are not supported by the description, as their scope is broader than justified by the description: only a limited number of poyhydroxy hydrocarbon compounds are mentioned in the description (Page 5, lines 12-19; Page 11, lines 15) and claims, and the acids, alkylesters, alkanols, alkylethers which can take part to the reactions described in the application can be fatty acids, "lower" alkylesters of "lower" carboxylic acids, "lower" alkanols, C1-C5 alkyl ethers.

3.1 Although **claims 1 and 2** have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought. The aforementioned claims therefore lack conciseness.

3.2 The same objection as the one under paragraph 3.1 above applies to independent **claims 15, 19, 22, 24 and 25** (See below paragraph 4).

4. **Claim 25** is written as a claim dependent on one or more of claims 15 to 24, but the feature "fatty acid triglyceride" is not present in this claim and is present in each one of claims 15 to 24, thus not all the features of each one of claims 15 to 24 are present in claim 25, thus claim 25 cannot be witten as a claim dependent on any one of claims 15 to 24.

5.1 In **claim 8**, the "motor fuel" is not a feature of the additive, product, subject-matter of the claim, thus the features of motor fuel mentioned in this claim do not limit the scope of the claim, which is then identical to one or more of claims 1 to 7; The claim could be written as a use claim, or as a fuel composition claim.

5.2 **Claim 13** is written as a product claim: The intended use of the product: "Co-solvent for a fuel composition..." does not limit the scope of the claim, which is then identical to one or more of claims 1 to 7; The claim could be written as a use claim.

6. The preferred forms of the invention defined in **claims 7, 11, 12, 15-20, 22-24** after the terms such as "preferably", should be removed, because not limiting the scope of the claims, and, if necessary, be the subject-matter of new dependent claims, for the requirements of clarity and conciseness of the claims to be fulfilled.

7.1 In **claim 15**, a product disclosed in **claim 7** is prepared; In claim 7, only acetates are disclosed, thus, in claim 15, only C_1-C_5 alkylacetates can be used.

7.2 In **claims 22 and 24**, a product disclosed in **claim 6** is prepared; In claim 6, only ethers with tert. butyl or tert. amyl groups are disclosed, thus, in claims 22 and 24, only ethers of tert. butyl or tert. amyl and a C1-C5 alkyl can be used.

8. The relative term "lower" ("lager(e)") used in **claims 15, 19 and 24** has no well-recognised meaning and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear.

9. Description of the present application: page 10, line 5: "...stoichiometric insufficient amount of a C1-C5 alkyl ether,...". In claim 22: "...stoechiometrische overmaat C1-C5 alkylether,..". Present claim 22 as it is has been searched. The subject-matter of the claim must be supported by the description, which is not the case here.