

- 1 -

FUEL COMPOSITIONS

Field of the Invention

The present invention relates to fuel compositions comprising a renewable fuel component. In particular, the fuel compositions of the present invention have improved cold flow properties.

Background of the Invention

Renewable fuel components, such as renewable diesel, can be manufactured by hydroprocessing of triglyceride fats, from vegetable oils or animal oils for example, to remove the glycerol backbone to produce fatty acids which on further hydrotreating produces paraffinic molecules. Esters of fatty acids can be treated in the same way, hence the name 'Hydrotreated Esters and Fatty Acids' or 'HEFA'.

Fatty acid synthesis in biological systems typically produces molecules of even numbers between C14-C24. Without additional hydrocracking, HEFA of a boiling point corresponding with diesel meeting the EN15940 specification for paraffinic fuels is rich in normal or n-paraffinic molecules.

However, mixtures of n-paraffinic molecules in this carbon range typically crystallise at the ambient temperatures experienced commonly in winter months. The crystallisation temperatures can be measured by using a 'cloud point' test such as ASTM D2500-05, ASTM D5771-05, ASTM D5772-05, ASTM D5773-05 or ASTM D7397-08. The crystals of n-paraffins at temperatures below the cloud point are typically flat and plate-like in appearance and by stacking upon themselves can result in fuel starvation issues arising from blocked fuel filters. One method to

- 2 -

measure the cold flow properties of diesel fuel is the cold filter plugging point (CFPP) laboratory test according to the standard test methods EN116, IP309 and ASTM D6371.

5 To avoid cold flow problems from crystallised n-paraffins, cold flow improving additives are commonly used in winter for diesel manufactured from mineral/crude oil sources. These additives do not typically alter the cloud point temperature, but result in the CFPP
10 temperature being depressed (improved) through a mechanism of interfering with the growth of n-paraffin crystals. These crystals now have altered morphology with slender/needle-like appearance which maintain an open structure when stacked together, permitting the flow
15 of fuel at temperatures well below the cloud point temperature.

 However, the very high concentration of n-paraffins found in renewable diesel manufactured by the HEFA process means that cold flow improving additives for
20 mineral diesel are typically ineffective in improving cold flow properties of HEFA.

 Cold flow properties of HEFA can alternatively be improved by introducing an energy intensive step into the manufacturing process, by hydrocracking and isomerizing
25 the n-paraffinic molecules into iso-paraffinic molecules. These iso-paraffins crystallise at colder temperatures than n-paraffins and hence a more isomerized HEFA has improved cold flow properties (depressed cloud point and depressed CFPP).

30 It would be desirable to reduce the overall carbon footprint of renewable fuel components such as HEFA, as well as reducing manufacturing costs. It has now been found by the present inventors that by using a particular

- 3 -

combination of additives in fuel compositions comprising renewable fuel components such as HEFA, the cold flow properties (both cloud point and CFPP) of the fuel compositions can be improved while reducing the need for severe hydrocracking/isomerization steps during the manufacture of the renewable fuel component, such as HEFA.

Summary of the Invention

According to the present invention there is provided a fuel composition comprising a base fuel and an additive mixture, wherein the base fuel comprises a renewable fuel component and wherein the additive mixture comprises:

- (i) a first additive which comprises a long chain carboxylic acid alkyl polyamine; and
- (ii) a second additive which comprises an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound having a single nitrogen atom per molecule;

wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.

According to the present invention there is also provided the use of an additive mixture in a fuel composition for the purpose of reducing the cloud point and the Cold Filter Plugging Point (CFPP) of the fuel composition, wherein the fuel composition comprises a base fuel and an additive mixture, and wherein the base fuel is a renewable fuel component and wherein the additive mixture comprises (i) a first additive comprising a long chain carboxylic acid alkyl polyamine and (ii) a second additive comprising an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound having a single nitrogen atom per molecule; wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.

- 4 -

According to the present invention there is also provided a method for reducing the cloud point and the Cold Filter Plugging Point of a fuel composition, wherein the method comprises adding an additive mixture to the fuel composition, wherein the fuel composition comprises a base fuel, wherein the base fuel comprises a renewable fuel component, wherein the additive mixture comprises (i) a first additive comprising a long chain carboxylic acid alkyl polyamine and (ii) a second additive comprising an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound having a single nitrogen atom per molecule; wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.

It has been found that by using a particular combination of additives in fuel compositions comprising HEFA, the cold flow properties of HEFA and said fuel compositions can be improved, in particular a reduction in both the cloud point and CFPP, while reducing the need for severe hydrocracking/isomerization steps during the manufacture of HEFA. In particular, the use of the specified combination of additives have been found to improve the cold flow properties of HEFA and HEFA-containing fuel compositions such that European winter fuel specifications can be met.

Brief Description of the Drawings

Figure 1 shows typical cold-flow properties for Automotive Gasoil (AGO) (0 to 30% FAME) when treated and untreated with conventional cold-flow improving additives. In AGO treated with conventional cold-flow improvers, the CFPP is depressed (improved) with minimal to no change to cloud point.

Figure 2 shows typical cold-flow properties for HEFA

- 5 -

(0% FAME) when treated and untreated with the cold-flow improving additive mixture disclosed herein. Unlike the AGO example shown in Figure 1, HEFA treated with the cold-flow improving additive mixture disclosed herein exhibits depression (improvement) to both cloud point and CFPP.

Figure 3 shows the average CFPP performance benefit in HEFA for individual additivation (KF4990 alone) vs average incremental changes seen for combining the first additive and the second additive in differing ratios.

Figure 4A to 4D: Compositional analysis of Renewable Diesel Blends for concentration of n-paraffins, and ratio of iso- to n-paraffins, and the correlation of these parameters with Cold-Flow Properties (Cloud Point and Cold Filter Plugging Point) with and without the presence of the cold-flow improving additive mixture disclosed herein.

Figure 5 is a graphical representation of the experimental data presented in Table 1, showing improvement in Cold-Flow Properties (Cloud Point and Cold Filter Plugging Point) for HEFA in the presence of the cold-flow improving additive mixture disclosed herein.

Detailed Description of the Invention

The fuel composition of the present invention comprises a base fuel and an additive mixture, wherein the base fuel comprises a renewable fuel component.

The additive mixture used herein has advantageously been found to reduce both the Cloud Point and the Cold Filter Plugging Point of the fuel composition. In doing so, it is possible to make use of renewable paraffinic fuel components having lower isomerization ratios, hence avoiding the need for energy intensive hydroisomerization steps in the manufacture of the renewable fuel components,

- 6 -

lowering the overall carbon footprint of the renewable paraffinic fuel.

As used herein, the term 'Cloud Point' of a fuel means the temperature at which the heaviest n-paraffins are no longer soluble but precipitate out from the fuel, giving it a cloudy appearance. Cloud Point can be measured by any suitable test method, such as ASTM D2500, D5771, D5772, D5773, D7689, EN3015, DIN EN ISO 3015. A preferred test method herein for measuring the Cloud Point is DIN EN ISO 3015.

As used herein, the term 'Cold Filter Plugging Point (CFPP)' of a fuel is the temperature at and below which was in the fuel will cause severe restrictions when flowing through a filter. CFPP can be measured by any suitable test method such as ASTM D6371 or EN 116, DIN EN 116. A preferred test method herein for measuring CFPP is DIN EN 116.

Both cloud point and cold filter plugging point are measured and given as temperature (T, here C). The lower the cloud point and cold filter plugging point, the better the cold properties of the fuel.

In the context of this aspect of the invention, the term "reducing the Cloud Point and the Cold Filter Plugging Point" embraces any degree of reduction in the Cloud Point and the Cold Filter Plugging Point of the fuel composition. The reduction in the Cloud Point of the fuel composition may be of the order of 1°C or more, preferably 2°C or more, more preferably 3°C or more, and especially 4°C or more compared to the Cloud Point of an analogous fuel composition which does not contain the specified additive mixture. Even a 1°C reduction in Cold Filter Plugging Point is worthwhile, as such a reduction can bring a material within seasonal specifications for

- 7 -

EN15940 Paraffinic Fuel, which it would not otherwise meet.

5 The addition of the specified additive package obviates the need to use isomerisation or hydrocracking to increase the ratio of iso- to n-paraffins of a C14-C20 HEFA renewable fuel component. In particular, a reduction in Cloud Point by 1°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 HEFA renewable fuel component by 9.2%, a reduction in
10 Cloud Point by 2°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 HEFA renewable fuel component by 19%, a reduction in Cloud Point by 3°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 renewable HEFA fuel component by 29.4% and a
15 reduction in Cloud Point by 4.0°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 HEFA renewable fuel component by 40.5%.

 The reduction in the Cold Filter Plugging Point of the fuel composition may be of the order of 1°C or more,
20 preferably 2°C or more, more preferably 3°C or more, and especially 4°C or more compared to the Cold Filter Plugging Point of an analogous fuel composition which does not contain the specified additive mixture.

 The addition of the specified additive package
25 obviates the need to use isomerisation or hydrocracking to increase the ratio of iso- to n-paraffins of a C14-C20 HEFA renewable fuel component. In particular, a reduction in CFPP by 1.0°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 HEFA
30 renewable fuel component by 9.2%, a reduction in CFPP by 2.0°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 HEFA renewable fuel component by 18.3%, a reduction in CFPP by 3.0°C is equivalent to

- 8 -

increasing the ratio of iso- to n-paraffins in a C14-C20 renewable HEFA fuel component by 28.4% and a reduction of CFPP by 4.0°C is equivalent to increasing the ratio of iso- to n-paraffins in a C14-C20 HEFA renewable component by 39%.

The base fuel used in the fuel composition of the present invention comprises a renewable fuel component. In one embodiment, the renewable fuel component is present in the fuel composition herein at a level in the range from 20% v/v to 100% m/m, preferably from 50% v/v to 100% v/v, more preferably from 80% v/v to 100 %v/v, even more preferably from 90% v/v to 100% v/v, based on the total fuel composition.

The renewable fuel component preferably comprises or consists of hydrotreated vegetable oil, hydrotreated animal fat, hydrotreated fish fat, hydrotreated fish oil, hydrotreated algae oil, hydrotreated microbial oil, hydrotreated wood and/or other plant based oil, hydrotreated recyclable waste and/or residue or a combination thereof. Preferably, the fresh feed of renewable fuel is selected from plant oils/fats, animal fats/oils, fish fats/oils, fats contained in plants bred by means of gene manipulation, recycled fats of food industry and combinations thereof. Hydrotreating vegetable oils or animal fats is an alternative process to esterification for producing bio-based middle distillate fuels. Hydrotreated renewable middle distillate fuels are also referred to as 'hydrotreated vegetable oil fuels', 'hydrotreated renewable diesels', 'renewable fuels', 'renewable diesels' or 'renewable diesel components' instead of 'biodiesel', which is reserved for fatty acid methyl esters (FAME). Chemically, hydrotreated renewable middle distillates are mixtures of paraffinic hydrocarbons

- 9 -

and have very low quantities of sulfur and aromatics.

Preferably, the renewable fuel component for use herein is a hydrotreated vegetable oil (HVO) derived gasoil or a mixture of hydrotreated vegetable oil (HVO) derived gasoils.

The isomerization ratio of the renewable fuel such as hydrotreated renewable middle distillate can be, for example, at least 50%, or at least 60%. The isomerization ratio means the total sum of iso-paraffins (weight %) divided by the total sum of paraffins (weight %). Higher isomerization ratios typically improves cold properties but such a hydrotreated renewable middle distillate consumers more resources during its production.

Isomerization ratios of more than 80% may be achieved, but may not be necessary in the context of the present invention in view of the cold properties being improved by use of the specified additive mixture. Preferably, the isomerization ratio of renewable fuel, such as hydrotreated renewable middle distillate is less than 69%, giving advantageous ranges from 50 to 69 and from 60 to 69% respectively.

Since hydrotreated renewable middle distillates are hydrocarbons, they may be used as conventional middle distillate fuels. The fatty acid methyl ester specifications (EN 14214, ASTM D6751) do not apply for hydrotreated renewable middle distillates and therefore there is no volume percent limitation on how much hydrotreated renewable middle distillates may be blended with diesel fuel.

The base fuel present in the fuel composition can contain about 100% renewable fuel or can comprise a blend of renewable fuel and mineral middle distillate components. Where the base fuel contains 100% renewable

- 10 -

fuel, it can comprise a mixture of renewable fuel components.

In one embodiment herein, the renewable fuel component is present in the fuel composition as a blend together with a mineral diesel, such as an EN590 or ASTM D975 refinery diesel. In this embodiment, the renewable fuel component is preferably present in the fuel composition at a level in the range from 1% v/v to 99% v/v, more preferably from 20% v/v to 70% v/v, even more preferably from 20% v/v to 50% v/v, and especially from 20% v/v to 30% v/v, based on the total fuel composition.

Mineral middle distillate components are naturally occurring fuel components and derived from non-renewable sources. Examples of non-renewable sources include petroleum oil or shale oil, or combinations thereof. Middle distillate is typically diesel fuel or kerosene fuel. In the present invention, the mineral middle distillate component is preferably mineral diesel. Diesel fuel is any liquid fuel which can be used in diesel engines and is typically a specific fractional distillate of petroleum fuel oil. The diesel fuel used herein preferably meets the EN590 specification for diesel fuels. Mineral diesel may also be called petrodiesel, fossil diesel, or petroleum distillate. Mineral diesel can comprises atomphstric or vacuum distillates. The distillate can comprises cracked gas oil or a blend of straight run or thermally or catalytically cracked distillates. The distillate fuel can be subjected to further processing sch as hydrotreatment or oether propoecsces to improve the fuel properties, e.g. cold flow properties. Typically, mineral diesel comprises n-paraffins and iso-paraffins at a level of 10-70% weight, naphthenic at a level of 10-50% weight, monaromatics at a

- 11 -

level of 5-30% weight, diaromatics at a level of 0-11 % weight and other aromatics at 0-5% weight.

5 A preferred mineral diesel for use herein is petroleum derived low sulphur diesel comprising <50 ppm of sulphur, for example, an ultra-low sulphur diesel (ULSD) or a zero sulphur diesel (ZSD). Preferably, the low sulphur diesel comprises <10 ppm of sulphur. The petroleum derived low sulphur diesel preferred for use in the present invention will typically have a density from 10 0.81 to 0.865, preferably 0.82 to 0.85, more preferably 0.825 to 0.845 g/cm³ at 15°C; a cetane number (ASTM D613) of at least 51; and a kinematic viscosity (ASTM D445) from 1.5 to 4.5, preferably 2.0 to 4.0, more preferably from 2.2 to 3.7 mm²/s at 40°C.

15 Preferably, the renewable fuel and mineral middle distillate components are blended in a volume percent ratio of less than 95:5, more preferably less than 90:10 (renewable fuel:mineral middle distillate). In one embodiment, the renewable fuel and mineral middle 20 distillate components are blended in a volume percent ratio of 20:80 to 80:20 (renewable fuel:mineral middle distillate). In another embodiment, the renewable fuel and mineral middle distillate components are blended in a volume percent ratio of 20:80 to 60:40.

25 The renewable fuel component and the mineral middle distillate component are preferably present in the fuel composition at a total level of at least 90 vol%, based on the total fuel composition. Other fuel components suitable for use in diesel engines can also be included in 30 the fuel compositions herein, such as Fischer-Tropsch derived paraffinic gasoils and fatty acid methyl esters (FAME).

The fuel composition of the present invention

- 12 -

comprises an additive mixture as an essential component, in order to improve the cold properties of the renewable fuel component and the final fuel composition. The additive mixture is preferably present at a level from 50
5 mg/kg to 5000 mg/kg, more preferably from a 50 mg/kg to 2000 mg/kg, even more preferably from 50 mg/kg to 750 mg/kg, especially 63 mg/kg to 500 mg/kg by weight of the fuel composition.

The additive mixture comprises (i) a first additive
10 which comprises a long chain carboxylic acid alkyl amine; and (ii) a second additive which comprises an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound; wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.

15 In a preferred embodiment, the weight ratio of the first additive to the second additive is in the range from 4:1 to 2:1, preferably from 3.5:1 to 2.5:1, even more preferably from 3:1 to 2.5:1. In a particularly preferred embodiment herein, the weight ratio of the first additive
20 to the second additive is 3:1.

The first additive comprises a long chain carboxylic acid alkyl polyamine. Preferably, the long chain carboxylic acid alkyl polyamine is a reaction product of C14-C18 fatty acids with a linear, branched or cyclic
25 alkylene amine, preferably a linear alkylene amine. In one embodiment, the C14-C18 fatty acids comprise a mixture of linear and branched C14-C18 fatty acids and C18 unsaturated fatty acid. In another embodiment, the C14-C18 fatty acids comprises isooctadecanoic acid, octadecanoic
30 acid or mixtures thereof, preferably octadecanoic acid. Preferably, the alkylene amine is an ethyleneamine, especially tetraethylenepentamine. In an especially preferred embodiment herein, the long chain carboxylic

- 13 -

acid alkyl amine is a reaction product of isooctadecanoic acid or octadecanoic acid, or mixtures thereof with tetraethylenepentamine. In an especially preferred embodiment, the long chain carboxylic acid alkyl polyamine is a reaction product of octadecanoic acid with tetraethylenepentamine.

The long chain carboxylic acid alkyl polyamine is preferably present in the first additive at a level of 30 to 60 wt%, by weight of the first additive. Preferably, the first additive also comprises a heavy aromatic solvent such as petroleum naphtha. Preferably, the heavy aromatic solvent is present at a level from 30 to 60 wt%, by weight of the first additive. Other preferred components in the first additive include naphthalene and 1,2,4-trimethyl benzene.

The first additive is commercially available under the tradename Infineum R536A, from Infineum.

The second additive comprises an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound, containing a single nitrogen atom per molecule, preferably selected from one or more compounds (a) to (c) as follows:

(a) an amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride;

(b) a compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system

$$-A-NR^1R^2 \quad (I)$$

where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R^1 and R^2 are the

- 14 -

same of different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally
5 being in the form of a salt thereof; and
(c) a condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

Further details of compounds (a), (b) and (c) are provided below:

10 Compound (a)

(a) An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride.
15 Esters/amides may be used containing 30 to 300, preferably 50 to 150 total carbon atoms. Suitable amines are usually long chain C12-C40 primary, secondary, tertiary or quaternary amines or mixtures thereof, but shorter chain amines may be used provided the resulting
20 nitrogen compound is oil soluble and therefore normally contains about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C8 to C40, preferably C14 to C24, alkyl segment.

25 Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocamine, and hydrogenated tallow amine. Examples of secondary
30 amines include dioctadecyl amine and methyl-behenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine of the formula HNR₁R₂

- 15 -

wherein R1 and R2 are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C14, 31% C16, 59% C18.

5 Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include cyclohexane 1,2-dicarboxylic acid, cyclohexene 1,2-dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobis lactone. Generally, these
10 acids have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid and its anhydride is particularly preferred. The
15 particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dehydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

20 Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monamides of substituted succinic acids, examples of which are known in the art and described in US-A-4,147,520, for example. Suitable amines may be
25 those described above.

Other examples are condensates such as described in EP-A-327,423.

Compound (b)

30 b) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system

- 16 -



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R¹ and R² are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof. Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

As used herein, the term 'hydrocarbyl' refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms.

- 17 -

Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents of the general formula (I) may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S, or O atom, in which case or cases the compound is a heterocyclic compound.

Examples of such polycyclic assemblies include:

- (i) Condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;
- (ii) Condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene oxide;
- (iii) Rings joined 'end-on' such as diphenyl;
- (iv) Heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiodiphenylamine;
- (v) Non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene), alpha-pinene, cardinene, and bornylene; and

- 18 -

(vi) Three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

5 Each hydrocarbyl group constituting R1 and R2 in the invention (Formula I) may for example be an alkyl or alkylene group or a mono- or poly-alkoxylalkyl group. Preferably, each hydrocarbyl group is a straight-chain alkyl group. The number of carbon atoms in each
10 hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

 Also, it is preferred that the cyclic system is substituted with only two substituents of the general formula (I) and that A is a methylene group.

15 Examples of salts of the chemical compounds are the acetate and the hydrochloride.

 The compounds may conveniently be made by reducing the corresponding amide which may be made by reacting a secondary amine with the appropriate acid chloride; and

20

Compound (c)

c) A condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

25 Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telemer acid and alkanolamines such as described in US-A-4,639,256; a long chain epoxide/amine reaction product which may optionally be further reacted
30 with a polycarboxylic acid; and the reaction product of an amine containing a branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A-4,631,071.

- 19 -

Further examples of suitable second additives for use herein include those compounds disclosed in WO93/18115 and WO2008/113757.

5 A preferred second additive for use herein is an unsaturated and conjugated carboxylic acid compound having the formula $\text{HOOC-CH=CH-C(X)=NR}$ wherein R is a C₆ to C₂₂ alkyl group and wherein X is a hydroxy group or an alkoxy group. Preferably, R is a C₈ to C₁₈ alkyl group, preferably a C₁₂ to C₁₈ alkyl group, especially a C₁₃
10 alkyl group. Preferably the X group is hydroxy.

In an especially preferred embodiment, the second additive comprises 2-Butenoic, 4-oxo-4-(tridecylamino)-, (Z)-, branched (molecular formula: C₁₇H₃₁NO₃). Such an additive is commercially available from BASF under the
15 tradename Keroflux (RTM) 4990.

The first additive is preferably present in the fuel composition at a level from 63 ppmw to 2000 ppmw, more preferably from 125 ppmw to 1000 ppmw, even more preferably from 188 ppmw to 500 ppmw, based on the fuel
20 composition.

The second additive is preferably present present in the fuel composition at a level from 31 ppmw to 2000 ppmw, more preferably from 63 ppmw to 1000 ppmw, even more preferably from 63 ppmw to 375 ppmw, based on the fuel
25 composition.

The fuel compositions described herein are particularly suitable for use as a diesel fuel, and can be used for arctic applications, as winter grade diesel fuel due to the excellent cold flow properties.

30 For example, a cloud point of -10°C or lower (EN 23015) or a cold filter plugging point (CFPP) of -20°C or lower (as measured by EN 116) may be possible with fuel compositions herein.

- 20 -

The diesel base fuel may be any petroleum derived diesel suitable for use in an internal combustion engine, such as a petroleum derived low sulphur diesel comprising <50 ppm of sulphur, for example, an ultra-low sulphur diesel (ULSD) or a zero sulphur diesel (ZSD).
5 Preferably, the low sulphur diesel comprises <10 ppm of sulphur.

The petroleum derived low sulphur diesel preferred for use in the present invention will typically have a
10 density from 0.81 to 0.865, preferably 0.82 to 0.85, more preferably 0.825 to 0.845 g/cm³ at 15°C; a cetane number (ASTM D613) of at least 51; and a kinematic viscosity (ASTM D445) from 1.5 to 4.5, preferably 2.0 to 4.0, more preferably from 2.2 to 3.7 mm²/s at 40°C.

15 In one embodiment, the diesel base fuel is a conventional petroleum-derived diesel.

Generally speaking, in the context of the present invention the fuel composition may be additivated with fuel additives, in addition to the additive mixture
20 described hereinabove. Unless otherwise stated, the (active matter) concentration of each such additive in a fuel composition is preferably up to 10000 ppmw, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to
25 150 ppmw. Such additives may be added at various stages during the production of a fuel composition; those added to a base fuel at the refinery for example might be selected from anti-static agents, pipeline drag reducers, middle distillate flow improvers (MDFI) (e.g.,
30 ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers), lubricity enhancers, anti-oxidants and wax anti-settling agents.

The fuel composition may include a detergent, by

- 21 -

which is meant an agent (suitably a surfactant) which can act to remove, and/or to prevent the build-up of, combustion related deposits within an engine, in particular in the fuel injection system such as in the injector nozzles. Such materials are sometimes referred to as dispersant additives. Where the fuel composition includes a detergent, preferred concentrations are in the range 20 to 500 ppmw active matter detergent based on the overall fuel composition, more preferably 40 to 500 ppmw, most preferably 40 to 300 ppmw or 100 to 300 ppmw or 150 to 300 ppmw. Detergent-containing diesel fuel additives are known and commercially available. Examples of suitable detergent additives include polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

Other components which may be incorporated as fuel additives, for instance in combination with a detergent, include lubricity enhancers; dehazers, e.g. alkoxyated phenol formaldehyde polymers; anti-foaming agents (e.g. commercially available polyether-modified polysiloxanes); ignition improvers (cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in US4208190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g. a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted

- 22 -

aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives; anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); metal deactivators; static dissipator additives; and mixtures thereof.

The present invention may in particular be applicable where the fuel composition is used or intended to be used in a direct injection diesel engine, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, or in an indirect injection diesel engine. The fuel composition herein may be suitable for use in heavy-and/or light-duty diesel engines, and in engines designed for on-road use or off-road use.

In order to be suitable for at least the above uses, the diesel fuel composition herein preferably has one or more of the following characteristics:

- a kinematic viscosity at 40°C of 1.9 mm²/s or greater, more preferably in the range from 1.9 to 4.5 mm²/s;
- a density of 800 kg/m³ or greater, more preferably in the range from 800 to 860, even more preferably 800 to 845 kg/m³;
- a T95 of 360°C or less;
- a cloud point in the range from 0°C to -13°C, more preferably from -5°C to -8°C;
- a CFPP in the range of from -8°C to -30°C, more preferably from -15°C to -20°C.

The invention is illustrated by the following non-limiting examples.

Examples

- 23 -

Commercially sourced samples of HEFA of varying cold-flow properties were used in their pure form and in binary mixtures to understand the correlations between their hydrocarbon composition and cold-flow properties. The distribution of normal and isomerised paraffins with different carbon chain lengths was measured by gas-chromatography. Cold-flow properties were measured by standard methods for Cloud point (DIN EN ISO 3015) and Cold Filter Plugging Point (DIN EN 116). Analysis of these data (Figures 4A-4D) revealed that n-paraffin concentration was related to Cloud Point and Cold Filter Plugging Point by a logarithmic relationship. Similarly, the ratio of iso- to n-paraffins in carbon chain lengths C14 to C20 was related to Cloud Point and Cold Filter Plugging Point by a second order polynomial relationship. These blend rules allowed creation of binary mixtures of HEFA at targeted Cloud Point and Cold Filter Plugging Point temperatures.

Example 1

A binary mixture of 79.4 wt% HEFA with high isomerisation (11.6% n-paraffin content by mass; iso-/n-paraffin ratio = 8.05) with 20.4 wt% of HEFA with low isomerisation (98.0% n-paraffin content by mass; iso-/n-paraffin ratio = 0.02) was blended. Testing confirmed this had the predicted desired Cold Filter Plugging Point of -5°C and Cloud Point of -3.4°C.

To this HEFA blend, cold-flow additives (Infineum R536A from Infineum and Keroflux KF4990 from BASF) were blended individually, and in combination with each other at concentrations of 63 to 2000 mg/kg, and at weight ratios ranging from 1:1 to 3:1 (R536A to KF4990). Cold-flow properties were measured for these samples using the same methods as above.

- 24 -

Results showed that Cold Filter Plugging Point for HEFA could be improved (reduced) by up to 2°C to -7°C and Cloud Point improved (reduced) by up to 3°C to -6.4°C. Unexpected and advantageous observations were that dose-reponse was non-linear, with greatest improvements in Cold Filter Plugging Point being achieved at moderate dose-rates (<250 mg/kg of additive) and that preferable combinations of the two additives (3:1 of R536A to KF4990) delivered incremental improvements in Cold Filter Plugging Point compared to less preferable combinations of the two additives (1:1 of R536A to KF4990).

Example 2

Binary mixtures of HEFA with high isomerisation (11.6% n-paraffin content by mass; iso-/n-paraffin ratio = 8.05) with HEFA with low isomerisation (98.0% n-paraffin content by mass; iso-/n-paraffin ratio = 0.02) were blended to give 4 blends with Cloud Points of 0 to -21°C and Cold Filter Plugging Points of 0 to -22°C.

To these HEFA blends, cold-flow additives (Infineum R536A from Infineum and Keroflux KF4990 from BASF) were blended individually, and in combination with each other as per Table 1.

The results in Table 1 showed that Cold Filter Plugging Point for HEFA could be improved (reduced) by up to 2°C and Cloud Point improved (reduced) by up to 4°C by addition of the cold-flow additive mixture.

Table 1

	HEFA with High Isomerisation (weight %)	HEFA with Low Isomerisation (weight %)	Infineum R506A (mg/kg)	Keroflux KF4990 (mg/kg)	Cloud Point (°C)	CFPP (°C)	Cloud Point Change (Δ°C)	CFPP Change (Δ°C)
No CFI Reference HEFA Blends	33.1%	66.9%	0	0	0	0	N/A	N/A
	11.4%	88.6%	0	0	-9	-10	N/A	N/A
	4.7%	95.3%	0	0	-14	-17	N/A	N/A
	0.0%	100.0%	0	0	-21	-22	N/A	N/A
A	33.1%	66.9%	250	0	0	-2	0	-2
	11.4%	88.6%	250	0	12	12	3	2
	4.7%	95.3%	250	0	-17	-17	-3	0
	0.0%	100.0%	250	0	-23	-22	-2	0
B	33.1%	66.9%	0	250	1	1	1	1
	11.4%	88.6%	0	250	-11	-11	-2	-1
	4.7%	95.3%	0	250	-16	-16	-2	1
	0.0%	100.0%	0	250	-22	-22	-1	0
C	33.1%	66.9%	750	0	0	1	0	1
	11.4%	88.6%	750	0	-12	-12	-3	-2
	4.7%	95.3%	750	0	-18	-17	-4	0
	0.0%	100.0%	750	0	-23	-22	-2	0
D	33.1%	66.9%	0	750	1	-1	1	-1
	11.4%	88.6%	0	750	-11	-12	-2	-2
	4.7%	95.3%	0	750	-16	-17	-2	0
	0.0%	100.0%	0	750	-22	-22	-1	0
E	33.1%	66.9%	375	125	1	-1	1	-1
	11.4%	88.6%	375	125	-12	-12	-3	-2
	4.7%	95.3%	375	125	-18	-17	-4	0
	0.0%	100.0%	375	125	-23	-21	-2	1

- 26 -

Unexpected and advantageous observations were that:

- (i) dose-response was non-linear, with greatest improvements in Cloud Point and Cold Filter Plugging Point being achieved at moderate dose-rates (250 mg/kg of additive; aligned with Example 1);
- (ii) At a preferable ratio of the two additives (3:1 of 375 mg/kg R536A with 125 mg/kg KF4990; Example 2E) incremental improvements in Cold Filter Plugging Point were measured to be the same as a higher dose of a single additive (750 mg/kg R536A; Example 2C, or 750 mg/kg KF4990; Example 2D).
- (iii) at a fixed dose-rate of additive, or fixed dose-rate of additives at a preferred ratio, improvements (reduction) in Cloud Point and Cold Filter Plugging Point were dependent on the original cold-flow properties of the HEFA. The largest improvements (reduction) in Cloud Point and Cold Filter Plugging Point being achieved for HEFA with Cloud Point of between -9°C and -14°C and Cold Filter Plugging Point of between -10°C and -17°C (as shown in Figure 5);
- (iv) at a fixed dose-rate of additive, or fixed dose-rate of additives at a preferred ratio, improvements (reduction) in Cloud Point and Cold Filter Plugging Point result in a breakdown of the previously observed relationship between these cold-flow properties and the concentration of n-paraffin in HEFA. This is illustrated in Figure 4A and 4B, where changes are seen for both the logarithmic coefficient of x (the n-paraffin concentration) as well as the vertical offset. Hence, reinforcing the unexpected and advantageous observation in point (iv) (above) and showing that when the example additives are present, the concentration of n-paraffin

- 27 -

can no longer be used as an effective predictor of cold-flow properties of HEFA.

(v) at a fixed dose-rate of additive, or fixed dose-rate of additives at a preferred ratio, improvements

5 (reduction) in Cloud Point and Cold Filter Plugging Point result in a breakdown of the previously observed polynomial relationship between these cold-flow properties and the ratio of iso-/n-parafins in the C14-C20 carbon chain length in HEFA. This is illustrated in
10 Figure 4C and 4D, where changes are seen for both the first and second order coefficient of x (ratio of iso-/n-parafins in the C14-C20 carbon chain length) as well as the vertical offset. Hence, reinforcing the unexpected and advantageous observation in point (iv) (above) and
15 showing that when the example additives are present, the ratio of iso-/n-parafins in the C14-C20 carbon chain length can no longer be used as an effective predictor of cold-flow properties of HEFA.

Discussion

20 Typically, when no cold-flow improving (CFI) additives are used, a strong linear correlation is found between Cloud Point and Cold Filter Plugging Point in both mineral derived diesel (0 to 30% bio-diesel content; Figure 1) and HEFA (Figure 2).

25 The addition of CFI additives to mineral derived diesel (0 to 30% bio-diesel content) decorrelates the link between Cloud Point and Cold Filter Plugging Point, which is illustrated in Figure 1.

30 At reduced temperatures, without the use of CFI additives, normal paraffin wax crystals in mineral derived diesel (0 to 30% bio-diesel content) quickly grow at temperatures below the Cloud Point (DIN EN ISO 3015) into flat, dinnerplate-like crystals, which block the

- 28 -

filtration media in the Cold Filter Plugging Point test (DIN EN 116) at a temperatures close to the Cloud Point.

CFI additives dosed into mineral derived diesel (0 to 30% bio-diesel content) result in wax crystals with long, needle-like shapes, which form an open matrix and allow for continued flow of fuel at temperatures well below the Cloud Point.

A further unexpected and advantageous observation was seen for the use of the example CFI additives (individually, and in combination) in HEFA, where the correlation between Cloud Point and Cold Filter Plugging Point was maintained (Figure 2), suggesting a different and unique mechanism for HEFA compared to mineral derived diesel (0 to 30% bio-diesel content).

15

C L A I M S

1. A fuel composition comprising a base fuel and an additive mixture, wherein the base fuel comprises a renewable fuel component and the additive mixture comprises:
- 5 (i) a first additive which comprises a long chain carboxylic acid alkyl polyamine; and
- (ii) a second additive which comprises an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound containing a single nitrogen atom per molecule;
- 10 wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.
2. A fuel composition according to Claim 1 wherein the weight ratio of the first additive to the second additive is in the range from 4:1 to 2:1.
- 15 3. A fuel composition according to Claim 1 or 2 wherein the weight ratio of the first additive to the second additive is in the range from 3.5:1 to 2.5:1.
4. A fuel composition according to any of Claims 1 to 3 wherein the weight ratio of the first additive to the
- 20 second additive is 3:1.
5. A fuel composition according to any of Claims 1 to 4 wherein the ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound is selected from one or more compounds (a) to (c) as follows:
- 25 (a) an amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride;

- 30 -

(b) a compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system



- 5 where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R^1 and R^2 are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally
10 interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof; and
- (c) a condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.
- 15 6. A fuel composition according to any of Claims 1 to 5 wherein the ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound is an unsaturated and conjugated carboxylic acid compound having the formula $\text{HOOC-CH=CH-C(X)=NR}$ wherein R is a C6-C22 alkyl
20 group and wherein X is a hydroxy group or an alkoxy group.
7. A fuel composition according to Claim 6 wherein R is a C8-C18 alkyl group.
8. A fuel composition according to any of Claims 1 to
25 7 wherein the long chain carboxylic acid alkyl polyamine present in the first additive is a reaction product of C14-C18 fatty acids with an alkylenepolyamine.
9. A fuel composition according to any of Claims 1 to
30 8 wherein the long chain carboxylic acid alkyl polyamine present in the first additive is a reaction products of C14-C18 fatty acids with an ethylenepolyamine.
10. A fuel composition according to any of Claims 1 to 9 wherein the long chain carboxylic acid alkyl polyamine

- 31 -

present in the first additive is a reaction product of C14-C18 fatty acids with a tetraethylenepentamine.

11. A fuel composition according to any of Claims 8 to 10 wherein the long chain carboxylic acid amine present in the first additive is a reaction product of isooctadecanoic acid or octadecanoic acid or a mixture thereof with a tetraethylenepentamine.

12. A fuel composition according to any of Claims 1 to 11 wherein the renewable fuel component is a hydrotreated vegetable oil (HVO) derived gasoil or a mixture of hydrotreated vegetable oil (HVO) derived gasoils.

13. Use of an additive mixture in a fuel composition for the purpose of reducing the Cloud Point (as measured according to DIN EN ISO 3015) and the Cold Filter Plugging Point (as measured according to DIN EN 116) of the fuel composition, wherein the fuel composition comprises a base fuel and an additive mixture, wherein the base fuel comprises a renewable fuel component and wherein the additive mixture comprises (i) a first additive comprising a long chain carboxylic acid polyamine and (ii) a second additive comprising an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound having a single nitrogen atom per molecule;

wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.

14. Method for reducing the Cloud Point (as measured according to DIN EN ISO 3015) and the Cold Filter Plugging Point (as measured according to DIN EN 116) of a fuel composition, wherein the method comprises adding an additive mixture to the fuel composition, wherein the fuel composition comprises a base fuel, wherein the base fuel comprises a renewable fuel component, wherein the

- 32 -

additive mixture comprises (i) a first additive comprising a long chain carboxylic acid polyamine and (ii) a second additive comprising an ionic or non-ionic, oil-soluble polar organic, nitrogen-containing compound
5 having a single nitrogen atom per molecule;
wherein the weight ratio of the first additive to the second additive is in the range from 6:1 to 2:1.