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(54) Title: FUEL COMPOSITION

(57) Abstract: A fuel composition for powering a combustion engine, the composition comprising: a liquid base fuel; and a (co)polymer obtainable by (co)polymerizing at least the following monomers: • at least one bicyclic (meth)acrylate ester • optionally at least one lower-alkyl (meth)acrylate, • optionally at least one aromatic vinyl monomer, and • optionally other ethylenically unsaturated monomers.

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FUEL COMPOSITION

Field of Invention

The present invention relates to fuel compositions containing a certain (co)polymer. Aspects of the invention also relate to the use of the (co)polymer in fuel compositions, and to the use of fuel compositions containing the (co)polymer.

Background to the Invention

Polymers have previously been used for modifying the rheology of a fluid containing the polymer. There is a need for polymers that can be used to adjust the flow and spray characteristics of liquid fuels, such as gasoline and diesel fuels.

Liquid fuels must be vaporized and mixed with air, or oxygen, for effective combustion. As middle distillate or heavier fractions have low vapour pressures, efficient atomization is a particularly critical aspect of spray combustion of such fuels.

Atomization produces fine liquid fuel particles, whose large surface area leads to fast evaporation and thus rapid and efficient combustion. Even with efficient atomization stoichiometric combustion cannot be achieved. Limitation is imposed in this respect by the inability to reach a condition of perfect mixing in the time and size scale of the combustion process and equipment. In order to get complete combustion, therefore, it is necessary to supply excess air to the system.

Excess air, to the extent it provides complete combustion, serves to increase combustion efficiency. However, too much air can lead to a decrease in heat recovery. All of the oxygen not involved in the combustion process as well as all of the nitrogen in the air is heated and thus carries heat out of the stack. Further, the greater the excess air the greater the mass flow through the system and the shorter the time scale for heat transfer. Hence, achieving efficient combustion and heat recovery requires a delicate balance of atomization and excess air coupled with optimized combustion chamber and heat recovery system designs.

GB 1 569 344 relates to the use of polymers, especially poly-isobutylene, to modify fuel properties in an attempt to improve combustion efficiency. A problem with poly-isobutylene was found that it is very difficult to handle, which is exemplified by its glass transition temperature (Tg) of -75 °C. Other known polymers such as poly-lauryl methacrylate also suffer from such a low Tg.

Other polymers with higher Tg were found to suffer from insufficient solubility of the polymer in a fuel, as judged visually or via determination of cloud point, making them unsuitable for changing the fuel rheology.

There remains a need for alternative polymers with the ability of modifying the rheology of a petroleum based fuels, that can be handled easily and have adequate solubility in the fuel, and that can enable improved combustion efficiency.

Summary of the Invention

Therefore one object of the invention is to provide a fuel composition component comprising a polymer with the ability to modify the rheology of a base fuel of the composition in a manner that can positively influence combustion efficiency in an internal combustion engine run using the fuel.

The present inventors have found that this object can at least partly be met by a composition which will now be described in more detail.

According to a first aspect of the present invention there is provided a fuel composition for powering a combustion engine, the composition comprising: a liquid base fuel; and a (co)polymer obtainable by (co)polymerizing at least the following monomers:

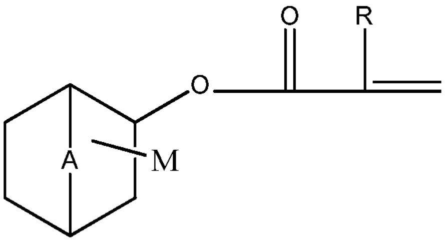
- one or more bicyclic (meth)acrylate esters (a);
- optionally, and preferably, one or more lower-alkyl (meth)acrylates (b);
- optionally, and preferably, one or more aromatic vinyl monomers (c);
- optionally further ethylenically unsaturated monomers.

Preferably, the copolymer has a weight averaged molecular weight from 100,000 to 10,000,000 Dalton.

In the context of the invention the term '(meth)acrylate' indicates acrylate or methacrylate, and '(co)polymer' indicates polymer or copolymer. The term 'polymer' and the term 'copolymer' are also used herein interchangeably.

Detailed Description of the Invention

The bicyclic (meth)acrylate ester contains a (meth)acryloyl radical bonded to any carbon atom of the bicyclic rings, preferably of the six-membered carbon atom bridged ring; said esters include products such as decahydronaphtyl (meth)acrylates, and adamantyl (meth)acrylates. Preferred are products according to the general formula (I)



(I)

wherein
R is H or $-CH_3$,
A is $-CH_2-$, $-CH(CH_3)-$ or $-C(CH_3)_2-$, and one or more M is covalently bonded to any carbon of the bicyclic rings, preferably to a carbon atom of the six-membered ring, and each M is independently selected from the group consisting of hydrogen, halogen, methyl, and methylamino or a plurality thereof.

Non-limiting examples of the bicyclic (meth)acrylate esters include isobornyl (meth)acrylate, bornyl (meth)acrylate, fenchyl (meth)acrylate, isofenchyl (meth)acrylate, norbornyl methacrylate, cis, (endo) 3-methylamino-2-bornyl (meth)acrylate, 1,4,5,6,7,7-hexachlorobicyclo [2.2.1]-hept-5-ene-2-ol methacrylate (HCBOMA) and 1,4,5,6,7,7-hexachlorobicyclo [2.2.1]-hept-5-ene-2 methanol methacrylate (HCBMA), and mixtures of such bicyclic methacrylates. The chlorinated compounds are less preferred since they can liberate corrosive HCl when burned. Preferably, the bicyclic methacrylate ester is isobornyl methacrylate. The bicyclic (meth)acrylate esters are known per se and may be prepared in known fashion or may be obtained from commercial sources.

The bicyclic (meth)acrylate is preferably chosen from monomers which, when polymerized, form a homopolymer that is soluble in a liquid fuel, more preferably in diesel fuel.

The lower-alkyl (meth)acrylate contains a (meth)acryloyl radical bonded to a lower alkyl group, herein defined as a C_1-C_7 alkyl group, preferably a C_1-C_4 alkyl group, which can be linear or branched, substituted or unsubstituted, saturated or unsaturated. Examples of the alkyl (meth)acrylate, include methyl methacrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)(acrylate) and hexyl (meth) acrylate. The currently preferred alkyl (meth)acrylate is iso-butyl methacrylate.

The lower-alkyl (meth)acrylate is preferably chosen from monomers which, when polymerized, form a homopolymer that is not soluble in a liquid fuel, more preferably not soluble in diesel fuel.

The aromatic vinyl monomer contains a vinyl group bonded to an aromatic group. Examples include styrene, substituted styrene, vinyl naphthalene, divinylbenzene, and mixtures thereof. Preferred substituted styrenes include ortho-, meta- and/or para- alkyl, alkyloxy or halogen substituted styrenes, such as methyl styrene, tert-butyloxy styrene, 2-chlorostyrene and 4-chlorostyrene. Preferably, the aromatic vinyl monomer is styrene.

The aromatic vinyl monomer is preferably chosen from monomers which, when polymerized, form a homopolymer that is not soluble in a liquid fuel, more preferably not soluble in diesel fuel.

Further monomers that may participate in the copolymerization process are ethylenically unsaturated monomers different from the monomers (a), (b) and (c) defined above. Examples of such other monomers include 4-tert-butyl styrene, cationic, nonionic and anionic ethylenically unsaturated monomers known to those skilled in the art, and include, but are not limited to, ethylenically unsaturated acids, such as (meth)acrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, N-[3-(dimethylamino) propyl] methacrylamide, N-[3-(dimethylamino) propyl] acrylamide, (3-acrylamidopropyl)-trimethyl-ammonium chloride, methacrylamido propyl trimethyl ammonium chloride, methacrylamide, N-alkyl (meth)acrylamides, N-vinyl pyrrolidone, N-vinyl caprolactams, vinyl formamide, vinyl acetamide, higher-alkyl(meth)acrylates, where higher-alkyl is herein defined as straight or branched, saturated or unsaturated, substituted or unsubstituted hydrocarbyl chain containing 8 or more, such as 8 to 24, carbon atoms.

The (co)polymer may be synthesized by conventional methods for vinyl addition polymerization known to those skilled in the art, such as but not limited to solution polymerization, precipitation polymerization, and dispersion polymerizations, including suspension polymerization and emulsion polymerization.

In an embodiment the polymer is formed by suspension polymerization, wherein monomers that are insoluble in water or poorly soluble in water are suspended as droplets in water. The monomer droplet suspension is maintained by mechanical agitation and the addition of stabilizers. Surface active polymers such as cellulose ethers, poly(vinyl alcohol-co-vinyl acetate), poly(vinyl pyrrolidone) and alkali metal salts of (meth)acrylic acid containing polymers and colloidal (water insoluble) inorganic powders such as tricalcium phosphate, hydroxyapatite, barium sulfate, kaolin, and magnesium silicates can be used as stabilizers. In addition, small amounts of surfactants such as sodium dodecylbenzene sulfonate can be used together with the stabilizer(s). Polymerization is initiated using an oil soluble initiator. Suitable initiators include peroxides such as benzoyl peroxide, peroxy esters such as tert-butylperoxy-2-ethylhexanoate, and azo compounds such as 2,2′-azobis(2-methyl¬butyro¬nitrile). At the completion of the polymerization, solid polymer product can be separated from the reaction medium by filtration and washed with water, acid, base, or solvent to remove unreacted monomer or free stabilizer.

In another embodiment the polymer is formed by emulsion polymerization, one or more monomers are dispersed in an aqueous phase and polymerization is initiated using a water soluble initiator. The monomers are typically water insoluble or very poorly soluble in water, and a surfactant or soap is used to stabilize the monomer droplets in the aqueous phase. Polymerization occurs in the swollen micelles and latex particles. Other ingredients that might be present in an emulsion polymerization include chain transfer agents such as mercaptans (e.g. dodecyl mercaptan) to control molecular weight and electrolytes to control pH. Suitable initiators include alkali metal or ammonium salts of persulfate such as ammonium persulfate, water-soluble azo compounds such as 2,2′-azobis(2-aminopropane)dihydrochloride, and redox systems such as Fe(II) and cumene hydroperoxide, and tert-butyl hydroperoxide-Fe(II)-sodium ascorbate. Suitable surfactants include anionic surfactants such as fatty acid soaps (e.g. sodium or potassium stearate), sulfates and sulfonates (e.g. sodium dodecyl benzene sulfonate), sulfosuccinates (e.g. dioctyl sodium sulfosuccinate); non-ionic surfactants such as octylphenol ethoxylates and linear and branched alcohol ethoxylates; cationic surfactants such as cetyl trimethyl ammonium chloride; and amphoteric surfactants. Anionic surfactants and combinations of anionic surfactants and non-ionic surfactants are most commonly used. Polymeric stabilizers such as poly(vinyl alcohol-co-vinyl acetate) can also be used as surfactants. The solid polymer product free of the aqueous medium can be obtained by a number of processes including destabilization/coagulation of the final emulsion followed by filtration, solvent precipitation of the polymer from latex, or spray drying of the latex.

One skilled in the art will recognize that certain surfactants and initiator systems could leave residues in the polymer that will be undesirable in the fuel. These might include sulfur containing species, mono- and multivalent metal ions, and halide ions. One can either select alternative surfactants and initiators that will not leave such residues, or choose an isolation/purification process that will remove or minimize any unwanted residues.

For the copolymers of the invention the amount of bicyclic (meth)acrylate ester (a) that is used in the monomer compostion is preferably 20 wt% or more, suitably 21, 23, 25, or 30 wt% or more, based on the weight of all monomers, because such copolymers were found to have the desired solubility, as determined by the cloud point, in fuels.

Preferably, the copolymer is polymerized from:
22 to 100, suitably 95, wt% of the bicyclic (meth)acrylate ester (a);
0, suitably 5, to 78 wt% of the lower-alkyl (meth)acrylate (b);
0 to 45 wt% of the aromatic vinyl monomer (c); and
up to 50 wt% of further ethylenically unsaturated monomers (d), not being a monomer (a), (b), or (c).

Throughout this document, the weight percentages of the monomer that constitute the (co)polymer, are based on the total weight of the monomers used, whereby the total weight of the monomers adds up to 100 wt%.

More preferably, the copolymer used in the invention is polymerized from 40 to 90 wt% of the bicyclic (meth)acrylate ester (a);
5, suitably 10, to 60 wt% of the lower-alkyl (meth)acrylate (b);
5 to 40 wt% of the aromatic vinyl monomer (c); and
up to 40 wt% of the further ethylenically unsaturated monomers (d), not being a monomer (a), (b), or (c).

In another embodiment the copolymer of the invention is polymerized from 50 to 80 wt% of the bicyclic (meth)acrylate ester (a);
15 to 45 wt% of the lower-alkyl (meth)acrylate (b);
10 to 30 wt% of the aromatic vinyl monomer (c); and
up to 30 wt% of the further ethylenically unsaturated monomers (d), not being a monomer (a), (b), or (c).

In the copolymer used in the invention, and most suitably for each of the embodiments which utilise monomers (a) and (c), it is preferred that the amount of monomer (a) is more than 15 wt%, preferably more than 20 wt%, more than the amount of monomer (c), since that was found to positively influence the solubility of the copolymer.

Preferably in the copolymer used in the invention, and most suitably for each of the embodiments, the amount of the other ethylenically unsaturated monomers (d) does not exceed 20 wt%, 15 wt%, 9 wt%, or 5 wt% and in certain embodiments, monomers a), b) and c) together constitute 100 wt% of the monomers used to form the polymer.

In one embodiment the polymer used in the present invention is a homopolymer of isobornyl methacrylate.

In a proviso, the copolymers may not be composed of at least one bicyclic (meth)acrylate ester, at least one fatty-alkyl (meth)acrylate, and at least one lower-alkyl (meth)acrylate. Also they may not be copolymers of at least one bicyclic (meth)acrylate ester, at least one fatty-alkyl (meth)acrylate, at least one lower-alkyl (meth)acrylate, and at least one aromatic vinyl monomer. In another proviso, they are not copolymers wherein the weight percentage of fatty-alkyl (meth)acrylate is 5-80, or 5-40 weight percent of the monomers polymerized. In another proviso, they are not copolymers wherein the sum of bicyclic (meth)acrylate ester and fatty-alkyl (meth)acrylate is greater than or equal to 35 wt.% more preferably, greater than or equal to 50%; and most preferably, greater than or equal to 55 wt.% of the total monomer composition that is polymerized.

In another proviso, the copolymers of the invention may not be copolymers of lauryl methacrylate, isobornyl methacrylate, 2-phenoxy ethylacrylate, 2-ethylhexyl acrylate, and isodecyl methacrylate, particularly not copolymers wherein the monomers are polymerized in the same molar amount, more particularly not such copolymers obtained by solution polymerization at 100°C using 1 part of Vazo® 67, per 216.4 parts of monomers, as the initiator, since such polymers were found not to have the desired properties.

It was noted that although the homopolymers of styrene and isobutyl methacrylate are not soluble in B7 diesel fuel, a surprisingly large amounts of these monomers can be copolymerized with isobornyl methacrylate to give highly soluble copolymers. For example, based on weight fraction of each comonomer in the examples and using a linear mixing model, one would expect the cloud points which are significantly higher than the ones actually found and reported herein. In a preferred embodiment the copolymer has a cloud point which is at least 5, more preferably at least 10 °C below the value calculated using the linear mixing model.

If so desired, particularly to control the molecular weight and the molecular weight distribution of the polymer and/or to control rheological behaviour of solutions of the polymer, small amounts of divinylbenzene can be used in the mix of monomers. Typically divinylbenzene levels are below 5 wt%, preferably below 2 wt%, more preferably below 1 wt%.

In the copolymer used in the invention, the monomers may be arranged in any fashion, such as in blocks or randomly. Preferably, the copolymer is a randomly arranged copolymer.

The weight averaged molecular weight (Mw) of the (co)polymer used in the invention, when measured in accordance with GPC-MALS method d) of the experimental section, is preferably at least 100,000 Dalton (D), suitably at least 200,000, 300,000, 400,000, 500,000, 600,000, 700,000, 800,000, 900,000, and/or at least 1,000,000 D. In another embodiment, the molecular weight (Mw) of the invention is at least 1,500,000, suitably 2,000,000 or more. The upper molecular weight is determined by the solubility in the fluid in which it is intended to be used. A suitable Mw is 10,000,000 or less, suitably less than 9,000,000, 8,000,000, 7,000,000, 6,000,000, and/or 5,000,000 D. Polymers with a composition defined for use in the invention and a weight averaged molecular weight of from 1,000,000 to 5,000,000, suitably from 2,000,000 to 5,000,000 D were found to be useful at low concentrations, which made them particularly suitable for application in fuel, particularly for use in additive packages for fuel.

Polymers with a Mw of 400 kD or more showed the desired effective control of rheology when dissolved in fluids. Particularly for copolymers of just isobornyl (meth)acrylate and C_1-C_4 alkyl (meth)acrylate the number-average molecular weight is suitably chosen to be greater than 400 kD, since only then are the desired properties obtained for controlling the rheology of a fluid in which they are dissolved. The polydispersity index (PDI), i.e. Mw/Mn of the copolymer used in the invention was found not to be critical and is suitably in the range of from 1, or 2, or 3, up to 10, or 8, or 6. In an embodiment the PDI is from 1 to 5 or from 1.5 to 4.

The glass transition temperature of the (co)polymer used in the invention is preferably in the range of from 50 to 205, more preferably from 50 to 190 °C, even more preferably from 65 to 150 °C, and especially preferably from 95 to 140 °C, as determined by Differential Scanning Calorimetry (DSC). Herein the glass transition temperatures (Tg) were measured using a DSC Q200 (TA Instruments, New Castle, Delaware) with the following program:

1) Start DSC run with isothermal of 15 min at 20 degree C;
2) Ramp the temperature at 10 degree C/min to roughly 20 degree C above the Tg of the material;
3) Run isothermal at that temperature for 5 min;
4) Ramp temperature down from 20 degree C above Tg at 20 degree C/min to 20 degree C;
5) Run isothermal at 20 degree C for 5 min;
6) Start the Modulate mode with the process condition of +/-1.280 degree C for every 60 second;
7) Ramp the temperature at 2 degree C/min to 180 degree C.

The composition of the polymer can be reliably estimated from the relative amounts of the monomers fed into the polymerization. Alternatively, the composition of the (co)polymer is suitably determined from carbon-13 NMR spectra using a Varian MR-400 MHz and/or an Agilent DD2 MR 500 MHz NMR spectrometer.

The polymer of the invention is advantageously added to a petroleum based fuel suitable for running combustion engines, such as fuels conventionally known as gasoline and diesel fuels. The polymer is preferably added to the fuel in an amount effective to obtain a combustion efficiency improving effect. Typically, the polymer used in the invention is added to the fuel to achieve concentrations below 1 wt%, or 5000 ppm (parts per million by weight), such as from 5, from 10, from 50, from 100 or from 500 ppm, preferably up to 3000 or 1000 ppm. The term "ppm" equates to one mg per kg.

The (co)polymers used in the invention have the advantages that (1) they are better suited to adjust the flow and spray characteristics of a petroleum based fuel than conventional polymers; (2) the Tg of the copolymers is high enough to allow handling of the polymer as solids; and (3) they can be used in additive packages for use in fuel.

It is noted that the copolymers used herein may also be added to fuel composition to modify the rheology of said fuels. Suitably, the viscosity of the fuel compositions is increased by dissolution of less than 1%w/w, preferably less than 0.5%w/w, of the copolymer, based on the weight of the total fuel composition.

Herein a polymer is considered to be soluble when at least a 2.0 wt% solution of the polymer in a diesel fuel, or diesel base fuel, at 25 °C can be made, if necessary after heating. Preferably a 2.0 wt% solution of the polymer in diesel or diesel base fuel, at 8 °C can be made. Preferably the (co)polymer of any embodiment herein, when analysed as described below in the experimental section, shows a cloud point below 25°C, more preferably a cloud point below 15 °C, and even more preferably a cloud point below 5 °C.

In an embodiment, the fuel composition of the invention comprises a copolymer component consisting of, or comprising, one or more copolymers obtainable by copolymerizing at least the following monomers:

- at least one bicyclic (meth)acrylate ester
- optionally at least one lower-alkyl (meth)acrylate,
- optionally at least one aromatic vinyl monomer, and
- optionally other ethylenically unsaturated monomers

In an embodiment, the copolymer is preferably present in a fuel composition in amount in the range of from 10 ppm to 300 ppm, more preferably in the range of from 10 to 100, for example 25 ppm to 80 ppm, based on the total weight of the fuel composition.

Preferably, said copolymer component consists of one or more (co)polymers as defined above.

The term "consisting" wherever used herein also embraces "consisting substantially", but may optionally be limited to its strict meaning of "consisting entirely".

The copolymer component is to be understood herein as a component added to the base fuel. Preferably, the copolymer component may be, or be taken to be, the sole source of the copolymer(s) that it consists of in the composition, but this is not essential.

In some embodiments of the invention, the copolymer component may comprise a small amount of impurities, for example by-products of polymer synthesis that have no substantive effect on the overall properties of the copolymer component. Such impurities may, for example, be present in the copolymer component in an amount of at most about 3 wt%. In embodiments of the invention, such impurities up to 3 wt% may be considered part of the copolymer component, in which case the component consists substantially of the copolymer compounds.

The base fuel may be a liquid base fuel of any suitable type.

The base fuel may be at least partly fossil fuel derived, such as derived from petroleum, coal tar or natural gas.

The base fuel may be at least partly bioderived. Bioderived components comprise at least about 0.1 dpm/gC of carbon-14. It is known in the art that carbon-14, which has a half-life of about 5700 years, is found in biologically derived materials but not in fossil fuels. Carbon-14 levels can be determined by measuring its decay process (disintegrations per minute per gram carbon or dpm/gC) through liquid scintillation counting.

The base fuel may be at least partly synthetic: for instance derived by a Fischer-Tropsch synthesis.

Conveniently, the base fuel may be derived in any known manner, e.g. from a straight-run stream, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons, hydrocracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

In an embodiment, the base fuel is a distillate.

Typically, the base fuel may be a hydrocarbon base fuel, i.e. comprise, or consist of, hydrocarbons. However, the base fuel may also comprise or consist of oxygenates, for example alcohols or esters, as is known in the art.

The base fuel may itself comprise a mixture of two or more different components, and/or be additivated, e.g. as described below.

The copolymer in the fuel offers particular advantages in the context of middle distillate or heavier base fuels. In an embodiment, the base fuel comprises a middle distillate, for example a diesel and/or kerosene base fuel.

Preferably, the base fuel may be a diesel base fuel. The diesel base fuel may be any fuel component, or mixture thereof, which is suitable and/or adapted for use in a diesel fuel composition and therefore for combustion within a compression ignition (diesel) engine. It will typically be a middle distillate base fuel.

A diesel base fuel will typically boil in the range from 150 or 180 to 370 or 410°C (ASTM D86 or EN ISO 3405), depending on grade and use.

The diesel base fuel may be derived in any suitable manner. It may be at least partly petroleum derived. It may be at least partly obtained by distillation of a desired range of fractions from a crude oil. It may be at least partly synthetic: for instance it may be at least partly the product of a Fischer-Tropsch condensation. It may be at least partly derived from a biological source.

A petroleum derived diesel base fuel will typically include one or more cracked products, obtained by splitting heavy hydrocarbons. A petroleum derived gas oil may for instance be obtained by refining and optionally (hydro)processing a crude petroleum source. The diesel base fuel may comprise 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.

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 preferably have a density at 15°C of 650 to 1000 kg/m^3, a kinematic viscosity at 20°C of 1 to 80 mm^2/s, and a boiling range of 150 to 410°C.

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.

The diesel base fuel may comprise or consist of a Fischer-Tropsch derived diesel fuel component, typically a Fischer-Tropsch derived gas oil.

In the context of the present invention, the term "Fischer-Tropsch derived" means that a material is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The term "non-Fischer-Tropsch derived" may be interpreted accordingly. A Fischer-Tropsch derived fuel or fuel component will therefore be a hydrocarbon stream in which a substantial portion, except for added hydrogen, is derived directly or indirectly from a Fischer-Tropsch condensation process.

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.

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

$n(CO + 2H_2) = (-CH_2-)_n + nH_2O + \text{heat}$,

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. 0.5 to 10 MPa, preferably 1.2 to 5 MPa). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

The carbon monoxide and hydrogen may themselves be derived from organic, inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane.

A Fischer-Tropsch derived diesel base fuel of use in the present invention may be obtained directly from the refining or the Fischer-Tropsch reaction, or indirectly for instance by fractionation or hydrotreating of the refining or synthesis product to give a fractionated or hydrotreated product. 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.

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 of the elements, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0583836.

An example of a Fischer-Tropsch based process is the

Shell™ "Gas-to-liquids" or "GtL" technology (formerly known as the SMDS (Shell Middle Distillate Synthesis) and described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al, paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985, and in the November 1989 publication of the same title from Shell International Petroleum Company Ltd, London, UK). This process produces middle distillate range products by conversion of a natural gas into a heavy long chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated.

For use in the present invention, a Fischer-Tropsch derived fuel component is preferably any suitable component derived from a gas to liquid synthesis (hereinafter a GtL component), or a component derived from an analogous Fischer-Tropsch synthesis, for instance converting gas, biomass or coal to liquid (hereinafter an XtL component). A Fischer-Tropsch derived component is preferably a GtL component. It may be a BtL (biomass to liquid) component. In general a suitable XtL component may be a middle distillate fuel component, for instance selected from kerosene, diesel and gas oil fractions as known in the art; such components may be generically classed as synthetic process fuels or synthetic process oils. Preferably an XtL component for use as a diesel fuel component is a gas oil.

The diesel base fuel may comprise or consist of a bioderived fuel component (biofuel component). Such fuel components may have boiling points within the normal diesel boiling range, and will have been derived - whether directly or indirectly - from biological sources.

It is known to include fatty acid alkyl esters (FAAEs), in particular fatty acid methyl esters (FAMEs), in diesel fuel compositions. An example of an FAAE included in diesel fuels is rapeseed methyl ester (RME). FAAEs are typically derivable from biological sources and may be added for a variety of reasons, including to reduce the environmental impact of the fuel production and consumption process or to improve lubricity. The FAAE will typically be added to the fuel composition as a blend (i.e. a physical mixture), conveniently before the composition is introduced into an internal combustion engine or other system which is to be run on the composition. Other fuel components and/or fuel additives may also be incorporated into the composition, either before or after addition of the FAAE and either before or during use of the composition in a combustion system. The amount of FAAE added will depend on the natures of any other base fuels and FAAE in question and on the target Cloud Point.

FAAEs, of which the most commonly used in the present context are the methyl esters, are already known as renewable diesel fuels (so-called "biodiesel" fuels). They contain long chain carboxylic acid molecules (generally from 10 to 22 carbon atoms long), each having an alcohol molecule attached to one end. Organically derived oils such as vegetable oils (including recycled vegetable oils) and animal fats (including fish oils) can be subjected to a transesterification process with an alcohol (typically a Ci to C5 alcohol) to form the corresponding fatty esters, typically mono-alkylated. This process, which is suitably either acid- or base-catalysed, such as with the base KOH, converts the triglycerides contained in the oils into fatty acid esters and free glycerol, by separating the fatty acid components of the oils from their glycerol backbone.

FAAEs can also be prepared from used cooking oils, and can be prepared by standard esterification from fatty acids.

In the present invention, the FAAE may be any alkylated fatty acid or mixture of fatty acids. Its fatty acid component(s) are preferably derived from a biological source, more preferably a vegetable source. They may be saturated or unsaturated; if the latter, they may have one or more, preferably up to 6, double bonds. They may be linear or branched, cyclic or polycyclic. Suitably they will have from 6 to 30, preferably 10 to 30, more suitably from 10 to 22 or from 12 to 24 or from 16 to 18, carbon atoms including the acid group(s) $-CO_2H$.

The FAAE will typically comprise a mixture of different fatty acid esters of different chain lengths, depending on its source.

The FAAE is preferably derived from a natural fatty oil, for instance tall oil. The FAAE is preferably a C1 to C5 alkyl ester, more preferably a methyl, ethyl, propyl (suitably iso-propyl) or butyl ester, yet more preferably a methyl or ethyl ester and in particular a methyl ester. It may suitably be the methyl ester of tall oil. In general it may be either natural or synthetic, refined or unrefined ("crude").

The FAAE may contain impurities or by-products as a result of the manufacturing process.

The FAAE suitably complies with specifications applying to the rest of the fuel composition, and/or to another base fuel to which it is added, bearing in mind the intended use to which the composition is to be put (for example, in which geographical area and at what time of year). In particular, the FAAE preferably has a flash point (IP 34) of greater than 101°C; a kinematic viscosity at 40°C (IP 71) of 1.9 to 6.0 mm^2/s, preferably 3.5 to 5.0 mm^2/s; a density from 845 to 910 kg/m^3, preferably from 860 to 900 kg/m^3, at 15°C (IP 365, EN ISO 12185 or EN ISO 3675); a water content (IP 386) of less than 500 ppm; a T95 (the temperature at which 95% of the fuel has evaporated, measured according to IP 123) of less than 360°C; an acid number (IP 139) of less than 0.8 mgKOH/g, preferably less than 0.5 mgKOH/g; and an iodine number (IP 84) of less than 125, preferably less than 120 or less than 115, grams of iodine (I2) per 100g of fuel. It also preferably contains (e.g. by gas chromatography (GC)) less than 0.2% w/w of free methanol, less than 0.02% w/w of free glycerol and greater than 96.5% w/w esters. In general it may be preferred for the FAAE to conform to the European specification EN 14214 for fatty acid methyl esters for use as diesel fuels.

Two or more FAAEs may be present in the base fuel of the present invention.

Preferably, the fatty acid alkyl ester concentration in the base fuel or total fuel composition accords with one or more of the following parameters: (i) at least 1%v; (ii) at least 2%v; (iii) at least 3%v; (iv) at least 4%v; (v) at least 5%v; (vi) up to 6%v; (vii) up to 8%v; (viii) up to 10%v, (xi) up to 12%v, (x) up to 35%v, with ranges having features (i) and (x) , (ii) and (ix), (iii) and (viii), (iv) and (vii), and (v) and (vi) respectively being progressively more preferred. The range having features (v) and (viii) is also preferred.

The diesel base fuel may suitably comply with applicable current standard diesel fuel specification(s) as set out below for the diesel fuel composition.

The fuel composition of the present invention may in particular be a diesel fuel composition. It may be used in, and/or may be suitable and/or adapted and/or intended for use in, any type of compression ignition (diesel) engine. It may in particular be an automotive fuel composition.

The diesel fuel composition may comprise standard diesel fuel components. It may include a major proportion of a diesel base fuel, for instance of the type described above. A "major proportion" means typically 85 % w/w or greater based on the overall composition, more suitably 90 or 95 % w/w or greater, most preferably 98 or 99 or 99.5 % w/w or greater.

In a diesel fuel composition according to the invention, the base fuel may itself comprise a mixture of two or more diesel fuel components of the types described above.

The fuel composition may suitably comply with applicable current standard diesel fuel specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA). By way of example, the overall composition may have a density from 820 to 845 kg/m^3 at 15°C (ASTM D4052 or EN ISO 3675); a T95 boiling point (ASTM D86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D613) of 40 or greater, ideally of 51 or greater; a kinematic viscosity at 40°C (VK40) (ASTM D445 or EN ISO 3104) from 2 to 4.5 centistokes (mm^2/s); a flash point (ASTM D93 or EN ISO 2719) of 55°C or greater; a sulphur content (ASTM D2622 or EN ISO 20846) of 50 mg/kg or less; a cloud point (ASTM D2500 / IP 219 / ISO 3015) of less than -10°C; and/or a polycyclic aromatic hydrocarbons (PAH) content (EN 12916) of less than 11% w/w. It may have a lubricity, measured using a high frequency reciprocating rig for example according to ISO 12156 and expressed as a "HFRR wear scar", of 460 µm or less.

Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the composition. Moreover the composition may contain individual fuel components with properties outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

A diesel fuel composition prepared according to the invention suitably contains no more than 5000 ppm (parts per million by weight) of sulphur, typically from 2000 to 5000 ppm, or from 1000 to 2000 ppm, or alternatively up to 1000 ppm. The composition may for example be a low or ultra-low sulphur fuel, or a sulphur free fuel, for instance containing at most 500 ppm, preferably no more than 350 ppm, most preferably no more than 100 or 50 or even 10 ppm, of sulphur.

A fuel composition according to the invention, or a base fuel used in such a composition, may 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 cetane boost additives, 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. Thus, the composition may contain a minor proportion (preferably 1 % w/w or less, more preferably 0.5 % w/w (5000 ppm) or less and most preferably 0.2 % w/w (2000 ppm) or less), of one or more fuel additives, in addition to the copolymer.

The composition may for example contain a detergent. 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. 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.

A fuel additive mixture useable in a fuel composition prepared according to the invention 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); 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-pphenylenediamine); metal deactivators; combustion improvers; static dissipator additives; cold flow improvers; and wax anti-settling agents.

Such a fuel additive mixture may contain a lubricity enhancer, especially when the fuel composition has a low (e.g. 500 ppm or less) sulphur content. In the additivated fuel composition, the lubricity enhancer is conveniently present at a concentration of less than 1000 ppm, preferably between 50 and 1000 ppm, more preferably between 70 and 1000 ppm. Suitable commercially available lubricity enhancers include ester- and acid-based additives.

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.

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

The (active matter) concentration of any dehazer in the fuel composition will preferably be in the range from 0.1 to 20 ppm, more preferably from 1 to 15 ppm, still more preferably from 1 to 10 ppm, advantageously from 1 to 5 ppm. The (active matter) concentration of any ignition improver present will preferably be 2600 ppm or less, more preferably 2000 ppm or less, conveniently from 300 to 1500 ppm. The (active matter) concentration of any detergent in the fuel composition will preferably be in the range from 5 to 1500 ppm, more preferably from 10 to 750 ppm, most preferably from 20 to 500 ppm.

If desired one or more additive components, such as those listed above, may be co-mixed - preferably together with suitable diluent(s) - in an additive concentrate, and the additive concentrate may then be dispersed into a base fuel or fuel composition. The copolymer may, in accordance with the present invention, be incorporated into such an additive formulation. The additive formulation or additive package is suitably a dissolution of the additive components in a solvent, because the controlled pre-dissolution of the copolymer allows easier mixing with/dissolution in a fuel.

In the diesel fuel composition, the fuel additive mixture will for example 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.

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

In this specification, amounts (concentrations, % v/v, ppm, % w/w) of components are of active matter, i.e. exclusive of volatile solvents/diluent materials.

The present invention may be used to give performance benefits similar to an increased cetane number of the fuel composition. The 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 composition (e.g. to shorten ignition delays, to facilitate cold starting and/or to reduce incomplete combustion and/or associated emissions in a fuel-consuming system running on the fuel composition) and/or to improve combustion noise, and/or to improve power.

In principle, the base fuel may also comprise or consist of a type of liquid base fuel other than a diesel base fuel.

Suitably, the base fuel may comprise or consists of a heavy distillate fuel oil. In an embodiment, the base fuel comprises an industrial gas oil or a domestic heating oil.

Suitably, the base fuel may comprise or consist of a kerosene base fuel, a gasoline base fuel or mixtures thereof.

Kerosene base 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/m^3, preferably from 780 to 830 kg/m^3, 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 mm^2/s.

A gasoline base fuel may be any fuel component, or mixture thereof, which is suitable and/or adapted for use in a gasoline fuel composition and therefore for combustion within a spark ignition (petrol) engine.

Typically, the gasoline base fuel is a liquid hydrocarbon distillate fuel component, or mixture of such components, containing hydrocarbons which boil in the range from 0 to 250°C (ASTM D86 or EN ISO 3405) or from 20 or 25 to 200 or 230°C. The optimal boiling ranges and distillation curves for such base fuels will typically vary according to the conditions of their intended use, for example the climate, the season and any applicable local regulatory standards or consumer preferences.

The gasoline base fuel may be derived from, for example, petroleum, coal tar, natural gas or wood, in particular petroleum. It may be synthetic: for instance it may be the product of a Fischer-Tropsch synthesis.

A gasoline base fuel will typically have a research octane number (RON) (ASTM D2699 or EN 25164) of 80 or greater, or of 85 or 90 or 93 or 94 or 95 or 98 or greater, for example from 80 to 110 or from 85 to 115 or from 90 to 105 or from 93 to 102 or from 94 to 100. It will typically have a motor octane number (MON) (ASTM D2700 or EN 25163) of 70 or greater, or of 75 or 80 or 84 or 85 or greater, for example from 70 to 110 or from 75 to 105 or from 84 to 95.

A gasoline base fuel suitably has a low or ultra low sulphur content, for instance at most 1000 ppm (parts per million by weight) of sulphur, or no more than 500 ppm, or no more than 100 ppm, or no more than 50 or even 10 ppm. It also suitably has a low total lead content, such as at most 0.005 g/l; in an embodiment it is lead free ("unleaded"), i.e. having no lead compounds in it.

A gasoline base fuel might typically have a density from 0.720 to 0.775 kg/m^3 at 15°C (ASTM D4052 or EN ISO 3675). For use in a summer grade gasoline fuel, a base fuel might typically have a vapour pressure at 37.8°C (DVPE) of from 45 to 70 kPa or from 45 to 60 kPa (EN 13016-1 or ASTM D4953-06). For use in a winter grade fuel it might typically have a DVPE of from 50 to 100 kPa, for example from 50 to 80 kPa or from 60 to 90 kPa or from 65 to 95 kPa or from 70 to 100 kPa.

The gasoline base fuel may comprise or consist of one or more biofuel components, which are derived from biological sources. For example, it may comprise one or more oxygenates as additional fuel components, in particular alcohols or ethers having boiling points below 210°C. Examples of suitable alcohols include C_1 to C_4 or C_1 to C_3 aliphatic alcohols, in particular ethanol. Suitable ethers include C_5 or C_{5+} ethers. The base fuel may include one or more gasoline fuel additives, of the type which are well known in the art. It may be a reformulated gasoline base fuel, for example one which has been reformulated so as to accommodate the addition of an oxygenate such as ethanol.

In and embodiment, the fuel composition of the present invention is a gasoline fuel composition.

The gasoline fuel composition can be suitable and/or adapted for use in a spark ignition (petrol) internal combustion engine. It may in particular be an automotive fuel composition.

It may for example include a major proportion of a gasoline base fuel as described above. A "major proportion" in this context means typically 85 % w/w or greater based on the overall fuel composition, more suitably 90 or 95 % w/w or greater, most preferably 98 or 99 or 99.5 % w/w or greater.

The gasoline fuel composition may suitably comply with applicable current standard gasoline fuel specification(s) such as for example EN 228 in the European Union. By way of example, the overall formulation may have a density from 0.720 to 0.775 kg/m^3

at 15°C (ASTM D4052 or EN ISO 3675); a final boiling point (ASTM D86 or EN ISO 3405) of 210°C or less; a RON (ASTM D2699) of 95.0 or greater; a MON (ASTM D2700) of 85.0 or greater; an olefinic hydrocarbon content of from 0 to 20% v/v (ASTM D1319); and/or an oxygen content of from 0 to 5% w/w (EN 1601).

Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the composition. Moreover the composition may contain individual fuel components with properties outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

The fuel composition may be prepared by simple blending of its components in any suitable order. From a second aspect, the invention provides a method of blending the fuel composition, the method comprising blending the copolymer with the base fuel. The method may comprise agitating the composition to disperse or dissolve the copolymer in the base oil.

In embodiments, the present invention may be used to produce at least 1,000 litres of the (co)polymer-containing fuel composition, or at least 5,000 or 10,000 or 20,000 or 50,000 litres.

According to a third aspect of the invention, there is provided the use of the (co)polymer in the fuel composition for the purpose of one or more of:

(i) aiding atomisation of the fuel composition;

(ii) decreasing the ignition delay of the composition; and

(iii) improving the power output of a combustion ignition engine run on the composition.

In the context of the present invention, "use" of the (co)polymer in a fuel composition means incorporating the (co)polymer into the composition, typically as a blend (i.e. a physical mixture) with one or more other fuel components, for example a base fuel and optionally one or more fuel additives, preferably a diesel base fuel and optionally one or more diesel fuel additives. The (co)polymer will conveniently be incorporated before the composition is introduced into an engine or other system which is to be run on the composition. Instead or in addition, the use of the (co)polymer may involve running a fuel-consuming system, typically an internal combustion engine, on a fuel composition containing the (co)polymer, typically by introducing the composition into a combustion chamber of an engine. It may involve running a vehicle which is driven by a fuel-consuming system, on a fuel composition containing the (co)polymer. In such cases the fuel composition is suitably a diesel fuel composition and the engine is suitably a compression ignition (diesel) engine. "Use" of the (co)polymer in the ways described above may also embrace supplying the (co)polymer together with instructions for its use in a fuel composition, in particular a diesel fuel composition. The (co)polymer may itself be supplied as part of a composition which is suitable for and/or intended for use as a fuel additive.

A fourth aspect of the invention provides for the use of a fuel composition according to the first aspect of the invention for the purpose of one or more of:

(i) aiding fuel atomisation;

(ii) decreasing ignition delay; and

(iii) improving the power output of a combustion ignition engine run on the composition.

The combustion engine is preferably an internal combustion engine, and more preferably the fuel composition is a diesel fuel composition and the combustion engine is compression ignition (diesel) engine.

The purposes of aiding, decreasing and improving may in particular be achieved relative to a fuel composition substantially free from said (co)polymer.

A fuel composition prepared or used according to the invention may be marketed with an indication that it benefits from an improvement, for example a decrease in ignition delay, and/or an improvement in power. The marketing of such a composition may comprise an activity selected from (a) providing the composition in a container that comprises the relevant indication; (b) supplying the composition with product literature that comprises the indication; (c) providing the indication in a publication or sign (for example at the point of sale) that describes the composition; and (d) providing the indication in a commercial which is aired for instance on the radio, television or internet. The improvement may optionally be attributed, in such an indication, at least partly to the presence of the (co)polymer. The use of the composition may involve assessing the relevant property (for example the ignition delay, and/or the power output) derived from the composition during or after its preparation. It may involve assessing the relevant property both before and after incorporation of the (co)polymer, for example so as to confirm that the (co)polymer contributes to the relevant improvement in the composition.

Throughout the description and claims of this specification, the words “comprise” and “contain” and variations of the words, for example “comprising” and “comprises”, mean “including but not limited to”, and do not exclude other moieties, additives, components, integers or steps. Moreover the singular encompasses the plural unless the context otherwise requires: in particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Preferred features of each aspect of the invention may be as described in connection with any of the other aspects. Other features of the invention will become apparent from the following examples. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. For example, for the avoidance of doubt, the optional and preferred features of the fuel composition, the base fuel or the (co)polymer apply to all aspects of the invention in which the fuel composition, the base fuel or the (co)polymer are mentioned.

Moreover unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

Where upper and lower limits are quoted for a property, for example for the concentration of a fuel component, then a range of values defined by a combination of any of the upper limits with any of the lower limits may also be implied.

In this specification, references to fuel and fuel component properties are - unless stated otherwise - to properties measured under ambient conditions, i.e. at atmospheric pressure and at a temperature from 16 to 22 or 25°C, or from 18 to 22 or 25°C, for example about 20°C.

The present invention will now be further described with reference to the following non-limiting examples.

Examples

A series of exemplary inventive (co)polymers and comparative polymers were made using different combinations of isobornyl methacrylate, styrene, and isobutyl methacrylate. Isobornyl methacrylate was obtained from Sigma-Aldrich or Evonik (VISIOMER® terra IBOMA). Styrene and isobutyl methacrylate were obtained from Sigma-Aldrich.

Molecular Weight:

Four different methods were used to determine polymer molecular weight.

Method A:

Molecular weight was determined by Gel Permeation Chromatography (GPC) using narrow range polystyrene calibration standards. Samples and narrow range polystyrene calibration standards were prepared by dissolving 14-17 mg in 5 mL of tetrahydrofuran (mobile phase).

Column: (300 mm x 7.5 mm ID), Polymer Labs PL Gel Mixed C;

Mobile phase (Mp); Tetrahydrofuran;

Flow: 0.8mL/min;

Injection: 50µL;

RI Detector and column temperature: 40°C.

Method B:

Molecular weight was determined by Gel Permeation Chromatography (GPC) using narrow range polystyrene calibration standards. Samples and narrow range polystyrene calibration standards were prepared by dissolving 12-15 mg in 10 mL of tetrahydrofuran (mobile phase).

Column: (300 mm x 7.5 mm ID), Phenomenex Phenogel, 5µm Linear (2) mixed;

Mobile phase (Mp): Tetrahydrofuran;

Flow: 0.6 mL/min;

Injection: 50µL;

RI Detector and column temperature: 40°C.

Method C:

Molecular weight was determined by GPC-MALS, 40°C. Quantitation was a semi-batch mode by analysis using a guard column only. Samples were prepared by dissolving about 10 mg in 10 mL of tetrahydrofuran (mobile phase). Samples were further diluted with tetrahydrofuran as needed.

Column: Phenogel Guard 10^6A (50mm x 7.8mm);

Flow Rate: 0.5 ml/min THF;

Injection: 50 µl;

Detection: Wyatt Dawn Heleos 18 angle MALS 633 nm; and Wyatt Optilab T-REX Refractive Index DetectorQuantitation Zimm or Debye 1st order of 2nd order, with 5 to 18 angles.

Method D:

Molecular weight was determined by GPC-MALS. Samples were prepared by dissolving about 8 mg in 8 mL of tetrahydrofuran (mobile phase).

Column: 30cm x 4mm 5µm Phenogel Linear 2 - nominal 10M exclusion;

Column Oven: 40°C;

Solvent: Stabilized THF at 0.30 ml/min;

Injection: 50 µl;

Detection: Wyatt Dawn Heleos 18 angle MALS 633 nm; and Wyatt Optilab T-REX Refractive Index Detector

Synthesis Example S1. Preparation of Copolymer by Suspension Polymerization Process

Materials:

Hydroxyapatite (HAP)	1.2060 g
Sodium dodecyl benzenesulfonate [1% solution in deionized water; made by dissolution of WITCONATE 90-Flake (ex AkzoNobel) in deionized water]	0.4883 g
Water	165.06 g
Isobornyl methacrylate (IBOMA)	33.0210 g
Isobutyl methacrylate (IBMA)	6.0023 g
Styrene	21.0154 g
Vazo® 67 [2,2'-Azobis(2-methylbutyronitrile); ex DuPont™)	0.2738 g

Polymerization Procedure

A 4-neck 500 mL round bottom flask was equipped with a mechanical stirring paddle; a Y-tube equipped with an N_2-inlet topped reflux condenser and thermometer; and two stoppers. To the flask was charged HAP. To 165.06 g deionized water was charged 0.4883 g 1% sodium dodecyl benzene sulfonate. The resulting solution was charged to the reaction vessel, and the resulting suspension was heated to 80 °C under a positive pressure of nitrogen using a thermostat-controlled heating mantle. In a 125 mL Erlenmeyer flask, a solution of Vazo® 67 in isobornyl methacrylate, styrene, and isobutyl methacrylate was prepared. The solution was added in one portion to the reaction vessel, and the stirring rate was set to 690 rpm for 3 minutes and then lowered to 375 rpm. The polymerization was held at 80 °C for a total of 6 hours. During the course of the polymerization very little build-up of solids was noted on the flask wall or the thermometer. After 6 h at 80 °C, the reaction was cooled in an ice water bath with stirring and then allowed to stand overnight. A large amount of polymer beads were seen to fall from suspension, and the supernatant was essentially clear.

The pH of the polymer suspension was measured and found to be 6.91 at ~21 °C. The pH was lowered to 1.51 by the addition of dilute nitric acid with vigorous stirring and held at this pH for 1 hour. At the end of the hold, the pH had drifted down to 1.48. The reaction mixture was transferred to a blender where it was homogenized for about 60 s. The solids were isolated by vacuum filtration (paper filter). The product was washed with many 200 mL portions of tap water on the filter until the pH of the filtrate was 6.5 to 7. The product was then washed with 200 mL deionized water; 200 mL 1:1 (v:v) methanol / water; 200 mL methanol; and 2 x 200 mL deionized water. The solid product was dried to a constant weight in a vacuum oven (~40 °C). The yield of solid product was 58.14 g. The non-volatile content of the product was 98.6.

The MW was measured by GPC Method A; results:

Mn: 94,677; Mw: 351,230; PDI: 3.71.

Carbon-13 NMR measured in $CDCl_3$. By NMR, the copolymer is composed of 55.6 wt.% isobornyl methacrylate, 34.1 wt.% styrene, and 10.3 wt.% isobutyl methacrylate. This is nearly identical to the monomer feed by weight, which was 55% isobornyl methacrylate, 35% styrene, and 10% isobutyl methacrylate.

Synthesis Example S2. Preparation of copolymer by emulsion polymerization process

Materials:

Initial Charge:	
Deionized water	632.6 g

Aerosol® OT-75 PG (sodium dioctyl sulfosuccinate, 75% in propylene glycol and water; available from Cytec)	10.91 g
1% NaOH	As needed
Co-solvent:	
Acetone	139.6 g
Monomer mix:	
Isobornyl methacrylate	165 g
Styrene	105.2 g
Isobutyl methacrylate	30.7 g
Oxidant solution:	
t-Butyl hydroperoxide, 70%	0.0395 g
Deionized water	3.7565 g
Reductant solution:	
Deionized water	7.5 g
Sodium ascorbate	0.0730 g
Iron (II) sulfate heptahydrate, 0.25% in deionized water	0.60 g

Polymerization Procedure

A 2 L, 4-neck round bottom flask is equipped with an overhead mechanical stirrer, a Y-tube equipped with a condenser and nitrogen purge line, a thermometer, and a stopper. To the flask were charged deionized water and surfactant. The pH was checked and found to be within the desired range of 4 to 5 so no pH adjustment was made. A sub-surface nitrogen purge was then initiated through the stopper.

In a separate container, isobornyl methacrylate, styrene, and isobutyl methacrylate were combined.

An oxidant solution was then prepared by dissolving 0.0395 g t-butyl hydroperoxide (70%) in 3.7565 g deionized water.

While maintaining nitrogen purge, the monomer mixture and the acetone co-solvent were slowly added to the reaction vessel. During the addition, the agitation rate was gradually increased to 350 rpm.

Several minutes after the monomer mixture and the acetone co-solvent additions were completed, the agitation rate was slowed to 225 rpm. Using a thermostatted water bath, the reaction temperature was brought to about 38°C.

When the reaction temperature was about 38 °C, the oxidizer solution was added to the reaction mixture in a single shot. In a separate container, a reductant solution was prepared by dissolving 0.0730 g sodium ascorbate and 0.60 g of an 0.25 wt.% solution of iron (II) sulfate heptahydrate in 7.5 g deionized water.

About 5 minutes after the oxidant solution was added to the reaction mixture, the dark blue reductant solution was added via syringe to the reaction vessel in one shot while maintaining nitrogen purge.

About 5 minutes after the addition of the reductant, the onset of an exotherm was noted. As the reaction progressed, a bluish tint was noted in the emulsion, and it became increasingly more translucent, and a slight increase in viscosity was noted. The bath temperature was maintained at about 40 °C by adding ice or cool water, as needed. The reaction temperature reached a maximum of about 41 °C before the exotherm began to subside after about 2 hours. The reaction temperature was maintained thereafter at 38 °C using the water bath. After a total of 6 hours reaction time, the reaction was cooled and poured through cheesecloth into a container. Coagulum (caught on the cheesecloth) was noted and grit was measured.

The yield of polymer latex was 945 g. Solids (measured gravimetrically): 29.1%. Molecular weight by GPC (Method A): Mn = 1,278,000; Mw = 2,568,000; PDI = 2.01.

Solid polymer was isolated by adding the undiluted emulsion polymer to a large excess of methanol. The resulting precipitate was collected by vacuum filtration and washed extensively with methanol.

Synthesis Example S3-S18.

Additional copolymers were prepared following the basic procedure used to prepare Synthesis Example S1. The compositions and properties of these polymers and those of Synthesis Examples S1 and S2 are summarized in the Table 1 below.

Table 1

Example	P#	IBXMA	Styrene	IBMA	Tg (°C)	Mw (kDa)	PDI
		(Wt %)					
S1		55.6	34.1	10.3		351[a]	3.71
S2		55	35	10	124.7	2,568[a]	2.01
S3		25.0	0.0	75.0	92.4	4,200	1.31
S4		50.0	0.0	50.0	117.8	4,950[c]	n.d.
S5		55.0	0.0	45.0	123.4	2,900[c]	n.d.
S6	P42	80.0	0.0	20.0	162.6	2,801[b]	2.12
S7		45.0	15.0	40.0	112.8	4,300[d]	1.34
S8		45.0	25.0	30.0	113.4	3,600[d]	1.29
S9	P64	50.0	25.0	25.0	110.0	2,964[b]	2.35
S10	P44	51.5	31.5	17.0	122.5	3,053[b]	2.14
S11	P62	55.0	35.0	10.0	128.3	3,217[b] 5,683[d]	2.15[a] 1.28[c]
S12	P65	55.0	35.0	10.0	120.6	3,220[b]	2.49
S13		58.8	33.1	8.1	131.3	n.d.	
S14	P39	63.0	23.0	14.0	133.8	2,731[b]	2.05
S15		67.5	24.4	8.1	142.9	3,800[d]	1.31
S16		69.0	15.5	15.5	138.0	2,919[b]	2.17
S17	P63	76.25	8.13	15.60	123.7	2,554[b]	2.37
S18	P40	81.5	11.5	7.0	159.7	2,511[b]	2.22

IBXMA=isobornyl methacrylate; IBMA=isobutyl methacrylate.
a. Measured by Method A. b. Measured Method B. c. Measured by Method C. d. Measured by Method D.
n.d. = not determined

Solubility Comparative Example CE1.

Polystyrene with a reported Mw of 280,000 was obtained from Sigma-Aldrich.

Solubility Comparative Example CE2.

Poly(isobutyl methacrylate) with a Mw of 300kD and an inherent viscosity of 0.60 was obtained from Polysciences.

Solubility Examples E3-E8.

These polymers were prepared following the procedure of Synthesis Example S2. The compositions and properties of these polymers and those of Solubility Comparative Examples 1 and 2 are summarized in the Table 2 below.

Table 2

Example	IBXMA	Styrene	IBMA	Tg (°C)	Mw (kDa)	PDI
	(Wt %)					
CE1	0.000	100.0	0.000	100*	280	n.d.
CE2	0.000	0.000	100.0	53*	n.d.	
E3	100.0	0.000	0.000	202.0	2,196^{b}	2.24
E4	40.0	40.0	20.0	111.4	2,891^{b}	2.30
E5	45.0	37.0	18.0	114.8	2,738^{b}	2.22
E6	33.0	22.0	45.0	101.8	n.d.	
E7	25.0	10.0	65.0	n.d.	n.d.	
E8	15.0	0.0	85.0	n.d.	n.d.	

IBXMA=isobornyl methacrylate; IBMA=isobutyl methacrylate.
b. Measured by Method B.

Evaluation of Polymer Solubility in Diesel Fuel.

Solubility Index Method:

In a 20 mL vial with a cap, 0.2 g of polymer was added to 9.8 g diesel fuel. The resulting mixture was loosely capped stirred vigorously for 1 h at ambient room temperature (about 25 °C). The mixture was then heated to about 90 °C with stirring for 1 h. The resulting mixture or solution was allowed to cool to ambient room temperature and stand for 24 h. Polymer solubility was then determined by visual examination; polymers that showed any haze, turbidity or other signs of phase separation were judged to be insoluble. The mixture/solution was then placed in a refrigerator set at 8 °C for 24 h. Polymer solubility was then determined by visual examination; polymers that showed any haze, turbidity or other signs of phase separation were judged to be insoluble.

Cloud Point Determination Method:

To a 4-neck 250 mL round bottom flask equipped with an overhead mechanical stirrer, thermometer, condenser and septum/stopper was charged 5.0 g of polymer to 50.0 g of B7 diesel fuel. The resulting mixture was heated to 70-80 °C with stirring until a homogeneous solution was obtained. In the case of Comparative Example CE1 (polystyrene), the polymer did not dissolve in B7 diesel fuel even after stirring at 140 °C for 3 hours. A portion of the resulting solution was transferred to a 40 mL vial while warm. For polymers with a cloud point above about 25 °C, the solution was allowed to cool to about 25 °C while it was manually stirred with a thermometer. The reported cloud point is the temperature at which the solution visibly became turbid or cloudy. For polymers with a cloud point below about 25 °C, the solution was cooled to a temperature below the point at which the solution became visibly turbid or cloudy using an ice/water bath or a dry ice/acetone bath. The resulting turbid/cloudy mixture was allowed to gradually warm up to 25 °C, while it was manually stirred with a thermometer. The reported cloud point is the temperature at which the solution became clear. As a check, once the cloud point of a polymer was determined, clear solutions were gradually cooled (using cooling baths, if necessary) while stirring with a thermometer and the cloud point was confirmed.

The B7 diesel base fuel used was a B7 EN590 specification diesel base fuel having the characteristics given in Table 3 below. The results of the solubility evaluations of all of the Examples are summarized in Table 4 below.

Table 3

Parameter	Method	Units	
Cetane Number	DIN 51773	-	53.5
Density @ 15°C	DIN EN ISO 12185	kg m^{-3}	836.9
Distillation	DIN EN ISO 3405		
IBP		°C	179.2
5% v/v		°C	203.2
10% v/v		°C	214.4
20% v/v		°C	232.0
30% v/v		°C	247.1
40% v/v		°C	261.9
50% v/v		°C	276.2
60% v/v		°C	290.3
70% v/v		°C	305.0
80% v/v		°C	319.7
90% v/v		°C	335.9
95% v/v		°C	349.1
FBP		°C	358.2
Residue & loss		% vol	1.9
Flash Point	DIN EN ISO 2719	°C	69.0
Viscosity @ 40°C	DIN EN ISO 3104	mm^2 s^{-1}	2.8687
Sulphur -	DIN EN ISO 20884	mg/kg	<10
CFPP	DIN EN 116	°C	-29
Cloud point	DIN EN 23015	°C	-8
Fatty acid methyl ester	DIN EN 14078	% vol	6.4

Table 4. Polymer Solubility Evaluation Results.

Example	IBXMA	Styrene	IBMA	Tg (°C)	Cloud point @ 9.1% in B7 (°C)
	(Wt %)				
CE1	0.000	100.0	0.000	100*	insoluble
CE2	0.000	0.000	100.0	53*	45
E3	100.0	0.000	0.000	202.0	-2
E4	40.0	40.0	20.0	111.4	37
E5	45.0	37.0	18.0	114.8	32
E6	33.0	22.0	45.0	101.8	32
E7	25.0	10.0	65.0		33
E8	15.0	0.0	85.0		34

Example	IBXMA	Styrene	IBMA	Tg (°C)	Cloud point @ 9.1% in B7 (°C)
	(Wt %)				
S1	55.6	34.1	10.3		<25
S2	55	35	10	124.7	18
S3	25.0	0.0	75.0		23
S4	50.0	0.0	50.0	117.8	6
S5	55.0	0.0	45.0	123.4	-2
S6	80.0	0.0	20.0	162.6	-1
S7	45.0	15.0	40.0	112.8	16
S8	45.0	25.0	30.0	113.4	22
S9	50.0	25.0	25.0	110.0	22
S10	51.5	31.5	17.0	122.5	<25
S11	55.0	35.0	10.0	128.3	<25
S12	55.0	35.0	10.0	120.6	<25
S13	58.8	33.1	8.1	n.d.	17
S14	63.0	23.0	14.0	133.8	<25
S15	67.5	24.4	8.1	n.d.	3
S16	69.0	15.5	15.5	138.0	0
S17	76.25	8.13	15.60	123.7	<25
S18	81.5	11.5	7.0	159.7	0

The homopolymers of styrene and isobutyl methacrylate, CE1 and CE2, respectively, are not soluble in the B7 diesel fuel, but surprisingly large amounts of these monomers can be copolymerized with isobornyl methacrylate to give highly soluble copolymers. For example, based on weight fraction of each comonomer in S16 one would expect the cloud point at 9.1 wt.% of this copolymer to be about 27 °C using a linear mixing model. Instead, it is 0 °C, which is significantly and usefully different from the predicted value. Similarly, the predicted cloud point of S2, which contains over 40 wt.% of the insoluble comonomers styrene and isobutyl methacrylate is about 52 °C, which is above the range of sufficient solubility, while the actual cloud point is 18 °C, which is within the range of sufficient solubility.

The polymer E3 has a high Tg and a low cloud point of -2 °C but is an expensive product. For cost reasons, the product of example S6 is also less preferred. The products of Examples E4 - E8 are all less preferred because of the undesirable cloud point above 25 °C.

Comparative Examples 3-6.

Examples of the prior art were reworked. In CE3 the polymer of Example 1 step 1 in WO 2015/091513 was evaluated. In CE4 Example 12 of EP-A-0626442 was analysed. The resulting polymers had an Mw (using method D) of 79 and 95 kD, respectively. The molecular weight was too low to efficiently influence the rheology of a fluid in which it is dissolved.

In CE5 Example 7 of EP1260278 was reworked. However, no polymer resulted.

In CE7 Embodiment 11 of CN103992428 was reworked. However, the resulting polymer could not be dissolved in B7 fuel at 85°C, indicating that the polymers have an undesired cloud point of >85°C.

Diesel Fuel Test

The following fuel blends were prepared for testing. First a concentrate was made in the diesel base fuel, which concentrate contains at least 2.5 wt% of the copolymer, which was subsequently diluted with further diesel base fuel to yield a fuel composition having the desired mg/kg concentration. The amount of copolymer present is indicated in ppm based on the total weight of the fuel composition. The base fuel used had the specification given in Table 3 above.

	Fuel blend composition	
Fuel/Fuel blend #	Copolymer #	Amount of copolymer (ppm)
B7	none	0
P39	S14	50
P40	S18	100
P42	S6	50
P44	S10	50
P62	S11	25
P63	S17	80
P64	S9	50

P65	S12	50

The fuel blends to be tested were subjected to ignition testing in a Combustion Research Unit (CRU) obtained from Fueltech Solutions AS/Norway The CRU can mimic combustion conditions in modern diesel engines. It is described in Proceedings of the Combustion Institute 35 (2015) 2967 - 2974. The CRU features an injection system based on industry-standard high pressure common rail injector. Fuels were injected into a constant volume combustion chamber preconditioned as set out in the table below.

Condition	Temp (°C)	Chamber pressure (bar)	Fuel pressure (bar)	Main injection period (µs)	Number of injections
1	590	30	900	900	5

The CRU delivers pressure-temperature charts of the ignition process from which the ignition delay (ID), burn period (BP) and maximum pressure increase (MPI) can be determined. The ignition delay is defined as the time taken for the pressure in the combustion chamber to rise to 0.2 bar above its initial value ($ID^{0.2}$). The burn period is defined as the time from the moment where the chamber pressure equals its initial value plus 10% of MPI to the moment when the chamber equals its initial value plus 90% of MPI.

The results obtained are set out in the table below. Data are also provided in the table for the maximum rate of heat release (Max ROHR) and the time taken to maximum rate of heat release (T of max ROHR) for each sample tested. Max ROHR is a measure of how vigorous is the combustion. A higher number indicates that once the fuel has ignited, the speed at which the flame moves through the fuel is faster.

Fuel/ Fuel blend	$ID^{0.2}$ (msec)	ID % change from base	BP (msec)	BP % change from base	Max ROHR (bar/ msec)	T of max ROHR (msec)	T of max ROHR % change from base
B7	1.690	0	0.655	0	15.344	2.236	0
P39	1.654	-2.17	0.689	5.20	15.024	2.197	-1.75
P40	1.660	-1.81	0.673	2.71	15.222	2.203	-1.47
P44	1.654	-2.14	0.689	5.12	15.035	2.199	-1.65
P62	1.654	-2.13	0.688	4.96	15.031	2.199	-1.65
B7	1.685	0	0.661	0	15.305	2.236	0
P63	1.652	-1.95	0.700	5.84	15.025	2.195	-1.82
P64	1.653	-1.95	0.705	6.68	15.129	2.202	-1.50
P65	1.674	-0.66	0.657	-0.70	15.145	2.221	-0.67
B7	1.677	0	0.678	0	15.209	2.222	0
P42	1.647	-1.76	0.736	8.60	15.088	2.191	-1.38

These data show that, when used in a diesel fuel, the copolymers provided a performance benefit. The percentage change over the base fuel is mostly quoted to a 99 or 95% confidence level.

These data show that the fuel compositions that incorporate the copolymer have improved combustion characteristics.

The fuel compositions of the invention display an earlier ignition (shorter ignition delay) than the base fuel without the copolymer. A shorter ignition delay is known in the art to improve cold start ability, & reduce combustion noise. By decreasing ignition delay, the thermal efficiency of an engine stroke is improved, providing better combustion. These benefits of a shorter ignition delay are the same type of benefit as that obtained from an increased cetane number in a diesel fuel.

An earlier ignition also provides more power and therefore a shorter ignition delay is an indicator of the additional benefit of improving the power output of an engine.

While the ignition delay data show changes in terms of fractions of a millisecond, that data is significant at a 95% confidence level. In a diesel engine the crankshaft revolves through a full 360 degrees. At a vehicle operating at 2,000 rpm there will be 12,000 degrees of crank rotation per second (360 x 2000/60). This corresponds to 12 degrees of crank rotation per millisecond. A shortening of ignition delay by a fraction of a millisecond can mean a big difference in the phasing of the combustion in the engine.

High ROHR is also known to correlate with high combustion noise and so a reduction in the Max ROHR, and in the time to achieve it, also shows reduced combustion noise.

While not wishing to be bound by this theory, it is believed that the improved performance benefits are because of a modified rheology due to the use of the polymer in the fuel, which leads to an improved atomization of the fuel and a more complete combustion.

CLAIMS

1. A fuel composition for powering a combustion engine, the composition comprising:

a liquid base fuel; and

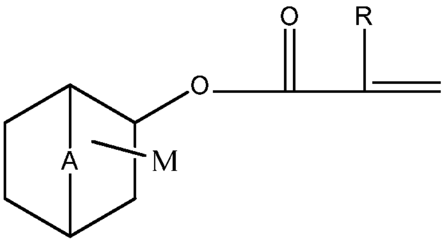
a (co)polymer obtainable by (co)polymerizing at least the following monomers:

- at least one bicyclic (meth)acrylate ester,
- optionally at least one lower-alkyl (meth)acrylate,
- optionally at least one aromatic vinyl monomer, and
- optionally other ethylenically unsaturated monomers.

2. A fuel composition according to Claim 1 wherein the bicyclic (meth)acrylate ester is present in an amount of more than 20% by weight, based on the weight of all monomers.

3. A fuel composition according to Claim 1 or 2 wherein the lower-alkyl (meth)acrylate is a C_1-C_7 alkyl (meth)acrylate.

4. The fuel composition according to any of claims 1 to 3, wherein the bicyclic (meth)acrylate ester is of the general formula (I)



(I)

wherein

R is H or $-CH_3$,

A is $-CH_2-$, $-CH(CH_3)-$ or $-C(CH_3)_2-$, and

M is covalently bonded to a carbon atom of the six-membered ring and is selected from the group consisting of hydrogen and a methyl group or a plurality thereof,

5. The fuel composition according to any of claims 1 to 4, wherein the copolymer comprises:

- 22 to 95 wt% of the bicyclic (meth)acrylate ester;
- 5 to 78 wt% of the lower-alkyl (meth)acrylate;
- 0 to 45 wt% of the aromatic vinyl monomer;
- 0 to 50 wt% of other ethylenically unsaturated monomers,

up to a total of 100 wt%, wherein the weight percentages of the monomer are based on the total weight of all the monomers.

6. The fuel composition according to any one of the preceding claims, wherein the copolymer comprises:

- 40 to 90 wt% of the bicyclic (meth)acrylate ester;
- 5 to 60 wt% of the lower-alkyl (meth)acrylate;
- 5 to 40 wt% of the aromatic vinyl monomer;
- 0 to 40 wt% of other ethylenically unsaturated monomers,

up to a total of 100 wt%, wherein the weight percentages of the monomer are based on the total weight of all the monomers.

7. The fuel composition according to any one of the preceding claims, wherein the copolymer comprises at most 20 wt% of other ethylenically unsaturated monomers.

8. The fuel composition according to any one of the preceding claims, wherein the weight percentage of bicyclic (meth)acrylate is at least 15% higher than the weight percentage of the aromatic vinyl monomer.

9. The fuel composition according to any one of the preceding claims, wherein the at least one bicyclic (meth)acrylate ester comprises, or is, isobornyl methacrylate.

10. The fuel composition according to any one of the preceding claims, wherein the at least one lower-alkyl

methacrylate comprises, or is, iso-butyl (meth)acrylate.

11. The fuel composition according to any one of the preceding claims, wherein the at least one aromatic vinyl monomer comprises, or is, styrene.

12. The fuel composition according to any one of the preceding claims, wherein the (co)polymer has a weight average molecular weight of at least 100,000 D.

13. A fuel composition according to any of Claims 1 to 3 wherein the copolymer has a weight averaged molecular weight of from 100,000 to 10,000,000 D, determined using GPC-MALS techniques for a solution in THF at 40°C, whereby copolymers of just isobornyl (meth)acrylate and C_1-C_4 alkyl (meth)acrylate have a number averaged molecular weight greater than 400 kD.

14. The fuel composition according to any one of the preceding claims, wherein the (co)polymer has a glass transition temperature in the range of from 50 to 205 °C.

15. The fuel composition according to any one of the preceding claims, wherein the base fuel is a diesel base fuel and the fuel composition is a diesel fuel composition.

16. The fuel composition according to any one of the preceding claims, wherein the amount of (co)polymer present in the fuel composition is in the range of from 10ppm to 300ppm, preferably 10ppm to 100ppm, more preferably 25ppm to 80ppm, by weight of the fuel composition.

17. A method of blending a fuel composition according to any preceding claim, the method comprising blending the (co)polymer, or an additive package containing the (co)polymer, with the base fuel.

18. Use of a (co)polymer or an additive package containing the (co)polymer as defined in any one of

claims 1 to 14 in a fuel composition, preferably a diesel fuel composition, for the purpose of one or more of:

(i) aiding atomisation of the fuel composition;

(ii) decreasing the ignition delay of the composition; and

(iii) improving the power output of a combustion ignition engine run on the composition.

19. Use of a fuel composition according to any one of claims 1 to 16 for the purpose of one or more of:

(i) aiding fuel atomisation;

(ii) decreasing ignition delay; and

(iii) improving the power output of a combustion ignition engine run on the composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/061251

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/192
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L C10M C10G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/064568 A1 (STOHR TORSTEN [DE] ET AL) 12 March 2009 (2009-03-12) paragraphs [0011], [0017], [0034], [0042] - [0053], [0059], [0073], [0079] -----	1-19
X	US 2011/192076 A1 (HESS BRIAN [US] ET AL) 11 August 2011 (2011-08-11) paragraphs [0033], [0055] - [0067], [0071], [0093], [0098] -----	1-19
X	AU 2013 361 819 A1 (BASF SE) 21 May 2015 (2015-05-21) pages 14, 18; table 1 -----	1,4-6,9, 17

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

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 14 June 2016	Date of mailing of the international search report 27/06/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pardo Torre, J

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/061251

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