(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 184 612 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.06.2017 Bulletin 2017/26

(51) Int Cl.:
C10L 1/23 (2006.01) *C10L 10/12* (2006.01)

(21) Application number: 15201686.1

(22) Date of filing: 21.12.2015

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(71) Applicant: Shell Internationale Research Maatschappij B.V.
2596 HR Den Haag (NL)

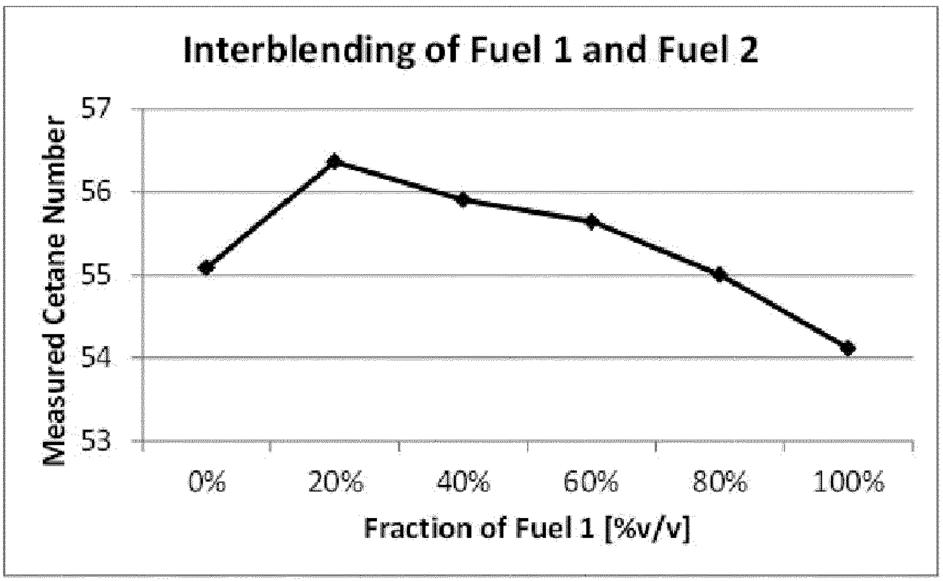
(72) Inventor: Stradling, Richard James
Manchester M22 0RR (GB)

(74) Representative: Matthezing, Robert Maarten et al
Shell International B.V.
Intellectual Property Services
P.O. Box 384
2501 CJ The Hague (NL)

(54) PROCESS FOR PREPARING A DIESEL FUEL COMPOSITION

(57) Process for preparing a diesel fuel composition comprising the steps of:
(i) providing a first diesel base fuel, wherein the first diesel base fuel comprises a first cetane improver and wherein the first diesel base fuel has a cetane number C_1;
(ii) providing a second diesel base fuel, wherein the second diesel base fuel optionally comprises a second cetane improver and wherein the second diesel base fuel has a cetane number C_2;
wherein the first cetane improver provides a cetane number increase to the first diesel base fuel of ΔC_1 and wherein the second cetane improver provides a cetane number increase to the second diesel base fuel of ΔC_2 and wherein $\Delta C_1 > \Delta C_2$; and
(iii) blending the first diesel base fuel with the second diesel base fuel in a volume ratio of $V_1:V_2$ to produce a diesel fuel composition having a cetane number C_{final} wherein $C_{final} > (V_1C_1 + V_2C_2)/(V1+V_2)$.

Figure 1



Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The present invention relates to a process for preparing a diesel fuel composition, in particular to a process for preparing a diesel fuel composition where the diesel fuel composition so prepared has an increased cetane number.

Background of the Invention

[0002] The cetane number of a fuel composition is a measure of its ease of ignition and combustion. With a lower cetane number fuel, a compression ignition (diesel) engine tends to be more difficult to start and may run more noisily when cold; conversely a fuel of higher cetane number tends to impart easier cold starting, to lower engine noise and to alleviate white smoke ("cold smoke") caused by incomplete combustion.

[0003] There is a general preference, therefore, for a diesel fuel composition to have a high cetane number, a preference which has become stronger as emissions legislation grows increasingly stringent, and as such automotive diesel specifications generally stipulate a minimum cetane number. To this end, many diesel fuel compositions contain ignition improvers, also known as cetane boost additives or cetane (number) improvers/enhancers, to ensure compliance with such specifications and generally to improve the combustion characteristics of the fuel.

[0004] Organic nitrates have been known for some time as ignition accelerants in fuels, and some are also known to increase the cetane number of diesel fuels. Perhaps the most commonly used diesel fuel ignition improver is 2-ethylhexyl nitrate (2-EHN), which operates by shortening the ignition delay of a fuel to which it is added.

[0005] It is known to blend diesel fuels together in order to obtain diesel fuel blends. Sometimes these diesel fuel blends have improved properties over either of the starting diesel fuels.

[0006] Cetane blending is a practice which involves the blending of two or more fuels, each having a certain cetane number. Cetane blending is normally considered to follow a linear-by-volume rule. This is the case for diesel fuels which don't contain 2-EHN cetane improvers or fuels that contain relatively similar 2-EHN concentrations.

[0007] It has now surprisingly been found that if a diesel base fuel containing zero or low levels of cetane improver is blended with a diesel base fuel containing a high concentration of cetane improver, a beneficial non-linear response can be achieved, thereby obtaining a cetane number that is greater than the cetane numbers of either of the starting diesel base fuels.

Summary of the Invention

[0008] According to the present invention there is provided a process for preparing a diesel fuel composition comprising the steps of:

(i) providing a first diesel base fuel, wherein the first diesel base fuel comprises a first cetane improver and wherein the first diesel base fuel comprising the first cetane improver has a cetane number C_1;
(ii) providing a second diesel base fuel, wherein the second diesel base fuel optionally comprises a second cetane improver, and wherein the second diesel base fuel optionally comprising the second cetane improver has a cetane number C_2;

wherein the first cetane improver provides a cetane number increase to the first diesel base fuel of Δc_1 and wherein the second cetane improver, when present, provides a cetane number increase to the second diesel base fuel of Δc_2 and wherein $\Delta c_1 > \Delta c_2$; and (iii) blending the first diesel base fuel with the second diesel base fuel in a volume ratio of v_1:v_2 to produce a diesel fuel composition having a cetane number C_{final} wherein $C_{final} > (v_1c_1 + v_2c_2)/(v_1+v_2)$.

[0009] It has been found that the process of the present invention leads to diesel fuel compositions which have much higher cetane numbers than would have been expected if a conventional linear-by-volume rule had been applied to the blending process.

[0010] Suitably, the process of the present invention has the effect of increasing the cetane number of the diesel fuel composition, such as to a desired or target cetane number.

[0011] According to another aspect of the present invention there is provided a method for increasing the cetane number of a diesel fuel composition obtained by blending at least two diesel base fuels wherein the method comprises:

(i) providing a first diesel base fuel, wherein the first diesel base fuel comprises a first cetane improver and wherein the first diesel base fuel has a cetane number c_1;
(ii) providing a second diesel base fuel, wherein the second diesel base fuel optionally comprises a second cetane improver and wherein the second diesel base fuel has a cetane number C_2;

wherein the first cetane improver provides a cetane number increase to the first diesel base fuel of Δc_1 and wherein the second cetane improver, when present, provides a cetane number increase to the second diesel base fuel of Δc_2 and wherein $\Delta c_1 > \Delta c_2$; and (iii) blending the first diesel base fuel with the second diesel base fuel in a volume ratio of $v_1:v_2$ to produce a diesel fuel composition having a cetane number C_{final} wherein $C_{final} > (v_1c_1 + v_2c_2)/(v_1+v_2)$.

[0012] The process and method of the present invention may additionally or alternatively be used to adjust any property of the fuel composition which is equivalent to or associated with cetane number, for example, to improve the combustion performance of the fuel composition, e.g. to modify/shorten ignition delays (i.e. the time between fuel injection and ignition in a combustion chamber during use of the fuel), to facilitate cold starting or to reduce incomplete combustion and/or associated emissions in a fuel-consuming system running on the fuel composition, and/or to improve fuel economy or exhaust emissions generally.

Detailed Description of the Drawings

[0013] Figure 1 is a graphical representation of the results shown in Table 1 below.

Detailed Description of the Invention

[0014] In order to assist with the understanding of the invention several terms are defined herein.

[0015] The term "diesel fuel composition" as used herein is a fuel composition in liquid form suitable for use in a diesel/compression ignition internal combustion engine.

[0016] The terms "cetane (number) improver" and "cetane (number) enhancer" are used interchangeably to encompass any component that, when added to a fuel composition at a suitable concentration, has the effect of increasing the cetane number of the fuel composition relative to its previous cetane number under one or more engine conditions within the operating conditions of the respective fuel or engine. As used herein, a cetane number improver or enhancer may also be referred to as a cetane number increasing additive / agent or the like.

[0017] In accordance with the present invention, the cetane number of a fuel composition may be determined in any known manner, for instance using the standard test procedure ASTM D613 (ISO 5165, IP 41) which provides a so-called "measured" cetane number obtained under engine running conditions. More preferably the cetane number may be determined using the more recent and accurate "ignition quality test" (IQT; ASTM D6890, IP 498), which provides a "derived" cetane number based on the time delay between injection and combustion of a fuel sample introduced into a constant volume combustion chamber. This relatively rapid technique can be used on laboratory scale (ca 100 ml) samples of a range of different fuels.

[0018] The person skilled in the art will appreciate that other instruments may be available in the future to measure derived cetane number.

[0019] Alternatively, cetane number may be measured by near infrared spectroscopy (NIR), as for example described in US5349188. This method may be preferred in a refinery environment as it can be less cumbersome than for instance ASTM D613. NIR measurements make use of a correlation between the measured spectrum and the actual cetane number of a sample. An underlying model is prepared by correlating the known cetane numbers of a variety of fuel samples with their near infrared spectral data.

[0020] In some embodiments, the process of the present invention is carried out so as to adjust the cetane number of the resulting diesel fuel composition or to achieve or reach a desired target cetane number for the resulting diesel fuel composition. In the context of the invention, to "reach" a target cetane number can also embrace exceeding that number. Thus, the target cetane number may be a target minimum cetane number.

[0021] The present invention suitably results in a fuel composition which has a derived cetane number (IP 498) of 40 or greater, preferably 50 or greater, more preferably of 51, 52, 53, 54 or 55 or greater. For example, in some embodiments the resultant fuel composition may have a cetane number of 60 or greater, 65 or greater or even 70 or greater.

[0022] The present invention may additionally or alternatively be used to adjust any property of the fuel composition which is equivalent to or associated with cetane number, for example, to improve the combustion performance of the fuel composition, e.g. to shorten ignition delays (i.e. the time between fuel injection and ignition in a combustion chamber during use of the fuel), to facilitate cold starting or to reduce incomplete combustion and/or associated emissions in a fuel-consuming system running on the fuel composition and/or to improve fuel economy or exhaust emissions generally.

[0023] The process of the present invention may be used to increase the cetane number of a diesel fuel composition. As used herein, an "increase" in the context of cetane number embraces any degree of increase compared to a previously measured cetane number under the same or equivalent conditions. Thus, the increase is suitably compared to the cetane number of an analogous fuel composition which has not been prepared according to the process of the present invention, or compared to the cetane number which would have been expected if at least two diesel base fuels were blended to produce a diesel fuel composition and if a conventional linear-by-volume rule had been applied to the blending process.

[0024] Alternatively, an increase in cetane number of a fuel relative to a comparative fuel may be inferred by a measured increase in combustibility or a measured decrease in ignition delay for the comparative fuels.

[0025] The increase in cetane number (or the decrease in ignition delay, for example) may be measured and/or reported in any suitable manner, such as in terms of a percentage increase or decrease, or such as in terms of an increase in cetane number units.

[0026] By way of example, the increase in cetane number may be at least 0.1 cetane number units, such as at least 0.5 cetane number units. Suitably, the increase in cetane number is at least 1 cetane number units, at least 2 cetane number units, at least 3 cetane number units, at least 4 cetane number units or at least 5 cetane number units. In some embodiments the increase in cetane number may be at least 9 or 10 cetane number units, or even at least 15 cetane number units. However, it should be appreciated that any measurable improvement in cetane number or modification of ignition delay may provide a worthwhile advantage, depending on what other factors are considered important, e.g. availability, cost, safety and so on.

[0027] The process of the present invention comprises the blending of two diesel base fuels, namely a first diesel base fuel and a second diesel base fuel.

[0028] The first diesel base fuel comprises a first cetane improver, preferably at a level of 0.01 wt% or greater, more preferably at a level of 0.05% or greater, and especially at a level of 0.1 wt% or greater, by weight of the first diesel base fuel. In one embodiment of the present invention the first diesel base fuel comprises a first cetane improver at a level of 0.3 wt% or greater, preferably 0.5 wt% or greater, by weight of the first diesel base fuel. The first diesel base fuel comprising the first cetane improver has a cetane number c_1.

[0029] The second diesel base fuel optionally comprises a second cetane improver. The second cetane improver can be present in the second diesel base fuel preferably at a level of 0.2 wt% or less, more preferably at a level of 0.1 wt% or less, even more preferably at a level of 0.05 wt% or less, and especially at a level of 0.01 wt% or less, by weight of the second diesel base fuel.

[0030] In a preferred embodiment of the present invention the second diesel base fuel is free of cetane improver.

[0031] The second diesel base fuel optionally comprising the second cetane improver has a cetane number c_2.

[0032] The first cetane improver can be any cetane improver suitable for use in a diesel fuel composition. A preferred first cetane improver is selected from nitrates, nitroalkanes, nitrocarbonates, peroxides, and mixtures thereof.

[0033] The second cetane improver can be any cetane improver suitable for use in a diesel fuel composition. A preferred second cetane improver is selected from nitrates, nitroalkanes, nitrocarbonates, peroxides, and mixtures thereof.

[0034] In one embodiment of the present invention the first cetane improver is the same as the second cetane improver.

[0035] In another embodiment of the present invention the first cetane improver is a nitrate, preferably 2-ethylhexyl nitrate.

[0036] In one embodiment of the present invention, the second diesel base fuel comprises a second cetane improver which is a nitrate, preferably 2-ethylhexyl nitrate.

[0037] The first cetane improver provides a cetane number increase to the first diesel base fuel of Δc_1. The second cetane improver provides a cetane number increase to the second diesel base fuel of Δc_2. In the process of the present invention $\Delta c_1 > \Delta c_2$. In the case where the second diesel base fuel is free of cetane improver, Δc_2 will be zero.

[0038] According to the process of the present invention, the first diesel base fuel is blended with the second diesel base fuel in a volume ratio of $v_1:v_2$ to produce a diesel fuel composition having a cetane number C_{final} wherein $C_{final} > (v_1c_1 + v_2c_2) /(v_1+v_2)$.

[0039] In a preferred embodiment of the present invention, $C_{final} > c_1$ and $C_{final} > C_2$.

[0040] The relative proportions of the two diesel base fuels, and any other components or additives present in a diesel fuel composition prepared according to the invention, may depend on other desired properties such as density, emissions performance and viscosity. In a preferred embodiment of the present invention, the first diesel base fuel is blended with the second diesel base fuel in a volume ratio in the range from 5:95 to 30:70, preferably in the range from 10:90 to 20:80.

[0041] In one embodiment of the present invention, the first diesel base fuel can itself be a blend of two or more diesel base fuels each optionally containing one or more cetane improvers. In another embodiment of the present invention, the second diesel base fuel can itself be a blend of two or more diesel base fuels each optionally containing one or more cetane improvers.

[0042] In a further embodiment of the present invention, the resulting diesel fuel formulation which is prepared according to the process of the present invention may be blended with one or more further diesel base fuels each optionally containing one or more cetane improvers before being used as a diesel fuel. In the latter embodiment, the diesel fuel formulation produced in step (iii) of the process of the present invention has a cetane number C_{final} and the further diesel base fuel optionally comprising one or more cetane improvers has a cetane number c_4. In the latter embodiment, the diesel fuel formulation produced in step (iii) is blended with the further diesel base fuel in a volume ratio of $v_3:v_4$ to produce a diesel fuel composition having a cetane number C_x wherein $C_x > (v_3C_{final} + v_4c_4)/(v_3 + v_4)$. The resulting diesel fuel composition produced in the latter embodiment can be blended with a further one or more further diesel base fuels each optionally containing one or more cetane improvers before being used as a diesel fuel, i.e. the process can be repeated as many times as desired, i.e. in a 'recursive' process.

[0043] The diesel base fuels used in the process of the present invention are diesel base fuels for use in automotive compression ignition engines, as well as in other types of engine such as for example off road, marine, railroad and stationary engines.

[0044] Such diesel base fuels will contain one or more base fuels which may typically comprise liquid hydrocarbon middle distillate gas oil(s), for instance petroleum derived gas oils. Such fuels will typically have boiling points within the usual diesel range of 150 to 400°C, depending on grade and use. They will typically have a density from 750 to 1000 kg/m^3, preferably from 780 to 860 kg/m^3, at 15°C (e.g. ASTM D4502 or IP 365) and a cetane number (ASTM D613) of from 35 to 120, more preferably from 40 to 85. They will typically have an initial boiling point in the range 150 to 230°C and a final boiling point in the range 290 to 400°C. Their kinematic viscosity at 40°C (ASTM D445) might suitably be in the range from 1.2 to 6, or in the range from 1.2 to 5, or in the range from 1.2 to 4.5 mm^2/s.

[0045] An example of a petroleum derived gas oil is a Swedish Class 1 base fuel, which will have a density from 800 to 820 kg/m^3 at 15°C (SS-EN ISO 3675, SS-EN ISO 12185), a T95 of 320°C or less (SS-EN ISO 3405) and a kinematic viscosity at 40°C (SS-EN ISO 3104) from 1.4 to 4.0 mm^2/s, as defined by the Swedish national specification EC1.

[0046] Optionally, non-mineral oil based fuels, such as biofuels or Fischer-Tropsch derived fuels, may also form or be present in the diesel fuel. Such Fischer-Tropsch fuels may for example be derived from natural gas, natural gas liquids, petroleum or shale oil, petroleum or shale oil processing residues, coal or biomass.

[0047] The amount of Fischer-Tropsch derived fuel used in the diesel fuel may be from 0% to 100%v of the overall diesel fuel, preferably from 5% to 100%v, more preferably from 5% to 75%v. It may be desirable for such a diesel fuel to contain 10%v or greater, more preferably 20%v or greater, still more preferably 30%v or greater, of the Fischer-Tropsch derived fuel. It is particularly preferred for such diesel fuels to contain 30 to 75%v, and particularly 30 to 70%v, of the Fischer-Tropsch derived fuel. The balance of the diesel fuel is made up of one or more other diesel fuel components.

[0048] Such a Fischer-Tropsch derived fuel component is any fraction of the middle distillate fuel range, which can be isolated from the (optionally hydrocracked) Fischer-Tropsch synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably, a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these products are easier to handle in for example domestic environments. Such products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400°C, preferably between 160 and about 370°C. Examples of Fischer-Tropsch derived kerosene and gas oils are described in EP-A-0583836, WO-A-97/14768, WO-A-97/14769, WO-A-00/11116, WO-A-00/11117, WO-A-01/83406, WO-A-01/83648, WO-A-01/83647, WO-A-01/83641, WO-A-00/20535, WO-A-00/20534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

[0049] The Fischer-Tropsch product will suitably contain more than 80 wt% and more suitably more than 95 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenic compounds. The content of sulphur and nitrogen will be very low and normally below the detection limits for such compounds. For this reason the sulphur content of a diesel fuel composition containing a Fischer-Tropsch product may be very low.

[0050] The diesel fuel composition preferably contains no more than 5000 ppmw sulphur, more preferably no more than 500 ppmw, or no more than 350 ppmw, or no more than 150 ppmw, or no more than 100 ppmw, or no more than 70 ppmw, or no more than 50 ppmw, or no more than 30 ppmw, or no more than 20 ppmw, or no more than 15 ppmw, or most preferably no more than 10 ppmw sulphur.

[0051] Other diesel fuel components for use herein include the so-called "biofuels" which derive from biological materials. Examples include fatty acid alkyl esters (FAAE). Examples of such components can be found in WO2008/135602.

[0052] Each diesel base fuel may itself be additivated (additive-containing) or unadditivated (additive-free). If additivated, e.g. at the refinery, it will contain minor amounts of one or more additives selected for example from anti-static agents, pipeline drag reducers, flow improvers (e.g. ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers), lubricity additives, antioxidants and wax anti-settling agents.

[0053] Preferably, the diesel fuel composition prepared according to the process of the present invention comprises a performance additive package comprising one or more additive components. The amount of the performance package present in the liquid fuel composition herein is in the range of 15 ppmw (parts per million by weight) to 10 %wt, based on the overall weight of the diesel fuel composition. More preferably, the amount of the performance package present in the diesel fuel composition herein additionally accords with one or more of the parameters (i) to (xv) listed below:

(i) at least 100 ppmw
(ii) at least 200 ppmw
(iii) at least 300 ppmw
(iv) at least 400 ppmw
(v) at least 500 ppmw
(vi) at least 600 ppmw
(vii) at least 700 ppmw
(viii)at least 800 ppmw
(ix) at least 900 ppmw

(x) at least 1000 ppmw
(xi) at least 2500 ppmw
(xii) at most 5000 ppmw
(xiii)at most 10000 ppmw
(xiv) at most 2 %wt
(xv) at most 5 %wt.

[0054] Typically, the diesel fuel composition and/or the performance additive package may contain additive components such as detergents, anti-foaming agents, corrosion inhibitors, dehazers etc.

[0055] Detergent-containing diesel fuel additives are known and commercially available. Such additives may be added to diesel fuels at levels intended to reduce, remove, or slow the build-up of engine deposits.

[0056] Examples of detergents suitable for use in diesel fuel additives for the present purpose include polyolefin substituted succinimides or succinimides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinimides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides.

[0057] Other examples of detergents suitable for use in diesel fuel additives for the present purpose include compounds having at least one hydrophobic hydrocarbon radical having a number-average molecular weight (Mn) of from 85 to 20 000 and at least one polar moiety selected from:

(A1) mono- or polyamino groups having up to 6 nitrogen atoms, of which at least one nitrogen atom has basic properties; and/or
(A9) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

[0058] Other detergents suitable for use in diesel fuel additives for the present purpose include quaternary ammonium salts such as those disclosed in US2012/0102826, US2012/0010112, WO2011/149799, WO2011/110860, WO2011/095819 and WO2006/135881.

[0059] The diesel fuel additive mixture may contain other components in addition to the detergent. Examples are lubricity enhancers; dehazers, e.g. alkoxylated phenol formaldehyde polymers; anti-foaming agents (e.g. polyether-modified polysiloxanes); 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 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; cold flow improvers; organic sunscreen compound, and wax anti-settling agents.

[0060] The diesel fuel additive mixture may contain one or more organic sunscreen compounds, such as those disclosed in European patent application no. 12199119.4. A wide variety of conventional organic sunscreen actives are suitable for use herein. Sagarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology (1972), discloses numerous suitable actives.

[0061] The diesel fuel additive mixture may contain a lubricity enhancer, especially when the diesel fuel composition has a low (e.g. 500 ppmw or less) sulphur content. In the additivated diesel fuel composition, the lubricity enhancer is conveniently present at a concentration of less than 1000 ppmw, preferably between 50 and 1000 ppmw, more preferably between 70 and 1000 ppmw. Suitable commercially available lubricity enhancers include ester- and acid-based additives. Other lubricity enhancers are described in the patent literature, in particular in connection with their use in low sulphur content diesel fuels, for example in:

- the paper by Danping Wei and H.A. Spikes, "The Lubricity of Diesel Fuels", Wear, III (1986) 217-235;
- WO-A-95/33805 - cold flow improvers to enhance lubricity of low sulphur fuels;
- US-A-5490864 - certain dithiophosphoric diester-dialcohols as anti-wear lubricity additives for low sulphur diesel fuels; and
- WO-A-98/01516 - certain alkyl aromatic compounds having at least one carboxyl group attached to their aromatic nuclei, to confer anti-wear lubricity effects particularly in low sulphur diesel fuels.

[0062] It may also be preferred for the diesel fuel composition to contain an anti-foaming agent, more preferably in combination with an anti-rust agent and/or a corrosion inhibitor and/or a lubricity enhancing additive.

[0063] Unless otherwise stated, the (active matter) concentration of each such optional additive component in the additivated diesel fuel composition is preferably up to 10000 ppmw, more preferably in the range from 0.1 to 1000 ppmw, advantageously from 0.1 to 300 ppmw, such as from 0.1 to 150 ppmw.

[0064] The (active matter) concentration of any dehazer in the diesel fuel composition will preferably be in the range from 0.1 to 20 ppmw, more preferably from 1 to 15 ppmw, still more preferably from 1 to 10 ppmw, and especially from 1 to 5 ppmw. The (active matter) concentration of any detergent in the diesel fuel composition will preferably be in the range from 5 to 1500 ppmw, more preferably from 10 to 750 ppmw, most preferably from 20 to 500 ppmw.

[0065] In the case of a diesel fuel composition, for example, the fuel additive mixture will typically contain a detergent, optionally together with other components as described above, and a diesel fuel-compatible diluent, which may be a mineral oil, a solvent such as those sold by Shell companies under the trade mark "SHELLSOL", a polar solvent such as an ester and, in particular, an alcohol, e.g. hexanol, 2-ethylhexanol, decanol, isotridecanol and alcohol mixtures such as those sold by Shell companies under the trade mark "LINEVOL", especially LINEVOL 79 alcohol which is a mixture of C_{7-9} primary alcohols, or a C_{12-14} alcohol mixture which is commercially available.

[0066] The total content of the additives in the diesel fuel composition may be suitably between 0 and 10000 ppmw and preferably below 5000 ppmw.

[0067] In the above, amounts (concentrations, % vol, ppmw, % wt) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

[0068] The engine in which the fuel composition herein is used may be any appropriate engine. Thus, where the fuel is a diesel or biodiesel fuel composition, the engine is a diesel or compression ignition engine. Likewise, any type of diesel engine may be used, such as a turbo charged diesel engine, provided the same or equivalent engine is used to measure cetane number/ignition delay/burn period for each diesel fuel composition being assessed. Similarly, the invention is applicable to an engine in any vehicle.

[0069] The present invention will be further understood from the following examples. Unless otherwise stated, all amounts and concentrations disclosed in the examples are based on weight of the fully formulated fuel composition.

<u>Examples</u>

[0070] In the examples below, two different diesel fuels (Fuel 1 and Fuel 2) were blended together using conventional blending techniques in the fractions (%v/v) shown in Table 1 below. Fuel 1 contains 0.12% v/v of 2-EHN and has a cetane number of 54.1. Fuel 2 is free of cetane improver and has a cetane number of 55.1. The cetane number of each blend is determined using the "Ignition Quality Test" (IQT; according to ASTM D6890, IP 498) which provides a "derived" cetane number based on the time delay between injection and combustion of a fuel sample introduced into a constant volume combustion chamber. The results of these cetane measurements for Fuel 1, Fuel 2 and four different blends (containing 20%v/v, 40%v/v, 60%v/v and 80%v/v of Fuel 1) are shown in Table 1 below.

<u>Table 1</u>

Fraction of Fuel 1 [%v/v]	0%	20%	40%	60%	80%	100%
Fraction of Fuel 2 [%v/v]	100%	80%	60%	40%	20%	0%
Measured Cetane Number	55.1	56.4	55.9	55.6	55.0	54.1

[0071] The results from Table 1 are plotted on a graph (see Figure 1). From Figure 1 it can be clearly seen that when Fuel 2 (containing no cetane improver) is blended with a diesel fuel containing a high concentration of cetane improver (Fuel 1 containing 0.12%v/v 2-EHN), a beneficial non-linear response can be achieved, thereby obtaining a diesel blend which has a cetane number that is greater than either of the starting diesel fuels.

Claims

1. Process for preparing a diesel fuel composition comprising the steps of:

(i) providing a first diesel base fuel, wherein the first diesel base fuel comprises a first cetane improver and wherein the first diesel base fuel comprising the first cetane improver has a cetane number c_1;
(ii) providing a second diesel base fuel, wherein the second diesel base fuel comprises a second cetane improver and wherein the second diesel base fuel optionally comprising the second cetane improver has a cetane number c_2;
wherein the first cetane improver provides a cetane number increase to the first diesel base fuel of Δc_1 and wherein the second cetane improver provides a cetane number increase to the second diesel base fuel of Δc_2 and wherein $\Delta c_1 > \Delta c_2$; and

(iii) blending the first diesel base fuel with the second diesel base fuel in a volume ratio of v_1:v_2 to produce a diesel fuel composition having a cetane number C_{final} wherein $C_{final} > (v_1c_1 + v_2c_2)/(v_1+v_2)$.

2. Process according to Claim 1 wherein the first cetane improver is selected from nitrates, nitroalkanes, nitrocarbonates, peroxides, and mixtures thereof.

3. Process according to Claim 1 or 2 wherein the second cetane improver is selected from nitrates, nitroalkanes, nitrocarbonates, peroxides, and mixtures thereof.

4. Process according to any of Claims 1 to 3 wherein the first cetane improver is the same as the second cetane improver.

5. Process according to any of Claims 1 to 4 wherein the first cetane improver is a nitrate, preferably 2-ethylhexyl nitrate.

6. Process according to any of Claims 1 to 5 wherein the second cetane improver is a nitrate, preferably 2-ethylhexyl nitrate.

7. Process according to any of Claims 1 to 6 wherein the first diesel base fuel comprises 0.01 wt% or greater, by weight of the first diesel base fuel, of the first cetane improver.

8. Process according to any of Claims 1 to 7 wherein the second diesel base fuel comprises 0.2 wt% or less, by weight of the second diesel base fuel, of the second cetane improver.

9. Process according to any of Claims 1 to 8 wherein the second diesel base fuel is free of cetane improver.

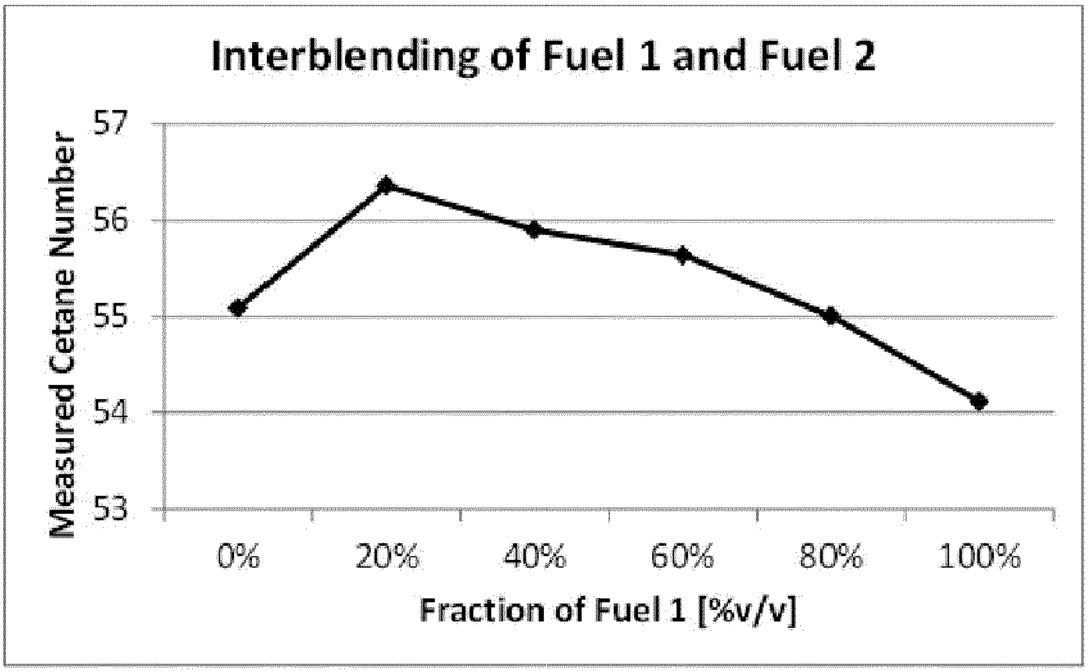
10. Process according to any of Claims 1 to 9 wherein the first diesel base fuel is blended with the second diesel base fuel in a volume ratio in the range from 5:95 to 30:70, preferably in the range from 10:90 to 20:80.

11. Process according any of Claims 1 to 10 wherein $C_{final} > c_1$ and $C_{final} > c_2$.

12. Method for increasing the cetane number of a diesel fuel composition obtained by blending at least two diesel base fuels wherein the method comprises:

(i) providing a first diesel base fuel, wherein the first diesel base fuel comprises a first cetane improver and wherein the first diesel base fuel comprising the first cetane improver has a cetane number c_1;
(ii) providing a second diesel base fuel, wherein the second diesel base fuel comprises a second cetane improver and wherein the second diesel base fuel comprising the second cetane improver has a cetane number C_2; wherein the first cetane improver provides a cetane number increase to the first diesel base fuel of Δc_1 and wherein the second cetane improver provides a cetane number increase to the second diesel base fuel of Δc_2 and wherein $\Delta c_1 > \Delta c_2$; and
(iii) blending the first diesel base fuel with the second diesel base fuel in a volume ratio of v_1:v_2 to produce a diesel fuel composition having a cetane number C_{final} wherein $C_{final} > (v_1c_1 + v_2c_2)/(v_1+v_2)$.

Figure 1



Interblending of Fuel 1 and Fuel 2
Measured Cetane Number
57
56
55
54
53
0%
20%
40%
60%
80%
100%
Fraction of Fuel 1 [%v/v]

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 15 20 1686

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 5 482 518 A (POIRIER MARC-ANDRE [CA]) 9 January 1996 (1996-01-09) * column 3, line 26 - column 5, line 22 * * examples; tables * -----	1-3,5,7, 8,10-12	INV. C10L1/23 C10L10/12
X	US 2 912 313 A (HINKAMP JAMES B ET AL) 10 November 1959 (1959-11-10) * column 1, line 71 - column 2, line 14 * * column 4, line 61 - column 6, line 59 * * tables * -----	1-3,7,8, 10-12	
X	WO 2008/000778 A1 (SHELL INT RESEARCH [NL]; CLARK RICHARD HUGH [GB]; STRADLING RICHARD JA) 3 January 2008 (2008-01-03) * examples; tables * -----	1-9,12	

TECHNICAL FIELDS SEARCHED (IPC)

C10L

1

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	23 May 2016	Keipert, Olaf

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 20 1686

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-05-2016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5482518 A	09-01-1996	NONE	
US 2912313 A	10-11-1959	NONE	
WO 2008000778 A1	03-01-2008	AR 061712 A1	17-09-2008
		BR PI0713577 A2	23-10-2012
		CN 101506337 A	12-08-2009
		EP 2038381 A1	25-03-2009
		JP 5550335 B2	16-07-2014
		JP 2009541560 A	26-11-2009
		SG 175556 A1	28-11-2011
		US 2008033220 A1	07-02-2008
		WO 2008000778 A1	03-01-2008

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5349188 A **[0019]**
- EP 0583836 A **[0048]**
- WO 9714768 A **[0048]**
- WO 9714769 A **[0048]**
- WO 0011116 A **[0048]**
- WO 0011117 A **[0048]**
- WO 0183406 A **[0048]**
- WO 0183648 A **[0048]**
- WO 0183647 A **[0048]**
- WO 0183641 A **[0048]**
- WO 0020535 A **[0048]**
- WO 0020534 A **[0048]**
- EP 1101813 A **[0048]**
- US 5766274 A **[0048]**
- US 5378348 A **[0048]**
- US 5888376 A **[0048]**
- US 6204426 A **[0048]**
- WO 2008135602 A **[0051]**
- GB 960493 A **[0056]**
- EP 0147240 A **[0056]**
- EP 0482253 A **[0056]**
- EP 0613938 A **[0056]**
- EP 0557516 A **[0056]**
- WO 9842808 A **[0056]**
- US 20120102826 A **[0058]**
- US 20120010112 A **[0058]**
- WO 2011149799 A **[0058]**
- WO 2011110860 A **[0058]**
- WO 2011095819 A **[0058]**
- WO 2006135881 A **[0058]**
- EP 12199119 A **[0060]**
- WO 9533805 A **[0061]**
- US 5490864 A **[0061]**
- WO 9801516 A **[0061]**

Non-patent literature cited in the description

- **SAGARIN et al.** Cosmetics Science and Technology. 1972, 189 **[0060]**
- **DANPING WEI ; H.A. SPIKES.** The Lubricity of Diesel Fuels. *Wear,* 1986, vol. III, 217-235 **[0061]**