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(54) **Fuel compositions**

(57) Use, in a fuel composition comprising a middle
distillate base fuel and a cold flow additive, of a Fischer-
Tropsch derived gas oil component for the purpose of
reducing the cold filter plugging point of said composition;

preparation of such a fuel composition; and operating a
fuel consuming system.

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Description

[0001] The present invention relates to fuel compositions and to their preparation and use, particularly to the use of combinations of certain types of fuel additives and components in such fuel compositions.

[0002] Low temperature operability is an important property of diesel fuels. In low winter temperatures, some of the longer chain hydrocarbons can solidify as waxes that may block filters or cause the fuel to gel and impede the free flow of fuel to an engine.

[0003] A number of tests is available to predict the low temperature operability of a fuel, namely Cloud Point, Cold Filter Plugging Point (CFPP), Pour Point and Low Temperature Flow Test. In Europe, CFPP is generally recognised as the best predictor of such operability, or cold flow performance.

[0004] Refineries may struggle to meet cold operability limits demanded by customers or by national certification bodies. They may employ cold flow additives, e.g. Middle Distillate Flow Improvers (MDFIs) or Wax Anti-Settling Agents (WASAs), to reduce the CFPP to an acceptable level.

[0005] Many Fischer-Tropsch derived diesel fuels, which are predominantly paraffinic, have rather poorer cold operability characteristics, e.g. Cloud Point or CFPP, than those of conventional, petroleum derived, diesel fuel, and are unresponsive to treatment with cold flow additives. Such properties can be improved by increasing, by hydrocracking, the degree of branching in the paraffins of said Fischer-Tropsch derived diesel fuel, so as to render it more suitable for use in severe winter conditions.

[0006] In recent years, there have been increasing legislative and environmental demands on middle distillate fuels, such as automotive gas oil (AGO) or industrial gas oil (IGO) and kerosene, and advancing vehicle technology. Furthermore, the addition of alternative components, such as fatty acid methyl esters (FAME), and the usage of high detergent dose rates, has been found to lead to a further deterioration in the cold flow properties, specifically the CFPP. Therefore, it has been found increasingly difficult to meet the stringent cold flow properties. Accordingly there is a need to be able to improve the response of middle distillate fuels to cold flow additives.

[0007] In "Increasing the Responsiveness of No. 2-D Diesel Fuels to Flow Improvers by Blending with Low Wax Diluents", Reddy, SAE 841351, Society of Automotive Engineers, 1984, it is described that the combined use of certain diluents and flow improvers synergistically reduced the filter plugging temperatures of No. 2-D fuels. The diluents described are a No. 1-D diesel fuel, a tar sands derived fuel, and an unleaded gasoline. However, there is no mention of the use of a Fischer-Tropsch derived gas oil component for the purpose of reducing the CFPP of a fuel composition which contains a flow improver.

[0008] It has now been surprisingly been found that a Fischer-Tropsch derived gas oil component, that has little or no effect on the CFPP of a middle distillate base fuel, for example a petroleum derived gas oil containing no cold flow additive, has the effect of reducing the CFPP of said middle distillate base fuel that does contain a cold flow additive. Moreover, it has surprisingly been found that when the CFPP of such a middle distillate base fuel containing a cold flow additive cannot be reduced any further by the inclusion of more cold flow additive, it can in fact be reduced further by the inclusion of a Fischer-Tropsch derived gas oil component.

[0009] The present invention relates to a fuel composition comprising a middle distillate base fuel, a cold flow additive, and a Fischer-Tropsch derived gas oil component.

[0010] "Base fuel" is defined as being a material that is in accordance with one or more published base fuel standard specifications.

[0011] Preferably, said one or more published base fuel standard specifications are selected from EN 590, Swedish Class 1 (as defined by the Swedish Standard for EC1), ASTM D975 and Defence Standard 91-91 (Def Stan 91-91) specifications. EN 590:2004 is the current European Standard for diesel fuels. SS 155435:2006 is the current Swedish Standard for EC1. ASTM D975-07a is the current United States Standard Specification for Diesel Fuel Oils. Def Stan 91-91 Issue 5 Amendment 2 is the current UK standard for Turbine Fuel, Aviation Kerosine Type, Jet A-1.

[0012] In accordance with the present invention there is provided the use, in a fuel composition comprising a middle distillate base fuel and a cold flow additive, of a Fischer-Tropsch derived gas oil component for the purpose of reducing the cold filter plugging point of said composition.

[0013] Preferably, the (active matter) concentration of the Fischer-Tropsch derived gas oil component in a fuel composition according to the present invention will be up to 30 %vol, more preferably up to 25 %vol, most preferably up to 20 %vol. Its (active matter) concentration will preferably be at least 1 %vol, more preferably at least 5 %vol, most preferably at least 10 %vol.

[0014] In the case, for example, of a diesel fuel composition intended for use in an automotive engine, a certain level of cold flow performance may be desirable in order for the composition to meet current fuel specifications, and/or to safeguard engine performance, and/or to satisfy consumer demand, in particular in cold climates or seasons.

[0015] In accordance with the present invention, the above-mentioned standard specifications may still be achievable even with reduced levels of cold flow additives, due to the Fischer-Tropsch gas oil component having the effect of reducing the CFPP of a fuel composition containing a middle distillate base fuel and a cold flow additive.

[0016] Middle distillate fuel compositions for which the present invention is used may include for example heating oils, industrial gas oils, automotive diesel fuels, distillate marine fuels or kerosene fuels such as aviation fuels or heating kerosene. Typically the composition will be either an automotive diesel fuel or a heating oil. Preferably, the fuel composition to which the present invention is applied is for use in an internal combustion engine; more preferably, it is an automotive fuel composition, yet more preferably a diesel fuel composition which is suitable for use in an automotive diesel (compression ignition) engine.

[0017] The fuel composition may in particular be adapted for, and/or intended for, use in colder climates and/or during colder seasons (for example, it may be a so-called "winter fuel").

[0018] In the context of the present invention, a middle distillate base fuel will typically contain a major proportion of, or consist essentially or entirely of, a middle distillate hydrocarbon base fuel. A "major proportion" means typically 80 %vol or greater, more suitably 90 or 95 %vol or greater, most preferably 98 or 99 or 99.5 %vol or greater.

[0019] The fuel compositions to which the present invention relates include diesel fuels for use in automotive compression ignition engines, as well as in other types of engine such as for example marine, railroad and stationary engines, and industrial gas oils for use in heating applications (e.g. boilers).

[0020] The base fuel may itself comprise a mixture of two or more different diesel fuel components, and/or be additivated as described below.

[0021] 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/m³, preferably from 780 to 860 kg/m³, 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 from 1.2 to 4.5 mm²/s.

[0022] 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/m³ 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 mm²/s, as defined by the Swedish national specification EC1.

[0023] Such industrial gas oils will contain a base fuel which may comprise fuel fractions such as the kerosene or gas oil fractions obtained in traditional refinery processes, which upgrade crude petroleum feedstock to useful products. Preferably, such fractions contain components having carbon numbers in the range 5 to 40, more preferably 5 to 31, yet more preferably 6 to 25, most preferably 9 to 25, and such fractions have a density at 15°C of 650 to 1000 kg/m³, a kinematic viscosity at 20°C of 1 to 80 mm²/s, and a boiling range of 150 to 400°C.

[0024] Kerosene fuels will typically have boiling points within the usual kerosene range of 130 to 300°C, depending on grade and use. They will typically have a density from 775 to 840 kg/m³, preferably from 780 to 830 kg/m³, at 15°C (e.g. ASTM D4502 or IP 365). They will typically have an initial boiling point in the range 130 to 160°C and a final boiling point in the range 220 to 300°C. Their kinematic viscosity at -20°C (ASTM D445) might suitably be from 1.2 to 8.0 mm²/s.

[0025] Optionally, non-mineral oil based fuels, such as biofuels or Fischer-Tropsch derived fuels, may also form or be present in the fuel composition. 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.

[0026] Such a Fischer-Tropsch derived fuel 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 to 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.

[0027] 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 naphthenics 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 fuel composition containing a Fischer-Tropsch product may be very low.

[0028] The 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 most preferably no more than 15 ppmw sulphur.

[0029] A petroleum derived gas oil may be obtained from refining and optionally (hydro)processing a crude petroleum source. It may be a single gas oil stream obtained from such a refinery process or a blend of several gas oil fractions obtained in the refinery process via different processing routes. Examples of such gas oil fractions are straight run gas oil, vacuum gas oil, gas oil as obtained in a thermal cracking process, light and heavy cycle oils as obtained in a fluid

catalytic cracking unit and gas oil as obtained from a hydrocracker unit. Optionally, a petroleum derived gas oil may comprise some petroleum derived kerosene fraction.

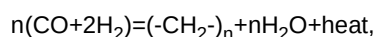
[0030] Such gas oils may be processed in a hydrodesulphurisation (HDS) unit so as to reduce their sulphur content to a level suitable for inclusion in a diesel fuel composition.

[0031] In the present invention, a base fuel may be or contain a so-called "biodiesel" fuel component, such as a vegetable oil or vegetable oil derivative (e.g. a fatty acid ester, in particular a fatty acid methyl ester) or another oxygenate such as an acid, ketone or ester. Such components need not necessarily be bio-derived. It may also contain fuels derived from hydrogenated vegetable oils.

[0032] A base fuel may contain a Fischer-Tropsch derived fuel, in particular a Fischer-Tropsch derived gas oil. Such fuels are known and in use in diesel fuel compositions. They are, or are prepared from, the synthesis products of a Fischer-Tropsch condensation reaction, as for example the commercially used gas oil obtained from the Shell Middle Distillate Synthesis (Gas-To-Liquid) process operating in Bintulu, Malaysia.

[0033] By "Fischer-Tropsch derived" is meant that a fuel is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. A Fischer-Tropsch derived fuel may also be referred to as a GTL (Gas-to-Liquid) fuel.

[0034] The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons :



in the presence of an appropriate catalyst and typically at elevated temperatures (e.g. 125 to 300°C, preferably 175 to 250°C) and/or pressures (e.g. 5 to 100 bar, preferably 12 to 50 bar). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

[0035] The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane. The gases which are converted into liquid fuel components using such processes can in general include natural gas (methane), LPG (e.g. propane or butane), "condensates" such as ethane, synthesis gas (CO/hydrogen) and gaseous products derived from coal, biomass and other hydrocarbons.

[0036] Gas oil, naphtha and kerosene products may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of Fischer-Tropsch synthesis products or from hydrotreated Fischer-Tropsch synthesis products. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, e.g., GB-B-2077289 and EP-A-0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired gas oil fraction(s) may subsequently be isolated for instance by distillation.

[0037] Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in US-A-4125566 and US-A-4478955.

[0038] Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0583836 (pages 3 and 4).

[0039] As indicated above, an example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described by van der Burgt et al in "The Shell Middle Distillate Synthesis Process", paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985 (see also the November 1989 publication of the same title from Shell International Petroleum Company Ltd, London, UK). This process (also sometimes referred to as the Shell "Gas-To-Liquids" or "GTL" technology) produces middle distillate range products by conversion of a natural gas (primarily methane) derived synthesis gas into a heavy long chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. A version of the SMDS process, utilising a fixed bed reactor for the catalytic conversion step, is that currently in use in Bintulu, Malaysia, and its gas oil products have been blended with petroleum derived gas oils in commercially available automotive fuels.

[0040] Gas oils, naphthas and kerosenes prepared by the SMDS process are commercially available for instance from Shell companies.

[0041] By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived fuel has essentially no, or undetectable levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed.

[0042] Generally speaking, Fischer-Tropsch derived fuels have relatively low levels of polar components, in particular

polar surfactants, for instance compared to petroleum derived fuels. Such polar components may include for example oxygenates, and sulphur- and nitrogen-containing compounds. A low level of sulphur in a Fischer-Tropsch derived fuel is generally indicative of low levels of both oxygenates and nitrogen containing compounds, since all are removed by the same treatment processes.

[0043] Where a Fischer-Tropsch derived fuel component is a naphtha fuel, it will be a liquid hydrocarbon distillate fuel with a final boiling point of typically up to 220°C or preferably of 180°C or less. Its initial boiling point is preferably higher than 25°C, more preferably higher than 35°C. Its components (or the majority, for instance 95% w/w or greater, thereof) are typically hydrocarbons having 5 or more carbon atoms; they are usually paraffinic.

[0044] In the context of the present invention, a Fischer-Tropsch derived naphtha fuel preferably has a density of from 0.67 to 0.73 g/cm³ at 15°C and/or a sulphur content of 5 mg/kg or less, preferably 2 mg/kg or less. It preferably contains 95% w/w or greater of iso- and normal paraffins, preferably from 20 to 98% w/w or greater of normal paraffins. It is preferably the product of a SMDS process, preferred features of which may be as described below in connection with Fischer-Tropsch derived gas oils.

[0045] A Fischer-Tropsch derived kerosene fuel is a liquid hydrocarbon middle distillate fuel with a distillation range suitably from 140 to 260°C, preferably from 145 to 255°C, more preferably from 150 to 250°C or from 150 to 210°C. It will have a final boiling point of typically from 190 to 260°C, for instance from 190 to 210°C for a typical "narrow-cut" kerosene fraction or from 240 to 260°C for a typical "full-cut" fraction. Its initial boiling point is preferably from 140 to 160°C, more preferably from 145 to 160°C.

[0046] A Fischer-Tropsch derived kerosene fuel preferably has a density of from 0.730 to 0.760 g/cm³ at 15°C - for instance from 0.730 to 0.745 g/cm³ for a narrow-cut fraction and from 0.735 to 0.760 g/cm³ for a full-cut fraction. It preferably has a sulphur content of 5 mg/kg or less. It may have a cetane number of from 63 to 75, for example from 65 to 69 for a narrow-cut fraction or from 68 to 73 for a full-cut fraction. It is preferably the product of a SMDS process, preferred features of which may be as described below in connection with Fischer-Tropsch derived gas oils.

[0047] A Fischer-Tropsch derived gas oil should be suitable for use as a diesel fuel, ideally as an automotive diesel fuel; its components (or the majority, for instance 95% v/v or greater, thereof) should therefore have boiling points within the typical diesel fuel ("gas oil") range, i.e. from 150 to 400°C or from 170 to 370°C. It will suitably have a 90% v/v distillation temperature of from 300 to 370°C.

[0048] A Fischer-Tropsch derived gas oil will typically have a density from 0.76 to 0.79 g/cm³ at 15°C; a cetane number (ASTM D613) greater than 70, suitably from 74 to 85; a kinematic viscosity (ASTM D445) from 2 to 4.5, preferably from 2.5 to 4.0, more preferably from 2.9 to 3.7, mm²/s at 40°C; and a sulphur content (ASTM D2622) of 5 mg/kg or less, preferably of 2 mg/kg or less.

[0049] Preferably, a Fischer-Tropsch derived fuel component used in the present invention is a product prepared by a Fischer-Tropsch methane condensation reaction using a hydrogen/carbon monoxide ratio of less than 2.5, preferably less than 1.75, more preferably from 0.4 to 1.5, and ideally using a cobalt containing catalyst. Suitably, it will have been obtained from a hydrocracked Fischer-Tropsch synthesis product (for instance as described in GB-B-2077289 and/or EP-A-0147873), or more preferably a product from a two-stage hydroconversion process such as that described in EP-A-0583836 (see above). In the latter case, preferred features of the hydroconversion process may be as disclosed at pages 4 to 6, and in the examples, of EP-A-0583836.

[0050] Suitably, a Fischer-Tropsch derived fuel component used in the present invention is a product prepared by a low temperature Fischer-Tropsch process, by which is meant a process operated at a temperature of 250°C or lower, such as from 125 to 250°C or from 175 to 250°C, as opposed to a high temperature Fischer-Tropsch process which might typically be operated at a temperature of from 300 to 350°C.

[0051] Suitably, in accordance with the present invention, a Fischer-Tropsch derived fuel will consist of at least 70 %wt, preferably at least 80 %wt, more preferably at least 90 or 95 or 98 %wt, most preferably at least 99 or 99.5 or even 99.8 %wt, of paraffinic components, preferably iso- and normal paraffins. The weight ratio of iso-paraffins to normal paraffins will suitably be greater than 0.3 and may be up to 40; suitably it is from 2 to 40. The actual value for this ratio will be determined, in part, by the hydroconversion process used to prepare the gas oil from the Fischer-Tropsch synthesis product.

[0052] The Fischer-Tropsch derived gas oil component which is used in the present invention to reduce the CFPP of a fuel composition comprising a middle distillate base fuel and a cold flow additive preferably comprises at least 75 %wt, more preferably at least 80 %wt, most preferably at least 85 %wt, of iso-paraffins.

[0053] The olefin content of the Fischer-Tropsch derived fuel component is suitably 0.5 %wt or lower. Its aromatics content is suitably 0.5 %wt or lower.

[0054] Said Fischer-Tropsch derived gas oil component which is used in the present invention so as to reduce the CFPP of a fuel composition comprising a middle distillate base fuel and a cold flow additive may be as described above. Also suitable as said Fischer-Tropsch derived gas oil component is a Fischer-Tropsch product that has been processed to produce a catalytically dewaxed gas oil or gas oil blending component. A suitable process for this purpose involves the steps of (a) hydrocracking/hydroisomerising a Fischer-Tropsch product; (b) separating the product of step (a) into

at least one or more fuel fractions and a gas oil precursor fraction; (c) catalytically dewaxing the gas oil precursor fraction obtained in step (b), and (d) isolating the catalytically dewaxed gas oil or gas oil blending component from the product of step (c) by means of distillation.

[0055] A fuel composition used in the present invention may include a mixture of two or more Fischer-Tropsch derived fuel components.

[0056] The proportion of Fischer-Tropsch derived fuel components in the composition may be from 0 to 50 %vol. It may, for example, be 0.5 or 1 %vol or greater, preferably 2 or 5 or 10 %vol or greater, more preferably 20 or 25 or 30 or 40 %vol or greater. Yet more preferably, the proportion of Fischer-Tropsch derived fuel components is up to 30 %vol, or up to 25 or 20 or 15 %vol.

[0057] Preferably, the Fischer-Tropsch derived gas oil component is present in the fuel composition in the amount of 10 to 30 %vol, more preferably 10 to 25 %vol, most preferably 10 to 20 %vol.

[0058] In general, other products of gas-to-liquid processes may be suitable for inclusion in a fuel composition prepared according to the present invention. The gases which are converted into liquid fuel components using such processes can include natural gas (methane), LPG (e.g. propane or butane), "condensates" such as ethane, synthesis gas (CO/hydrogen) and gaseous products derived from coal, biomass and other hydrocarbons.

[0059] The 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.

[0060] 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.

[0061] Examples of detergents suitable for use in fuel additives for the present purpose 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. 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.

[0062] The fuel additive mixture may contain other components in addition to the detergent. Examples are lubricity enhancers; dehazers, e.g. alkoxyated phenol formaldehyde polymers; anti-foaming agents (e.g. polyether-modified polysiloxanes); ignition improvers (cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in US-A-4208190 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 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; combustion improvers; static dissipator additives; cold flow improvers; and wax anti-settling agents.

[0063] The fuel additive mixture may contain a lubricity enhancer, especially when the fuel composition has a low (e.g. 500 ppmw or less) sulphur content. In the additivated 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;
- WO-A-94/17160 - certain esters of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has 1 or more carbon atoms, particularly glycerol monooleate and di-isodecyl adipate, as fuel additives for wear reduction in a diesel engine injection system;
- 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.

[0064] It may also be preferred for the 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.

[0065] Unless otherwise stated, the (active matter) concentration of each such additive component in the additivated 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.

[0066] The (active matter) concentration of any dehazer in the 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, advantageously from 1 to 5 ppmw. The (active matter) concentration of any ignition improver present will preferably be 2600 ppmw or less, more preferably 2000 ppmw or less, conveniently from 300 to 1500 ppmw. The (active matter) concentration of any detergent in the 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.

[0067] 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 C₇₋₉ primary alcohols, or a C₁₂₋₁₄ alcohol mixture which is commercially available.

[0068] The total content of the additives in the fuel composition may be suitably between 0 and 10000 ppmw and preferably below 5000 ppmw.

[0069] In this specification, amounts (concentrations, % vol, ppmw, % wt) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

[0070] The present invention is particularly 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 may be suitable for use in heavy and/or light duty diesel engines.

[0071] As mentioned above, it is also applicable where the fuel composition is used in heating applications, for example boilers. Such boilers include standard boilers, low temperature boilers and condensing boilers, and are typically used for heating water for commercial or domestic applications such as space heating and water heating.

[0072] A diesel base fuel may be an automotive gas oil (AGO). A diesel base fuel used in the present invention will preferably have a sulphur content of at most 2000 ppmw (parts per million by weight). More preferably, it will have a low or ultra low sulphur content, for instance at most 500 ppmw, preferably no more than 350 ppmw, most preferably no more than 100 or 50 or 10 ppmw, of sulphur.

[0073] The cold flow additive used in the present invention is defined as any material capable of improving the cold flow performance of the composition, as described below. The cold flow additive may for example be a middle distillate flow improver (MDFI) or a wax anti-settling agent (WASA) or more typically a mixture thereof.

[0074] MDFIs may for example comprise vinyl ester-containing compounds such as vinyl acetate-containing compounds, in particular polymers. Copolymers of alkenes (for instance ethylene, propylene or styrene, more typically ethylene) and unsaturated esters (for instance vinyl carboxylates, typically vinyl acetate) are for instance known for use as MDFIs.

[0075] Other known cold flow additives (also referred to as cold flow improvers) include comb polymers (polymers having a plurality of hydrocarbyl group-containing branches pendant from a polymer backbone), polar nitrogen compounds including amides, amines and amine salts, hydrocarbon polymers and linear polyoxyalkylenes. Examples of such compounds are given in WO-A-95/33805, at pages 3 to 16 and in the examples.

[0076] Yet further examples of compounds useable as cold flow additives include those described in WO-A-95/23200. These include the comb polymers defined at pages 4 to 7, in particular those consisting of copolymers of vinyl acetate and alkyl-fumarate esters; and the additional low temperature flow improvers described at pages 8 to 19, such as linear oxygen-containing compounds, including alcohol alkoxylates (e.g. ethoxylates, propoxylates or butoxylates) and other esters and ethers; ethylene copolymers of unsaturated esters such as vinyl acetate or vinyl hexanoate; polar nitrogen containing materials such as phthalic acid amide or hydrogenated amines (in particular hydrogenated fatty acid amines); hydrocarbon polymers (in particular ethylene copolymers with other alpha-olefins such as propylene or styrene); sulphur carboxy compounds such as sulphonate salts of long chain amines, amine sulphones or amine carboxamides; and hydrocarbylated aromatics.

[0077] Ideally compounds used as cold flow additives will have or be associated with available protons.

[0078] Particularly preferred cold flow additives for use in the present invention are those containing nitrogen atoms, preferably in association with protons. Suitable compounds are amines, amine salts and amides, in particular amines and their salts, most particularly protonated amines. Suitably, at least one such compound is present in a fuel composition prepared according to the present invention.

[0079] Cold flow additives are conventionally included in middle distillate fuel compositions, such as diesel fuel compositions, so as to improve their performance at lower temperatures, and thus to improve the low temperature operability of systems (typically vehicles) running on the compositions.

[0080] The (active matter) concentration of the cold flow additive in a fuel composition prepared according to the present invention may be up to 1000 ppmw, preferably up to 500 ppmw, more preferably up to 400 ppmw. Its (active

matter) concentration will suitably be at least 20 ppmw, preferably at least 30 or 50 ppmw, more preferably at least 100 ppmw.

[0081] As indicated above, the cold flow performance of a fuel composition can suitably be assessed by measuring its CFPP, preferably using the standard test method IP 309 or an analogous technique. The CFPP of a fuel indicates the temperature at and below which wax in the fuel will cause severe restrictions to flow through a filter screen, and can correlate with vehicle operability at lower temperatures. A reduction in CFPP will correspond to an improvement in cold flow performance, other things being equal. Improved cold flow properties increase the range of climatic conditions or seasons in which a fuel can efficiently be used.

[0082] Cold flow performance may be assessed in any other suitable manner, for example using the Aral short sediment test (EN 23015), and/or by assessing the low temperature performance of a diesel engine, vehicle or other system running on the fuel composition. The temperature at which such performance is measured may depend on the climate in which the fuel composition is intended to be used - in Greece, for example, "low temperature performance" may be assessed at -5°C, whereas in Finland low temperature performance may be required at -30°C; in hotter countries where fuels are generally used at higher ambient temperatures, "low temperature" performance may need to be assessed at only 5 to 10 degrees below the ideal ambient temperature. In general, an improvement in cold flow performance may be manifested by a reduction in the minimum temperature at which a system running on the fuel composition can perform to a given standard.

[0083] An improvement in cold flow performance may be manifested by a reduction in, ideally suppression of, so-called "hesitation" effects which can occur in a CFPP test at temperatures higher than the CFPP value of a fuel. "Hesitation" may be understood as an at least partial obstruction of the CFPP test filter occurring at a temperature higher than the CFPP. Such an obstruction will be manifested - in a CFPP machine modified to allow such measurements - by an increased filtration time, albeit at a level below 60 seconds. If severe enough, hesitation causes the test to terminate early and the CFPP value to be recorded as the higher temperature - thus when hesitation occurs to a great enough extent, it is not recognised as hesitation but simply as a higher CFPP. References in this specification to CFPP values may generally be taken to include values which take account of - i.e. are raised as a result of - such hesitation effects.

[0084] A reduction in hesitation effects may be manifested by complete elimination of a hesitation effect which would be observed when measuring the CFPP of the fuel composition; and/or by a reduction in severity of such a hesitation effect (e.g. severe hesitation becomes only mild hesitation); and/or by a lowering of the temperature at which such a hesitation effect occurs. Since hesitation effects can cause variability in the measured CFPP of a fuel composition, in severe test machines triggering an increase in the recorded value, such a reduction may be beneficial because it can allow the CFPP of the composition to be more reliably and accurately measured, in turn allowing the composition to be more readily tailored to meet, and proven to meet, specifications such as industry or regulatory standards.

[0085] References to a "deterioration" in cold flow properties may be construed in accordance with the above. Such an effect will typically correspond to an increase in the CFPP of the fuel composition, and/or an increase in hesitation effects when measuring the CFPP of the composition, and/or poorer performance of an engine or vehicle or other system running on the composition, particularly at low temperatures as described above.

[0086] In the context of the present invention, "reducing" the CFPP embraces any degree of reduction. This can be assessed by measuring the cold flow performance of the composition (including the cold flow additive) both before and after incorporation of the Fischer-Tropsch derived gas oil component.

[0087] In the context of the present invention, "improving" the cold flow performance of the fuel composition embraces any degree of improvement compared to the performance of the composition before the Fischer-Tropsch derived gas oil component is incorporated. This may, for example, involve adjusting the cold flow performance of the composition, by means of the Fischer-Tropsch derived gas oil component, in order to meet a desired target, for instance a desired target CFPP value.

[0088] By using the present invention, the CFPP of the composition may be reduced by at least 1°C compared to its value prior to addition of the Fischer-Tropsch derived gas oil component, preferably by at least 2°C, more preferably by at least 3°C and most preferably by at least 4 or 5 or in cases 6 or 7 or 8°C.

[0089] A fuel composition prepared according to the present invention may have a CFPP of -5°C or lower, preferably -10 or -15°C or lower. In a preferred embodiment, it may have a CFPP of -20°C or lower, preferably -24°C or lower.

[0090] In the context of the present invention, "use" of an additive in a fuel composition means incorporating the additive into the composition, typically as a blend (i.e. a physical mixture) with one or more other fuel components. An additive will conveniently be incorporated before the composition is introduced into an internal combustion engine or other system which is to be run on the composition. Instead or in addition the use of an additive may involve running a fuel-consuming system, typically a diesel engine, on a fuel composition containing the additive, typically by introducing the composition into a combustion chamber of an engine.

[0091] Additives may be added at various stages during the production of a fuel composition; those added at the refinery for example might be selected from anti-static agents, pipeline drag reducers, flow improvers, lubricity enhancers, anti-oxidants and wax anti-settling agents. When carrying out the present invention, a base fuel may already contain

such refinery additives. Other additives may be added downstream of the refinery.

[0092] In accordance with the present invention there is further provided a method of reducing the CFPP of a fuel composition comprising a middle distillate base fuel and a cold flow additive by adding a Fischer-Tropsch derived gas oil component to the fuel composition.

[0093] In accordance with the present invention, there is further provided a process for the preparation of a fuel composition, which process comprises blending a middle distillate base fuel with a cold flow additive and a Fischer-Tropsch derived gas oil component, the Fischer-Tropsch derived gas oil component being included for the purpose of reducing the CFPP of the fuel composition.

[0094] In accordance with the present invention there is further provided a method of operating a fuel consuming system, which method comprises reducing the CFPP of a fuel composition comprising a middle distillate base fuel and a cold flow additive by adding a Fischer-Tropsch derived gas oil component to the fuel composition, and then introducing into the system said fuel composition. The fuel composition is preferably introduced for one or more of the purposes described above in accordance with the present invention. Thus, the system is preferably operated with the fuel composition of the present invention for the purpose of improving the low temperature performance of the system.

[0095] The system may in particular be an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, in which case the method involves introducing the relevant fuel composition into a combustion chamber of the engine. The engine is preferably a compression ignition (diesel) engine. Such a diesel engine may be of the types described above.

[0096] The present invention will now be further described by reference to the following Examples, in which, unless otherwise indicated, parts and percentages are by weight, and temperatures are in degrees Celsius.

[0097] A commercially available diesel fuel was sampled. When included, a representative cold flow additive was blended into the fuel in accordance with the additive supplier's instructions (typically at 45 to 65°C, followed by cooling to an ambient temperature of approximately 20°C) - in these cases the cold flow additive was an MDFI, although it could also be any suitable cold flow additive, such as a WASA, at concentrations of 400 and 500mg/kg (ppmw).

[0098] Cold flow performance was assessed by measuring cold filter plugging points (CFPPs) for the fuel blends, using a 5GS CFPP test machine (ex. ISL) and a method analogous in key respects to the standard test method IP 309.

[0099] Blends were prepared from the following components:-

- A Winter-grade, ultra low sulphur European specification diesel fuel (ULSD) (ex. Shell);
- B Fischer-Tropsch derived gas oil fraction (86 %wt iso-paraffins) (ex. Shell);
- C Fischer-Tropsch derived gas oil fraction (88 %wt iso-paraffins) (ex. Shell);
- D Catalytically dewaxed Fischer-Tropsch derived gas oil (93 %wt iso-paraffins) (ex. Shell);
- E Catalytically dewaxed Fischer-Tropsch derived gas oil (95 %wt iso-paraffins) (ex. Shell); and
- F Middle distillate flow improver, 'R343' (MDFI) (ex. Infineum)

[0100] Components B and C had been obtained from natural gas by a process that combined syngas manufacture, Fischer-Tropsch synthesis and hydrocracking.

[0101] Components D and E had been obtained by further catalytic treatment (hydroisodewaxing) of the vacuum distillate (also referred to as Waxy Raffinate) which had been produced by hydrocracking Fischer-Tropsch paraffins. The gas oil molecules had been distilled off from the isodewaxed vacuum distillate. Alternatively, it would have been possible to further process components B and C over a similar isodewaxing catalyst.

Examples

[0102] The properties of components A to E are shown in Table 1:

Table 1

Fuel property	Test method	A	B	C	D	E
Density @ 15°C (g/ml)	IP 365/ ASTM D4052	0.824	0.792	0.794	0.787	0.797
Distillation (°C)	IP 123/ ASTM D86					
IBP		170.6	267	267	219	237
10%		203.5	281	282	252	283

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(continued)

Distillation (°C)	IP 123/ ASTM D86					
30%		239.5	291	293	278	316
50%		266.7	302	307	300	337
70%		292.7	318	327	320	349
90%		332.8	340	351	340	359
95%		353	348	359	346	362
FBP		367.5	352	364	350	365
Sulphur (ppmw)	ASTM D2622	36	-	-	-	-
Cloud Point (°C)	IP 219	-6	-11	-9	-33	-24
CFPP (°C)	IP 309	-9	-12	-11	-44.5	-31.5

[0103] A number of blends B1 to B10 of components A to F were prepared as shown in Table 2 and the CFPP of each blend was measured as described above, in accordance with standard test method IP 309.

Table 2

	A (% vol)	B (% vol)	C (% vol)	D (% vol)	E (% vol)	F (mg/kg)	CFPP (°C)
B1	100					400	-20
B2	80	20					-10
B3	80	20				400	-24
B4	80		20				-9
B5	80		20			400	-26
B6	80			20			-10
B7	80			20		400	-26
B8	80				20		-9
B9	80				20	400	-28
B10	80	10		10			-10
B11	80	10		10		400	-25
B12	80	10			10		-10
B13	80	10			10	400	-26
B14	80		10		10		-10
B15	80		10		10	400	-27
B16	100					500	-20

[0104] It can be seen from Tables 1 and 2 that in respect of each of blends B2, B4, B6, B8, B10, B12 and B14, the addition of components B, C, D and E to component A had very little effect on the CFPP of component A (-9°C). The most that the CFPP was lowered was 1°C.

[0105] However, it is shown in Table 2 that surprisingly the addition of components B, C, D and E to component A where component F was present caused at least 4°C lowering of the CFPP. This can be seen by comparing the CFPP of each of blends B3, B5, B7, B9, B11, B13 and B15 with the CFPP of blend B1. This surprising effect is particularly noticeable in the case of components B and C which had CFPPs of -12°C and -11°C, respectively, i.e. much higher than that of blend B1 (-20°C), but which lowered the CFPP to -24°C and -26°C, respectively (as shown by blends B3 and

B5). Furthermore, whilst the CFPPs of components D and E were -44.5°C and -31.5°C, respectively, they had little effect on the CFPP of component A (as shown by blends B6 and B8). Therefore, it was surprising that they lowered the CFPP of a blend of components A and F (as shown by blends B7 and B9).

[0106] This clearly demonstrates that whilst the Fischer-Tropsch derived gas oil component had little effect on the CFPP of the ULSD itself, it had a clear effect on the ULSD containing the MDFI.

[0107] It is also shown that when the addition of further MDFI caused no further lowering of the CFPP of the ULSD (as shown by blends B1 and B16), addition of a Fischer-Tropsch derived gas oil component instead did further lower the CFPP (as shown, for example, by blends B3, B5, B7 and B9).

[0108] This also shows that the addition of a Fischer-Tropsch derived gas oil component can give (i) a greater CFPP benefit for the same treat rate of cold flow additive, or (ii) allow the use of less cold flow additive for a similar CFPP benefit.

Claims

1. Use, in a fuel composition comprising a middle distillate base fuel and a cold flow additive, of a Fischer-Tropsch derived gas oil component for the purpose of reducing the cold filter plugging point of said composition.
2. Use according to claim 1, wherein the middle distillate base fuel is a base diesel fuel.
3. Use according to claim 1 or 2 wherein the Fischer-Tropsch derived gas oil component is present in the fuel composition in the amount of 10 to 30% by volume.
4. Use according to claim 1, 2 or 3 wherein the Fischer-Tropsch derived gas oil component comprises at least 80% by weight, preferably at least 85% by weight, of iso-paraffins.
5. Use according to any one of the preceding claims wherein the cold flow additive is present in the fuel composition in the amount of up to 1000 ppmw, preferably up to 500 ppmw.
6. Use according to any one of the preceding claims wherein the cold flow additive is selected from middle distillate flow improvers and wax anti-settling agents.
7. A method of reducing the CFPP of a fuel composition comprising a middle distillate base fuel and a cold flow additive by adding a Fischer-Tropsch derived gas oil component to the fuel composition.
8. A process for the preparation of a fuel composition, which process comprises blending a middle distillate base fuel with a cold flow additive and a Fischer-Tropsch derived gas oil component, the Fischer-Tropsch derived gas oil component being included for the purpose of reducing the CFPP of the fuel composition.
9. A method of operating a fuel consuming system, which method comprises reducing the CFPP of a fuel composition comprising a middle distillate base fuel and a cold flow additive by adding a Fischer-Tropsch derived gas oil component to the fuel composition, and then introducing into the system said fuel composition.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 08 10 0309

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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