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(54) Title: FUEL AND METHOD OF PRODUCTION THEREOF.

(57) Abstract: The present invention relates to a method of producing a jet engine fuel comprising, mixing a first bio-fuel (for example bio-diesel) with a different second fuel in the presence of a co-solvent capable of effecting a substantially single phase solution of the bio-fuel and two or more different fuels.



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DESCRIPTIONFUEL AND METHOD OF PRODUCTION THEREOF

The present invention relates to a fuel and a method of producing a fuel.

Conventional automotive fuels are hydrocarbon molecules derived from
5 fractional distillates of crude oil. Crude oil is a finite resource that is rapidly
dwindling. Additionally, the burning of crude oil distillates has been shown to be
increasing the concentration of atmospheric carbon dioxide, and there is growing
concern about the consequences of climate change that this may cause. Bio-fuels
represent a renewable alternative to these types of fuel.

10 Bio-ethanol is an example of a bio-fuel. Ethanol is produced by the
fermentation of biomass products and is purified by filtration, distillation and then
subjected to drying. It can be used to fuel conventional petrol engines.

Bio-diesel is another example of bio-fuel. Bio-diesel, which comprises fatty
acid alkyl esters and can be manufactured from biologically produced triglycerides
15 such as vegetable oils, rendered animal fats and micro-algal oils. Conventional diesel
engines can be fuelled with bio-diesel. Chemically unchanged triglycerides such as
vegetable oils can be used to fuel diesel engines (*Knothe et al., (1997) Biodiesel: The
use of vegetable oils and their derivatives as alternative diesel fuels. Fuels and
Chemicals from Biomass. Washington, D.C.: American Chemical Society*).

20 Many other chemicals can be produced from renewable resources and would
be suitable for use as bio-fuels. Butanol, which can be used as an alternative to
petroleum can be produced by biomass fermentation, usually by utilising the
bacterium *Clostridium acetobutylicum*. Hexane can be produced by from sugars such
as glucose, through the intermediate sorbitol.

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There is worldwide interest and considerable amounts of money being invested in finding a bio-fuel that can be used as an alternative to jet engine fuel. So far, there is no evidence to suggest that a bio-fuel having the key characteristics of jet engine fuel has been identified. Furthermore, methods to produce an alternative jet engine fuel from bio-fuel and other renewable resources have proved to be either
5 impractical and/or too expensive.

Co-solvents have been proposed in the context of biofuels, but only as a means to accelerate the mixing of vegetable oils with alcohols. For example, Dunn and Bagby have disclosed using co-solvent blending to reduce the viscosity of vegetable
10 oils with a low molecular weight alcohol (*Dunn and Bagby (2000) JAOCS, Vol. 77, No. 12, 1315-1323*). US 6,712,867 discloses a process for forming a single phase solution of triglyceride in an alcohol by employing a co-solvent, so as to produce a bio-fuel.

It is an object to provide a jet engine fuel, which has a bio-fuel component or
15 is manufactured completely from bio-fuels.

In accordance with the present invention, there is provided a method of producing a jet engine fuel comprising, mixing a first bio-fuel with two or more different second fuels in the presence of a co-solvent capable of effecting a substantially single phase solution of the first and second fuels.

20 The present invention therefore provides a fuel that can have a number of desirable characteristics from a range of existing fuels, which would not usually mix to form a single-phase solution. One desirable characteristic which has been seen in experiments involving the fuel of the present invention, is a reduced requirement for oxygen during combustion in an engine. The fuel therefore appears to be suitable for
25 use at high altitudes.

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Whilst two or more bio-fuels may be mixed to form a “homogeneous” mixture having a uniform appearance and composition throughout, the mixture may not necessarily be a single-phase mixture and may settle into separate phases over time. For example, if bio-diesel and bio-ethanol in equal volumes are placed in a blending machine and mixed vigorously and thoroughly, then a mixture will be formed that initially appears to be homogeneous. In time the mixture will separate into two phases, and the ethanol light phase will float on the bio-diesel heavy phase. The provision of a co-solvent allows two or more fuels (one of which may be a bio-fuel) to form and remain in a single-phase. Without the co-solvent, the two or more fuels would either be immiscible or poorly miscible.

The term, “substantially single phase solution” should be taken to include microemulsions. A microemulsion is an equilibrium dispersion of optically isotropic fluid microstructures with an average diameter less than one quarter the wavelength of visible light that spontaneously form upon the addition of amphiphiles to a mixture of otherwise nearly immiscible liquids (*Schwab, A.W., et al., (1983), J. Dispersion Sci. Technol. 4: 1-17*). Unlike [macro]emulsions, microemulsions are thermodynamically stable and do not require agitation to remain in single-phase translucent solution at constant temperature and pressure (*Rosen, M.J., (1989), Surfactants and Interfacial Phenomena, 2nd edn., Wiley and Sons, New York, 322-324*).

A “bio-fuel” should be taken to mean any liquid fuel that is derived at least in part from a renewable source, for example bio-diesel.

The first bio-fuel may comprise bio-diesel.

In accordance with a further aspect of the present invention, there is provided a method of producing a jet engine fuel comprising, mixing a bio-diesel with one or

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more second fuels in the presence of a co-solvent capable of effecting a substantially single phase solution of the bio-diesel and the one or more second fuels.

Preferably, the second fuel is a bio-fuel. If needed, the fuel produced may include an existing crude oil distillate if a particular characteristic in the fuel is
5 required and no bio-fuel (or combination of bio-fuels) would be able to provide the desired characteristic.

The presence of the co-solvent enables a single-phase mixture to be formed between the fuels. The co-solvent may act as a surfactant. The co-solvent(s) used may potentially be any substance (or combination of substances) which is miscible
10 with the different types of bio-fuels (and oil distillate fuels where appropriate) to be mixed. It will be evident to the skilled addressee that the co-solvent used may vary depending upon which fuels are to be mixed together. The co-solvent may be amphiphilic, thereby combining hydrophilic and lipophilic properties so that it will be miscible with (i) long chain hydrocarbon molecules (such as vegetable oil and bio-
15 diesel) and (ii) short chain alcohols. More preferably, the co-solvent is tetrahydrofuran (THF) or an isobutyl alcohol (such as isobutanol, 2-methyl-1-propanol). The co-solvent may also have certain desirable characteristics so that it is compatible with the various jet engines which are to be powered by the fuel. For example, it is preferred that the co-solvent is ashless (i.e. burn without residue).

20 The method may further comprise the step of adding one or more additives to the fuel. Preferably, an additive will be a multi-functional fuel additive. Any number of additives may be added to the fuel for a variety of purposes. For example, LUBRIZOL® 8041F is a multifunctional fuel additive formulated for use at an optimum treat rate of 200ppm m/m (190 ppm v/v). The product provides dispersant,

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demulsifier, anti-foam, anti-corrosion, anti-oxidant and conductivity improver functionality.

An additive may be selected from one or more of the following additives: viscosity modifier, anti-oxidant/fuel stabiliser, biocide, corrosion inhibitor, injector cleaner, cold flow improver, demulsifier, antifoaming agent, dispersant, antistatic/conductivity improver and cetane/combustion improver. The use of a viscosity modifier will reduce the fuels viscosity at low temperature. An example of such a viscosity modifier would be malan-styrene copolymers.

One or more anti-oxidants may be used in accordance with the present invention and they may either be naturally occurring compounds (such as Carotenes and the Vitamin E family i.e. Tocopherols and Tocotrienols), or synthetic compounds selected from one or more of the following: Baynox (20% 2,6-di-tert-butyl-4-methylphenol, Vulkanox BKF (2,2'-methylenebis-(4-methyl-6-tert-butylphenol)) Vulkanox ZKF(2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol)); Ionox 75 (2,6-di-tert-butylphenol 75%); Ionox 99 (2,6-ditert-butylphenol 99%); Ionox 103 (2,6-di-tert-butyl-N,Ndimethylamino-p-cresol); Ionox 220 (4,4'-methylene-bis-(2,6-di-tert-butylphenol)); Ionol K65 (6-tert-butyl-2,4-dimethylphenol); MBP-K (2-tert-butyl-4-methylphenol); and MBM-K (2-tert-butyl-5-methylphenol). A corrosion inhibitor, may for example, comprise dimerised fatty acids.

Biocides may be conventional compounds, or enzyme based anti-contamination additives i.e. enzymes derived from hydrocarbon utilising micro-organisms which digest contaminants and prevent microbial growth. Soltron and Fuel Clean-BD are examples of such additives.

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Potential cold flow improvers may be selected from one or more of the following improvers: Generally viscosity-modifying polymers such as carboxy-containing interpolymers, styrene-maleic anhydride copolymer, polymethacrylates, polyacrylates, nitrogen-containing polyacrylates, poly[alkyl(meth)acrylates],

5 ethylene-vinyl ester (acetate) copolymers, fumarate or itaconate polymers and copolymers, polyoxyalkylene and polar nitrogen compounds.

If required, the method may further comprise a step of cold filtering the fuel. If such a filtering step is employed, it is preferred that the cold filtering removes particles larger than about 1 micron. It will be apparent to the skilled addressee that

10 cold filtration improves the cold flow properties of the fuel. Cold filtration involves cooling the fuel to a temperature below its cloud point (i.e. a temperature at which the fuel appears cloudy rather than clear but yet it will still flow) and then filtering it using a very fine filter media. Filtering in this way (e.g. filtering out particles larger than 1 micron) removes the molecules that have started to crystallize. Performing the

15 filtering lowers the cloud point, cold filter plugging point, pour point and importantly freeze point of the fuel.

The second fuel may be selected from one or more of the following group of bio-fuels: ethanol, butanol and hexane. It will be apparent that the precise formulation of the fuel will largely depend upon the fuels application and characteristics that is

20 required. For example, the energy content of the fuel can be improved by addition of high-energy hydrocarbons, such as hexane. Certain types of bio-diesel with superior cold flow properties may be selected if the fuel is to be used in cold conditions. For example, bio-diesel produced from canola oil. Furthermore, bio-diesels produced from ethanol (fatty acid ethyl esters) may be selected, as they tend to have better cold

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flow characteristics than bio-diesels produced from methanol (fatty acid methyl esters).

The fuel will preferably be used as a liquid fossil fuel substitute for jet engine fuel. For example, it may be used as a replacement, substitute or blend stock for jet
5 fuel (including Jet A, Jet A1, Jet B (enhanced cold weather performance) and military blends) and other aviation fuels. Therefore, by using a co-solvent, a fuel that possesses the key characteristics of jet engine fuel may be produced from bio-fuels which alone would not be suitable for use as jet engine fuel.

In accordance with a further aspect of the present invention, there is provided
10 a substantially single-phase jet engine fuel comprising a mixture of a bio-fuel, two or more different second fuels and a co-solvent capable of effecting a substantially single phase solution of the bio-fuel and two or more different fuels. Such a fuel may be produced by the method as herein above described.

The bio-fuel may comprise bio-diesel.

15 In accordance with yet a further aspect of the present invention, there is provided a jet engine fuel comprising a mixture of bio-diesel, one or more second fuels and a co-solvent capable of effecting a substantially single phase solution of the bio-diesel and one or more second fuel.

Preferably, the different second fuel comprises a bio-fuel. The co-solvent may
20 act as a surfactant. Such a surfactant may be amphiphilic and amphipathic. The fuel may further comprise one or more fuel additives. Such additives may be selected from one or more of the following additives: viscosity modifier, anti-oxidant, biocide, corrosion inhibitor, injector cleaner or cold flow improver, demulsifier, antifoaming agent, dispersant, antistatic/conductivity improver and cetane/combustion improver.
25 Examples of additives are described herein above.

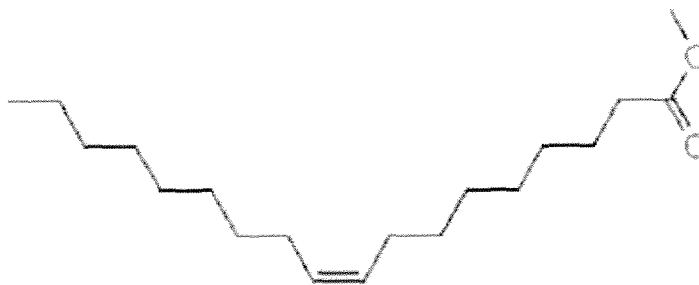
The first bio-fuel and at least one of the two or more second fuels may be selected from the following group of bio-fuels: ethanol, butanol and hexane.

The present invention will now be described by way of example only with reference to the following experimental example:

5 EXAMPLE 1

In this example, the ratio of bio-diesel to bio-ethanol that best matches the target specification of the required fuel is first determined. The required amount of bio-diesel and bio-ethanol are then mixed together vigorously and thoroughly. The co-solvent is gradually added to this mixture whilst it is agitated until the mixture
10 becomes clear i.e. it's appearance changes from that of a cloudy two-phase mixture to a clear single-phase mixture. The fuel produced has a lower freeze point, lower viscosity and lower flash point than standard bio-diesel.

In practice, the bio-diesel molecule may be a fatty acid methyl ester (methyl oleate) as shown below:

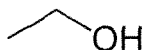


15

The long chain of carbon and hydrogen atoms (fatty acid / hydrocarbon chain) terminates at the top right of the diagram with a methyl ester group. Here the final carbon of the fatty acid chain has a double bonded oxygen attached to it as well as a single bonded oxygen atom to which the methyl group is attached. Bio-diesel can be
20 esters of any alcohol / fatty acid combination, such as an ethyl ester if ethanol is used to produce the bio-diesel.

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An ethanol molecule is shown below:



- which chemically is no different to bio-ethanol. At the top right of this diagram is the hydroxide group i.e. the oxygen atom and attached hydrogen atom at
5 the end of the chain.

A tetrahydrofuran (THF) molecule is shown below:

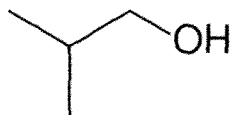


The structure of the THF molecule makes it a suitable co-solvent. The oxygen atom is said to be hydrophilic. It is able to form hydrogen bonds with water and
10 alcohols. The remainder of the molecule is a hydrocarbon portion that is said to be hydrophobic or lipophilic. This portion of the molecule is capable of solubilising many organic compounds. In simple terms, this molecule can combine with alcohols (such as ethanol) as well as molecules that are predominantly hydrocarbon (such as bio-diesel). Amphiphilic and amphipathic are words used to describe this type of
15 behaviour and types of molecules that exhibit this behaviour i.e. molecules that contain both hydrophilic and lipophilic groups. The addition of THF to a mixture of methyl oleate and ethanol allows a single phase solution of both components to be formed – which can be used as a fuel having a combination of desirable characteristics.

20 As an alternative to THF, an isobutyl alcohol (such as isobutanol, 2-methyl-1-propanol) may be used as the co-solvent.

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An isobutyl alcohol molecule is shown below:



Isobutyl alcohol itself has a fairly high heat of combustion (31.4 MJ/Kg) and is known to be stable under a number of conditions. Furthermore, isobutyl alcohol

5 can be produced by fermentation.

EXAMPLE 2

Table 1 below shows a comparison between crude oil distillate jet fuel and a range of bio-fuels.

	Form	Energy	Viscosity	Flash point	Freeze point	Cu corrosion
Jet fuel	Liquid Ash-less ¹	(*)Minimum 42.8 MJ/Kg ¹	Max 8 cSt @ -20°C ¹	Min +38°C ¹	Max -47°C ¹	Strip 1 max ¹
Ethanol	Liquid Ash-less ²	27 MJ/Kg ⁴	1.52 cSt @ +20°C ²	+14°C ²	Max -114°C ²	
Butanol	Liquid Ash-less ²	36 MJ/Kg ³	3.64 cSt @ +20°C ²	+34°C ²	-89°C ²	
Hexane	Volatile liquid Ash-less ⁴	44.7 MJ/Kg ²	0.51 cSt @ +20°C ²	-22°C ²	-95°C ²	Strip 1 max ²
Biodiesel	Liquid Ash-less ²	~40 MJ/Kg ³	~8 cSt @ +20°C ⁴	Generally above +130°C ⁴	Typically above -12°C ⁴	Strip 1 max ²

Table 1

10 Key

¹Target specification

²Within specification

³Close to specification

⁴Outside specification

15

It can be seen that a fuel having similar characteristics (see key to Table 1) to that of jet fuel can be formulated by mixing a number of bio-fuels having specifications which are on target, within or close to those required. By using a co-solvent (such as THF), a fuel that possesses the key characteristics of jet engine fuel
5 can produced from bio-fuels that alone would not be suitable for use as jet engine fuel.

It is worthy to note that with regard to the energy content, bio-diesel and bio-ethanol molecules both contain oxygen and are considered oxygenated fuels. This is not the case with conventional jet engine fuel or most other fuels derived from crude
10 oil distillates. Oxygenated bio-fuels allow for leaner combustion and have been shown to yield a gain in thermal efficiency. For this reason, it is not considered necessary to have an energy content as high as that specified for jet engine fuel, if it is produced from oxygenated bio-fuels.

CLAIMS

1. A method of producing a jet engine fuel comprising, mixing a first bio-fuel with two or more different second fuels in the presence of a co-solvent capable of effecting a substantially single phase solution of the first and second fuels.
5
2. A method as claimed in claim 1, wherein the first bio-fuel comprises bio-diesel.
3. A method of producing a jet engine fuel comprising, mixing a bio-diesel with one or more second fuels in the presence of a co-solvent capable of effecting a substantially single phase solution of the bio-diesel and the one or more second fuels.
10
4. A method as claimed in claim 3, wherein the second fuel comprises a bio-fuel.
5. A method as claimed in any preceding claim, wherein the co-solvent acts as a surfactant.
15
6. A method as claimed in any preceding claim, wherein the co-solvent is amphiphilic.
7. A method as claimed in any preceding claim, wherein the co-solvent comprises tetrahydrofuran (THF).
8. A method as claimed in any one of claims 1 to 6, wherein the co-solvent comprises an isobutyl alcohol.
20
9. A method as claimed in any preceding claim, wherein the method further comprises the step of adding one or more additives to the fuel.
10. A method as claimed in claim 9, wherein an additive is selected from one or more of the following additives: viscosity modifier, anti-oxidant/fuel
25

stabiliser, biocide, corrosion inhibitor, injector cleaner, cold flow improver, demulsifier, antifoaming agent, dispersant, antistatic/conductivity improver and cetane/combustion improver.

11. A method as claimed in any preceding claim, wherein the method further
5 comprises a step of cold filtering the fuel.
12. A method as claimed in claim 11, wherein the cold filtering removes particles larger than about 1 micron.
13. A method as claimed in any preceding claim, wherein the second fuel is selected from one or more of the following group of bio-fuels: ethanol,
10 butanol and hexane.
14. A jet engine fuel comprising a mixture of a bio-fuel, two or more different second fuels and a co-solvent capable of effecting a substantially single phase solution of the bio-fuel and the two or more different fuels.
15. A fuel as claimed in claim 14, wherein the bio-fuel comprises bio-diesel.
- 15 16. A jet engine fuel comprising a mixture of bio-diesel, one or more second fuels and a co-solvent capable of effecting a substantially single phase solution of the bio-diesel and one or more second fuel.
17. A fuel as claimed in any one of claims 14 to 16, wherein the second fuel comprises bio-fuel.
- 20 18. A fuel as claimed in any one of claims 14 to 17, wherein the co-solvent acts as a surfactant.
19. A fuel as claimed in any one of claims 14 to 18, wherein the surfactant is amphiphilic.
- 20 20. A fuel as claimed in any one of claims 14 to 19, wherein the fuel further
25 comprises one or more fuel additives.

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21. A fuel as claimed in claim 20, wherein an additive is selected from one or more of the following additives: viscosity modifier, anti-oxidant, biocide, corrosion inhibitor, injector cleaner or cold flow improver.
22. A fuel as claimed in any one of claims 14 to 23, wherein the second fuel is selected from one or more of the following group of bio-fuels: ethanol, butanol and hexane.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2008/050008

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/02 C10L1/18

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	KR 100 655 101 B1 (LEE YONG MAN [KR]) 1 December 2006 (2006-12-01) the whole document	1-22
P, X	& WO 2007/142475 A (LEE YONG MAN [KR]) 13 December 2007 (2007-12-13) page 3, line 24 - page 4, line 19; claims 1-14; examples 1-6	1-6, 8-22
P, X	& WO 2007/004789 A (PURE LIFE CO LTD [KR]; LEE YONG MAN [KR]) 11 January 2007 (2007-01-11) claims 1-10; examples 1-5	1-6, 8-22
	-/--	

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

☒ See patent family annex.

* Special categories of cited documents:

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G document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2008/050008

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	-----	7,8
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2008/050008

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