COMPOSITION

The present invention relates to an additive composition for fuel, a fuel composition, and methods and uses of such compositions. In particular, the present invention relates to compositions which may be used to reduce soot content and ash content of an exhaust of a combustion system for fuel. The invention also relates to an essentially hydrocarbon mixture (HC mixture) which burns so as to produce very little soot, particularly heating oil and a corresponding additive concentrate.

Ferrocene and its derivatives are known from the literature. Ferrocene and its manufacture were described for the first time in Nature 168 (1951), Page 1039. Since then, ferrocene and its derivatives as well as corresponding manufacturing procedures have been the object of numerous patents, e.g. US 2 769 828, US 2 834 796, US 2 898 360 and US 3 437 634.

In addition to many other compounds, DE 34 18 648 names ferrocene (dicyclopentadienyl iron) as a possible additive in order to optimise combustion of heating oil. This optimised combustion encourages complete combustion of the heating oil.

In US 4 389 220, a two stage process for conditioning a diesel motor is described. According to this patent, an initial high dosage of ferrocene, 20 to 30 ppm, in the diesel fuel can remove carbon deposits in the combustion chamber and also deposit a layer of catalytic iron oxide on the combustion surfaces. Subsequently, a lower dosage of ferrocene, 10 to 15 ppm, maintains this catalytic iron oxide coating. At the same time it was found that with these measures, fuel consumption is lower by up to 5 %. As it is difficult to add organic iron compounds such as ferrocene to fuels in solid form, concentrated solutions are generally used.

DE 30 31 158 A1 teaches that a mixture consisting of 70 to 85% of water by volume and 0.1 to 1% of camphor can be added to heating oil immediately before combustion.

DE 21 47 994 teaches that additives which among others contain camphor can be used in the combustion air of internal combustion engines.

US 3 925 031 teaches that an additive which contains camphor and naphthalene among others can be added to a gasifier fuel, a diesel fuel or a lubricating oil.

In the art, camphor has been used in fuel to provide a reduction in either fuel consumption or hazardous emissions. However, camphor is not known to reduce soot. Rather, as discussed in US 5 116 390, a disadvantage of using camphor is that additional soot formation is noted on burning fuel that contains camphor as an additive. Similarly, US 3 925 031 teaches that use of camphor in gasoline in sufficient quantities to increase the effective octane rating of the gasoline also results in a reduction of combustion efficiency and a corresponding increase in the quantity of unburned carbon, leading to sooty exhaust particles.

It is also known that combustion catalysts can lead to the production of ash, see for example US 6 948 926. Thus, additives which reduce soot formation may lead to an increase in the formation of ash. H. Jungbluth, B. Richter, "Neue Ergebnisse zur Regeneration von Dieselpartikelfiltern mit Additiven", Mineralöltechnik, July 1998; Regeneration von Partikelfiltern mit Additiven, FUELS 1999, 2nd International Colloquium, 20-21.01.1999, page 489-495, shows how using such additives in the fuel of heavy duty diesel engines provides an increased peak in the emissions caused by the ash derived from combustion of the additive.

CN 1597873 discloses a fuel which includes methanol, hydrogen peroxide, ferrocene and camphor that reduces the harmful emissions.

The present invention alleviates the problems of the prior art.

In one embodiment the present disclosure provides an additive composition for a fuel comprising:

(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and

(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;

wherein the additive composition comprises at least 100 ppm of the organic compound (ii).

In one aspect, there is provided a fuel composition comprising:
(i) at least 0.1 ppm of a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof;
(ii) at least 1 ppm of an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and
(iii) a fuel selected from biofuel, diesel, marine fuel, heating oil, middle distillate oil and heavy fuel oil and including such fuels containing renewable or bio-derived components and commonly termed biofuel; wherein the fuel composition comprises 9 ppm or less of metal compound (i).

In another aspect, there is provided a method for combustion of a fuel composition in a combustion system with an exhaust, comprising providing the fuel composition comprising:
(i) at least 0.1 ppm of a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof;
(ii) at least 1 ppm of an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and
(iii) a fuel; and
combusting the same such that soot content and ash content of the exhaust is reduced; wherein the fuel composition comprises 9 ppm or less of metal compound (i).

In another aspect, there is provided the use of:
(i) at least 0.1 ppm of a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and
(ii) at least 1 ppm of an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
in a fuel composition comprising 9 ppm or less of metal compound (i) for reducing the soot content and the ash content of an exhaust of a combustion system for fuel.

In a further embodiment the present disclosure provides a fuel composition comprising an additive composition as disclosed herein and a fuel.

In a further embodiment the present disclosure provides a fuel composition comprising:

(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof;

(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and

(iii) a fuel selected from biofuel, diesel, marine fuel, heating oil, middle distillate oil and heavy fuel oil.

In a further embodiment the present disclosure provides a method for combustion of a fuel composition in a combustion system with an exhaust, comprising providing the fuel composition comprising:

(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof;

(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and

(iii) a fuel; and

combusting the same such that soot content and ash content of the exhaust is reduced.

In one embodiment, the task of the invention is to provide a hydrocarbon mixture which contains an organic iron compound in combination with a further component which leads to a considerable reduction in soot. That is the combination of the iron compound and the further component produces a greater reduction in the amount of soot compared to that observed if the same quantity of iron compound is used alone, or to that observed if the same quantity of the further component is used alone. Thus, the quantity of the iron compound used in the mixture may be reduced to a level where, if the iron compound were used on its own, its catalytic effect in respect of soot reduction would be minimal. This task is fulfilled by means of a hydrocarbon mixture which produces little soot on combustion with at least 0.1 ppm ferrocene and at least 1 ppm camphor added.

Thus, it is known in the art that metal compounds, such as ferrocene, can improve combustion in a combustion system and reduce carbon deposits leading to a reduction in the amount of soot observed in the exhaust of the combustion system. However, the

quantity of iron compound required to produce an adequate reduction in soot also leads to an increased amount of ash being formed. In contrast, organic compounds, such as camphor, do not produce ash, but are known to increase the amount of soot observed. The present disclosure surprisingly shows that compositions comprising a metal compound in small quantities, such as ferrocene, and an organic compound, such as camphor, can provide good reductions in soot whilst only producing low amounts of ash. Surprisingly, such a composition provides significantly better soot reduction than is observed if the same amount of metal compound is used in the absence of the organic compound.

Various embodiments of the invention are defined in the appended claims.

Metal compound (i)

The metal compound (i) is selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof.

Preferably, the metal compound (i) is selected from an iron compound, methylcyclopentadienyl manganese tricarbonyl, manganese(II) 2-ethylhexanoate, manganese naphthenate, calcium 2-ethylhexanoate, calcium napthenate, calcium sulfonate, cerium(III) 2-ethylhexanoate, cerium sulfonate, and mixture thereof.

It is important that the metal compound (i) for use in the invention are fuel soluble or dispersible and preferably fuel stable. The precise nature of the metal containing compounds is less important.

Manganese compound

Preferably the manganese compound is selected from a manganese carbonyl compound, manganese(II) 2-ethylhexanoate, manganese naphthenate, and mixtures thereof.

The most desirable general type of manganese carbonyl compounds utilised in accordance with this invention comprise organomanganese polycarbonyl compounds. For best results, use should be made of a cyclopentadienyl manganese tricarbonyl

compound of the type described in U.S. Pat. Nos. 2,828,417 and 3,127,351. Thus use can be made of such compounds as cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, butylcyclopentadienyl manganese tricarbonyl, pentylcyclopentadienyl manganese tricarbonyl, hexylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, dimethyloctylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and like compounds in which the cyclopentadienyl moiety contains up to about 18 carbon atoms.

In one aspect, the manganese compound is an organomanganese compound.

A preferred organomanganese compound is cyclopentadienyl manganese tricarbonyl. Particularly preferred for use in the practice of this invention is methylcyclopentadienyl manganese tricarbonyl.

Methods for the synthesis of cyclopentadienyl manganese tricarbonyls are well documented in the literature. See for example, in addition to U.S. Pat. Nos. 2,818,417 and 3,127,351 noted above, U.S. Pat. Nos. 2,868,816; 2,898,354; 2,960,514; and 2,987,529, among others.

Other organomanganese compounds which may be employed include the acyl manganese tricarbonyls such as methylacetyl cyclopentadienyl manganese tricarbonyl and benzoyl methyl cyclopentadienyl manganese tricarbonyl, described in U.S. Pat No. 2,959,604; the aryl manganese pentacarbonyls such as phenyl manganese pentacarbonyl, described in U.S. Pat. 3,007,953; and the aromatic cyanomanganese dicarbonyls such as mesitylene cyanomanganese dicarbonyl, described in U.S. Pat. No. 3,042,693. Likewise, use can be made of cyclopentadienyl manganese dicarbonyl compounds of the formula $RMn(CO)_2L$, where R is a substituted or unsubstituted cyclopentadienyl group having 5 to 18 carbon atoms, and L is a ligand, such as an olefin, an amine, a phosphine, SO_2, tetrahydrofuran, or the like. Such compounds are referred to, for example in, Herberhold, M., *Metal π-Complexes,* Vol. II, Amsterdam, Elsevier, 1967 or Giordano, P.J. and Weighton, M. S., *Inorg. Chem.*, 1977, 16, 160. Manganese

pentacarbonyl dimer (dimanganese decacarbonyl) can also be employed if desired.

Preferably the manganese compound is a manganese complex.

Preferably the manganese compound is selected from cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl.

The manganese compound may be cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl, wherein the substituents can be, for example, one or more C_{1-5} alkyl groups, preferably C_{1-2} alkyl groups. A combination of such manganese complexes may also be used.

Preferably the manganese compound is selected from cyclopentadienyl manganese tricarbonyl and substituted cyclopentadienyl manganese tricarbonyl.

Preferably the manganese compound is methylcyclopentadienyl manganese tricarbonyl (MMT).

Calcium compound

Preferably the calcium compound is selected from calcium 2-ethylhexanoate, calcium napthenate, calcium sulfonate, and mixtures thereof.

Preferably the calcium compound is calcium sulfonate.

Other suitable calcium compounds are disclosed in GB2248068 and GB2254610 and are discussed therein.

Cerium compound

Preferably the cerium compound is selected from cerium(III) 2-ethylhexanoate, cerium sulfonate, and mixtures thereof.

Most preferably, the metal compound (i) is an iron compound or a mixture of iron compounds.

Iron compound

Preferably the iron compound is an iron complex selected from bis-cyclopentadienyl iron; substituted bis-cyclopentadienyl iron; overbased iron soaps, such as iron tallate and iron octoate; and mixtures thereof.

Preferably the iron compound is an iron complex selected from bis-cyclopentadienyl iron, substituted bis-cyclopentadienyl iron and mixtures thereof.

Preferably the iron compound is a substituted bis-cyclopentadienyl iron selected from adamantyl bis-cyclopentadienyl iron, bis(dicyclopentadienyl-iron) dicarbonyl and mixtures thereof. Bis(dicyclopentadienyl-iron) dicarbonyl is also known as cyclopentadienyliron dicarbonyl dimer.

In one aspect, the iron compound is an iron complex selected from bis-cyclopentadienyl iron, adamantyl bis-cyclopentadienyl iron, bis(dicyclopentadienyl-iron)dicarbonyl, iron tallate and iron octoate; and mixtures thereof.

Other suitable substituted bis-cyclopentadienyl iron complexes are those wherein the substituents can be, for example, one or more C_{1-30} alkyl groups, preferably C_{1-20} alkyl groups, preferably C_{1-10} alkyl groups, C_{1-5} alkyl groups, preferably C_{1-2} alkyl groups. A combination of such iron complexes may also be used.

Suitable alkyl-substituted-dicyclopentadienyl iron complexes are cyclopentadienyl-(methylcyclopentadienyl) iron, cyclopentadienyl(ethyl-cyclopentadienyl) iron, bis-(methylcyclopentadienyl) iron, bis-(ethylcyclopentadienyl) iron, bis-(1,2-dimethyl-cyclopentadienyl) iron, and bis-(1-methyl-3-ethylcyclo-pentadienyl) iron. These iron complexes can be prepared by the processes taught in US-A-2680756, US-A-2804468, GB-A-0733129 and GB-A-0763550. Another volatile iron complex is iron pentacarbonyl.

Suitable iron complexes are bis-cyclopentadienyl iron and/or bis-(methylcyclo-pentadienyl)

iron.

The co-ordination chemistry relevant to the solubilisation of transition metals, including iron, in hydrocarbon solvents, e.g. diesel fuel, is well known to those skilled in the art (see e.g. WO-A-87/01720 and WO-A-92/20762).

Substituted bis-cyclopentadienyl complex of iron (substituted ferrocenes) for use in the invention include those in which substitution may be on either or both of the cyclopentadienyl groups. Suitable substituents include, for example, one or more C_{1-5} alkyl groups, preferably C_{1-2} alkyl groups.

Particularly suitable alkyl-substituted-dicyclopentadienyl iron complexes (substituted ferrocenes) include cyclopentadienyl(methylcyclopentadienyl) iron, bis-(methylcyclopentadienyl) iron, bis-(ethylcyclopentadienyl) iron, bis-(1,2-dimethylcyclopentadienyl) iron and 2,2-diethylferrocenyl-propane.

Other suitable substituents that may be present on the cyclopentadienyl rings include cycloalkyl groups such as cyclopentyl, aryl groups such as tolylphenyl, and acetyl groups, such as present in diacetyl ferrocene. A particularly useful substituent is the hydroxyisopropyl group, resulting in (α-hydroxyisopropyl) ferrocene. As disclosed in WO-A-94/09091, (α-hydroxyisopropyl)ferrocene is a room temperature liquid.

Ferrocenes linked by a "bridge" may be used in the present invention. Suitable compounds are taught in WO 02/018398 and WO 03/020733. Thus, a suitable "bridge" linking ferrocenes may be a unsubstituted or substituted hydrocarbyl group. The term "unsubstituted or substituted hydrocarbyl group" as used herein means a group comprising at least C and H and which may, optionally, comprise one or more suitable substituents. In a preferred embodiment one carbon atom of the "bridge" hydrocarbyl group is attached to two ferrocene moieties, hence, bridging the ferrocenes. Further ferrocene moieties may be attached via further "bridge" hydrocarbyl groups. A typical unsubstituted or substituted hydrocarbyl group is an unsubstituted or substituted hydrocarbon group. Here the term "hydrocarbon" means any one of an alkylene group, an alkenylene group, an alkynylene group, which groups may be linear, branched or cyclic, or an aryl group. For example, the unsubstituted or substituted hydrocarbon group may be an alkylene, branched alkylene or cycloalkylene group. The term

hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch. A preferred unsubstituted or substituted hydrocarbon group is an unsubstituted or substituted alkylene group having at least one carbon atom in the alkylene linkage. More preferably, the unsubstituted or substituted hydrocarbon group is an unsubstituted or substituted alkylene group having from 1 to 10 carbon atoms in the alkylene linkage, for example, having at least 2 carbon atoms in the alkylene linkage or having one carbon atom in the alkylene linkage. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the hydrocarbyl group may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur, nitrogen and oxygen, for example, oxygen.

Other organometallic complexes of iron may also be used in the invention, to the extent that these are fuel soluble and stable. Such complexes include, for example, iron pentacarbonyl, di-iron nonacarbonyl, (1,3-butadiene)-iron tricarbonyl, and (cyclopentadienyl)-iron dicarbonyl dimer. Salts such as di-tetralin iron tetraphenylborate ($Fe(C_{10}H_{12})_2(B(C_6H_5)_4)_2$) may also be employed.

A preferred iron complex is ferrocene (i.e. bis-cyclopentadienyl iron).

Instead of ferrocene, equivalent quantities of other organic iron compounds which are soluble in hydrocarbon mixtures can be used in respect of the iron content. This applies to all statements and descriptions which follow. Dicyclopentadienyl iron has proven to be particularly suitable. Ferrocene derivatives can be used at least in part instead of ferrocene. Ferrocene derivatives are compounds where, starting from a basic ferrocene molecule, further substituents are found on one or both of the cyclopentadienyl rings. Examples could be ethylferrocene, butylferrocene, acetylferrocene and 2,2-bis-ethylferrocenylpropane. Geminal bisferrocenylalkanes are also suitable, as described, for example, in DE 201 10 995 and DE 102 08 326.

As a result of a combination of their solubility, stability, high iron content and, above all, volatility, the substituted ferrocenes are preferred iron compounds for use in the

invention. Ferrocene itself is an especially preferred iron compound on this basis. Ferrocene of suitable purity is sold in a range of useful forms as PLUTOcen^{RTM} and as solutions, Satacen^{RTM} both by Innospec Deutschland GmbH.

The iron compounds for use in the invention need not feature iron-carbon bonds in order to be fuel compatible and stable. Salts may be used; these may be neutral or overbased. Thus, for example, overbased soaps including iron stearate, iron oleate and iron naphthenate may be used. Methods for the preparation of metal soaps are described in The Kirk-Othmer Encyclopaedia of Chemical Technology, 4th Ed, Vol. 8:432-445, John Wiley & Sons, 1993. Suitable stoichiometric, or neutral, iron carboxylates for use in the invention include the so-called 'drier-iron' species, such as iron tris(2-ethylhexanoate) [19583-54-1].

Iron complexes not featuring metal-carbon bonds and not prepared as in the preceding reference may also be used in the invention provided these are adequately fuel compatible and stable. Examples include complexes with β-diketonates, such as tetramethylheptanedionate.

Iron complexes of the following chelating ligands are also suitable for use in the invention:

- aromatic Mannich bases such as those prepared by reaction of an amine with an aldehyde or ketone followed by nucleophilic attack on an active hydrogen containing compound, e.g. the product of the reaction of two equivalents of (tetrapropenyl)phenol, two of formaldehyde and one of ethylenediamine,
- hydroxyaromatic oximes, such as (polyisobutenyl)-salicylaldoxime. These may be prepared by reaction of (polyisobutenyl)phenol, formaldehyde and hydroxylamine;
- Schiff bases such as those prepared by condensation reactions between aldehydes or ketones (e.g. (tert-butyl)-salicylaldehyde) and amines (e.g. dodecylamine). A tetradentate ligand may be prepared using ethylenediamine (half equivalent) in place of dodecylamine;
- substituted phenols, such as 2-substituted-8-quinolinols, for example 2-dodecenyl-8-quinolinol or 2-N-dodecenylamino-methylphenol;
- substituted phenols, such as those wherein the substituent is NR_2 or SR in which R is a long chain (e.g. 20-30 C atoms) hydrocarbyl group. In the case of both α- and β-substituted phenols, the aromatic rings may beneficially be further substituted with

hydrocarbyl groups, e.g. lower alkyl groups;

- carboxylic acid esters, in particular succinic acid esters such as those prepared by reaction of an anhydride (e.g. dodecenyl succinic anhydride) with a single equivalent of an alcohol (e.g. triethylene glycol);
- acylated amines. These may be prepared by a variety of methods well known to those skilled in the art. However, particularly useful chelates are those prepared by reaction of alkenyl substituted succinates, such as dodecenyl succinic anhydride, with an amine, such as N,N'-dimethyl ethylene diamine or methyl-2-methylamino-benzoate;
- amino-acids, for example those prepared by reaction of an amine, such as dodecylamine, with an α,β-unsaturated ester, such as methylmethacrylate. In cases where a primary amine is used, this may be subsequently acylated, such as with oleic acid or oleyl chloride;
- hydroxamic acids, such as that prepared from the reaction of hydroxylamine with oleic acid,
- linked phenols, such as those prepared from condensation of alkylated phenols with formaldehyde. Where a 2:1 phenol:formaldehyde ratio is used the linking group is CH_2. Where a 1:1 ratio is employed, the linking group is CH_2OCH_2;
- alkylated, substituted pyridines, such as 2-carboxy-4-dodecylpyridine;
- borated acylated amines. These may be prepared by reaction of a succinic acylating agent, such as poly(isobutylene)succinic acid, with an amine, such as tetraethylenepentamine. This procedure is then followed by boronation with a boron oxide, boron halide or boronic acid, amide or ester. Similar reactions with phosphorus acids result in the formation of phosphorus-containing acylated amines, also suitable for providing an oil-soluble iron chelate for use in the invention;
- pyrrole derivatives in which an alkylated pyrrole is substituted at the 2-position by OH, NH_2, NHR, CO_2H, SH or C(O)H. Particularly suitable pyrrole derivatives include 2-carboxy-t-butylpyrroles;
- sulphonic acids, such as those of the formula R^1SO_3H, where R^1 is a C_{10} to about C_{60} hydrocarbyl group, e.g. dodecylbenzene sulphonic acid;
- organometallic complexes of iron, such as ferrocene, substituted ferrocenes, iron naphthenate, iron succinates, stoichiometric or over-based iron soaps (carboxylate or sulphonate), iron picrate, iron carboxylate and iron -diketonate complexes.

Suitable iron picrates for use in the invention include those described in US-A-4,370,147

and US-A-4,265,639.

Other iron-containing compounds for use in the invention include those of the formula M(R)x.nL wherein: M is an iron cation; R is the residue of an organic compound RH in which R is an organic group containing an active hydrogen atom H replaceable by the metal M and attached to an O, S, P, N or C atom in the group R; x is 2 or 3; n is 0 or a positive integer indicating the number of donor ligand molecules forming a dative bond with the metal cation; and L is a species capable of acting as a Lewis base.

Organic compound (ii)

The organic compound (ii) is selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof.

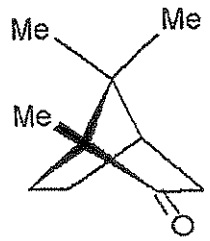
Preferably, the organic compound (ii) is selected from a bicyclic monoterpene, substituted bicyclic monoterpene and mixtures thereof.

Suitable substituted bicyclic monoterpenes are those wherein the substituents can be, for example, one or more of aldehyde, ketone, alcohol, acetate and ether functional groups.

Preferably, the organic compound (ii) is a bicyclic monoterpene or substituted bicyclic monoterpene selected from camphor, camphene, isobornyl acetate, dipropyleneglycol-isobornyl ether and mixtures thereof.

In one aspect, the organic compound (ii) is selected from camphor, camphene, isobornyl acetate, dipropyleneglycol-isobornyl ether, adamantane, propylene carbonate and mixtures thereof.

Preferably, the organic compound (ii) is camphor. Camphor has the systematic name 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one. Camphor has the following structure:



Additive composition

In one aspect, the present invention provides an additive composition for a fuel comprising:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
with the proviso that the composition is substantially free of methanol.

By the term "substantially free of methanol" is meant that the composition comprises less than 10 wt %, preferably less than 5 wt %, preferably less than 2 wt %, preferably less than 1 wt %, preferably less than 0.5 wt %, preferably less than 0.1 wt %, preferably less than 0.05 wt %, preferably less than 0.01 wt % methanol.

In another aspect, the present invention provides an additive composition for a fuel comprising:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
with the proviso that the composition is substantially free of C1 to C5 alcohol.

As used herein, the term "C1 to C5 alcohol" means a straight chain or branched alcohol containing between 1 and 5 carbon atoms, such as methanol, ethanol, propanol, butanol and pentanol. An example of a suitable branched alcohol is tertiary butanol.

By the term "substantially free of C1 to C5 alcohol" is meant that the composition comprises less than 10 wt %, preferably less than 5 wt %, preferably less than 2 wt %,

preferably less than 1 w t%, preferably less than 0.5 wt %, preferably less than 0.1 wt %, preferably less than 0.05 wt %, preferably less than 0.01 wt % C1 to C5 alcohol compounds.

In a further aspect, the present invention provides an additive composition for a fuel comprising:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
with the proviso that the composition is substantially free of any alcohol.

By the term "substantially free of any alcohol" is meant that the composition comprises less than 10 wt %, preferably less than 5 wt %, preferably less than 2 wt %, preferably less than 1 w t%, preferably less than 0.5 wt %, preferably less than 0.1 wt %, preferably less than 0.05 wt %, preferably less than 0.01 wt % alcohol.

In a further aspect the present invention provides an additive composition for a fuel comprising:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound, and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
with the proviso that the composition is substantially free hydrogen peroxide.

By the term "substantially free of hydrogen peroxide" is meant that the composition comprises less than 10 wt %, preferably less than 5 wt %, preferably less than 2 wt %, preferably less than 1 wt %, preferably less than 0.5 wt %, preferably less than 0.1 wt %, preferably less than 0.05 wt %, preferably less than 0.01 wt % of hydrogen peroxide.

In a preferred aspect, the metal compound (i) is bis-cyclopentadienyl iron and the organic compound (ii) is camphor.

Preferably the additive composition further comprises a solvent.

It is convenient for the additive composition to be added as a solution of the active components in a solvent. It is preferable for such solutions to exhibit a high concentration of the active components in the solvent. Ideal solvents are those in which all the active ingredients dissolve equally well and which form a solution which is stable over prolonged storage periods, and also under cold conditions.

Preferably the solvent is selected from an aromatic compound, a paraffin compound and mixtures thereof. As used herein, the term "paraffin compound" includes both straight chain and branched chain compounds. The branched chain compounds are also known as iso-paraffins.

Preferably the additive composition for a fuel comprises the metal compound or compounds (i) in an amount sufficient to provide less than 30,000 ppm of the metal; preferably less than 15,000 ppm; preferably less than 6,000 ppm.

Preferably the additive composition for a fuel comprises the metal compound or compounds (i) in an amount sufficient to provide from 3 ppm to 30,000 ppm of the metal; preferably from 15 ppm to 15,000 ppm; preferably from 60 ppm to 6,000 ppm.

Preferably the additive composition for a fuel comprises less than 90,000 ppm of the metal compound (i); preferably less than 45,000 ppm; preferably less than 18,000 ppm.

Preferably the additive composition for a fuel comprises from 10 ppm to 90,000 ppm of the metal compound (i); preferably from 50 ppm to 45,000 ppm; preferably from 200 ppm to 18,000 ppm.

Preferably the additive composition for a fuel comprises at least 100 ppm of the organic compound (ii); preferably at least 500 ppm; preferably at least 1,000 ppm; preferably at least 2,000 ppm; preferably at least 10,000 ppm; preferably at least 50,000 ppm; preferably at least 80,000 ppm; preferably at least 100,000 ppm.

Preferably the additive composition for a fuel comprises from 100 ppm to 700,000 ppm of the organic compound (ii); preferably from 500 ppm to about 350,000 ppm; preferably from about 2,000 ppm to about 140,000 ppm; preferably from about 50,000 ppm to about 130,000 ppm; preferably from about 80,000 ppm to about 120,000 ppm.

The fuel additives according to the invention may be added as part of a package to the fuel prior to combustion. This may be done at any stage in the fuel supply chain (for example, at the refinery or distribution terminal) or may be added via a dosing device associated with the combustion system, for examples, on-board the vehicle. If a dosing device is used it may dose the additives either to the fuel or even separately direct into the combustion chamber or inlet system. The fuel additives may be added to the fuel in the combustion systems' fuel tank by the user, a so-called 'aftermarket' treatment.

Preferably the additive composition is a solution. The additive composition is for addition to a fuel. Such an additive might be dosed at any stage in the fuel supply chain prior to combustion of the fuel. The fuel additives of the invention may be dosed to the fuel at any stage in the fuel supply chain. Preferably, each additive is added to the fuel close to the engine or combustion system, within the fuel storage system for the engine or combustion system at the refinery, distribution terminal or at any other stage in the fuel supply chain, including aftermarket use. The additive may be added to the fuel at the refinery or at the distribution terminal.

Where, however, the additive combination is intended to be added as an 'aftermarket' treatment, the volume of solvent used will be such as to provide a non-viscous solution, suitable for use in a dispenser bottle or syringe pack. The solvents to be used should be readily fuel soluble and compatible, including with respect to boiling point range, and preferably will have flash points in excess of 62°C for ease of storage.

In one aspect, the additive composition for a fuel is an additive concentrate composition.

Fuel

In one aspect of the present invention, the fuel is selected from gasoline, diesel, marine fuel, heating oil, middle distillate oil, ,heavy fuel oil and including such fuels containing renewable or bio-derived components and commonly termed bio-fuel, e.g. bio diesel.

In another aspect, preferably the fuel is selected from biofuel, diesel, marine fuel, heating oil, middle distillate oil and heavy fuel oil.

In another aspect, preferably the fuel is selected from diesel, marine fuel, heating oil, middle distillate oil and heavy fuel oil

In one aspect, the fuel is gasoline.

In one aspect the fuel is a fuel for spark ignition engines such as gasoline.

Preferably the fuel is a fuel for a high compression spontaneous ignition engine.

Preferably the fuel is diesel. The diesel may be biodiesel, low sulphur diesel and ultra-low sulphur diesel.

In another aspect, the fuel is marine fuel or bunker fuel.

In another aspect, the fuel is heating oil, for example, kerosene. Preferably a light heating oil. Preferably, the light heating oil is HEL: Heizöl extra leichtflüssig according to DIN 51603, Part 1.

In a further aspect, the fuel is a middle distillate oil.

In a further aspect, the fuel is a heavy fuel oil.

In another aspect, the fuel is a hydrocarbon mixture, preferably, a liquid hydrocarbon mixture.

Fuel composition

Preferably the fuel composition comprises at least 0.1 ppm of the metal compound (i).

Preferably the fuel composition comprises 9 ppm or less of the metal compound (i); preferably 8 ppm or less of the metal compound (i).

Preferably the fuel composition comprises the metal compound (i) in from about 0.1 ppm to about 9 ppm.

Preferably the fuel composition comprises the metal compound (i) in from about 0.5 ppm to about 8 ppm.

If, for example, the metal compound (i) is ferrocene, then 0.1 ppm of ferrocene is an amount sufficient to provide 0.03 ppm of the metal (iron). Thus, if the fuel composition comprises a metal compound (i) in an amount sufficient to provide 0.03 ppm of the metal, it would be present in an equivalent amount to 0.1 ppm of ferrrocene.

Preferably the fuel composition comprises the metal compound (i) in an amount sufficient to provide at least 0.03 ppm of the metal. Preferably the fuel composition comprises the metal compound (i) in an amount to provide 2.70 ppm or less of the metal. Preferably the fuel composition comprises the metal compound (i) in an amount to provide 2.40 ppm or less of the metal. Preferably the fuel composition comprises the metal compound (i) in an amount sufficient to provide from 0.03 ppm to 2.70 ppm of the metal. Preferably the fuel composition comprises the metal compound (i) in an amount sufficient to provide from 0.15 ppm to 2.40 ppm of the metal.

Preferably the fuel composition comprises 70 ppm or less of the organic compound (ii); preferably 60 ppm or less; preferably 50 ppm or less.

Preferably the fuel composition comprises at least 1 ppm of the organic compound (ii).

Preferably the fuel composition comprises the organic compound (ii) in from about 1 ppm to about 70 ppm; preferably from about 10 ppm to about 60 ppm; preferably from about 20 ppm to about 50 ppm.

In a further aspect, the fuel composition is provided by diluting an additive concentrate composition of the present invention in the fuel. Preferably, the ratio of additive concentrate composition to fuel is from 1: 100 to 1:10,000; preferably from 1:500 to 1:8,000; preferably from 1:1,000 to 1:5,000; preferably from 1:1,500 to 1:3000.

In a further aspect, the fuel composition is substantially free of methanol.

In a further aspect, the fuel composition is substantially free of C1 to C5 alcohol.

In a further aspect, the fuel composition is substantially free of alcohol.

In a further aspect, the composition is substantially free of hydrogen peroxide.

The meaning of the term "substantially free of" is as defined above in relation to additive composition.

In a preferred aspect, the metal compound (i) is bis-cyclopentadienyl iron and the organic compound (ii) is camphor.

Application areas

This system may be used in many different application areas.

In one aspect, the application area is diesel fuel.

In another aspect, the application area is marine fuels.

In another aspect, the application area is heating oil.

In another aspect, the application area is middle distillate oil.

In another aspect, the application area is heavy fuel oil

In another aspect, the application area is the regeneration of diesel particulate filters.

In another aspect, the application area is the reduction of soot content and ash content of an exhaust of a combustion system.

In another aspect, the application area is the improvement of combustion efficiency of a combustion system.

In another aspect, the application area is the improvement of fuel economy of a combustion system.

Hydrocarbon mixture

In one aspect, the present invention provides a hydrocarbon mixture which produces little soot on combustion with at least 0.1 ppm ferrocene and at least 1 ppm camphor added. In this aspect by camphor is meant a group of compounds consisting of double-ring-form, monoterpenic hydrocarbons such as camphene or phenzene, or analog aldehydes or monoterpenic ketones, for example phenzione. 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one is preferred.

Good results can be achieved with a hydrocarbon mixture with 7 ppm ferrocene and 40 ppm camphor.

In order to generate as little ash as possible during combustion, it is desirable to minimise the amount of ferrocene provided this does not adversely alter the soot reducing effect of the mixture.
A preferred ferrocene concentration therefore does not exceed 9 ppm, but is preferably 8 ppm or less.

The concentration of camphor should also not exceed 70 ppm and is preferably a maximum of 60 ppm, in particular a maximum of 50 ppm.

Preferably the majority of the hydrocarbons contained in the hydrocarbon mixture are petroleum derived. However, the hydrocarbon mixtures can also contain other natural or renewable materials, such as, for example, rapeseed oil methyl ester.

Particularly suitable hydrocarbon mixtures consist of middle distillates, as are manufactured in crude oil refineries. Such middle distillates are the main component of diesel oils and of heating oils, in particular heating oils with particularly low viscosity. The precise specification of such products is laid down in DIN standards.

The soot-reducing effects can be seen particularly clearly in heating oils, especially in so-called HEL: Heizöl extra leichtflüssig according to DIN 51603, Part 1 heating oils. Heating oils serve, as the name suggests, to provide heat. For this purpose they are burnt using special burners and with the addition of air. The advantages of the present

invention become particularly clear in such applications, as the present application produces less visible smoke, and less measurable soot.

A further object of the invention is an additive concentrate for manufacture of a hydrocarbon mixture with additive as described herein in numbered paragraph (1), with a content of 0.1-25 ppm ferrocene or, in relation to iron, an equivalent volume of another organic iron component which can dissolve in hydrocarbon, along with 1 to 80 ppm camphor.

The advantages of such an additive concentrate are quite clear. With the help of the concentrate, hydrocarbon mixtures to which no additive has been added can be transformed into hydrocarbon mixtures according to the invention, by adding a corresponding quantity of the concentrate to the hydrocarbon mixture and preferably mixing it so that it is homogeneous. It would also be possible to add corresponding amounts of ferrocene and camphor separately to the mixture. However, it would not only be necessary to ensure correct relation of the concentrate to the hydrocarbon mixture, but also the correct relation of the individual additive components to one another. Therefore it is simpler and more customer-friendly to offer an additive which already contains ferrocene and camphor in the correct relation to one another. Preferably the relation by weight of ferrocene to camphor is 7:40 in the additive concentrate.

Further Additives

The additive concentrate and/or the fuel may further comprise further additives, such as performance-enhancing additives. A non-limiting list of such further additives includes corrosion inhibitors, rust inhibitors, gum inhibitors, anti-oxidants, solvent oils, anti-static agents, dyes, anti-icing agents, ashless dispersants and detergents.

Ratio

In one aspect, preferably the ratio of metal compound (i) (measured in ppm) to organic compound (ii) (measured in ppm) is from 9:1 to 1:700.

Preferably the ratio of metal compound (i) to organic compound (ii) is from 2:1 to1:100; preferably from 1:1 to 1:10; preferably from 1:2 to 1:8; preferably from 1:3 to 1:7.

In a further aspect, preferably the ratio of metal provided by the metal compound (i) (measured in ppm) to organic compound (ii) (measured in ppm) is from 27:10 to 3:7000. Preferably the ratio of metal provided by the metal compound (i) to organic compound (ii) is from 6:10 to 3:1000; preferably from 3:10 to 3:100; preferably from 3:20 to 3:80; preferably from 3:30 to 3:70.

Methods

In a further aspect the present invention provides a method for combustion of a fuel composition in a combustion system, comprising providing a fuel composition comprising:

(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof;

(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and

(iii) a fuel; and

combusting the same such that combustion efficiency of the fuel is improved.

In a further aspect the present invention provides for combustion of a fuel composition in a combustion system, comprising providing a fuel composition comprising:

(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof;

(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and

(iii) a fuel; and

combusting the same such that fuel economy of the fuel is improved.

In a further aspect the present invention provides a method of regenerating a particulate filter located in an exhaust system of a combustion system for fuel, which comprises contacting carbon-based particulates, present in the particulate filter, with combustion products of a fuel composition comprising:

(i) a metal compound selected from an iron compound, , a manganese compound, a calcium compound, a cerium compound and mixtures thereof;

(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and
(iii) a fuel; and
combusting the fuel composition in the combustion system.

In a preferred aspect, the metal compound (i) is bis-cyclopentadienyl iron and the organic compound (ii) is camphor.

Combustion system

Preferably the combustion system is selected from a burner, engine and furnace.

Preferably the combustion system is selected from a burner and a furnace.

Preferably the combustion system is an engine. Preferably the engine is a compression ignition engine (diesel engine).

In one aspect, the combustion system is an engine. Preferably the engine is a spark ignition engine.

Use

In a further aspect, the present invention provides a use of:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
for reducing soot content and ash content of an exhaust of a combustion system for fuel.

In a further aspect, the present invention provides a use of an additive composition as herein defined for reducing soot content and ash content of an exhaust of a combustion system for fuel.

In a further aspect, the present invention provides a use of a fuel composition as herein defined for reducing soot content and ash content of an exhaust of a combustion system for fuel.

In a further aspect, the present invention provides a use of:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
for improving the combustion efficiency of a fuel.

In a further aspect, the present invention provides a use of an additive composition as herein defined for improving the combustion efficiency of a fuel.

In a further aspect, the present invention provides a use of a fuel composition as herein defined for improving the combustion efficiency of a fuel.

In a further aspect, the present invention provides a use of:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;
for improving the fuel economy of a combustion system.

In a further aspect, the present invention provides a use of an additive composition as herein defined for improving the fuel economy of a combustion system.

In a further aspect, the present invention provides a use of a fuel composition as herein defined for improving the fuel economy of a combustion system.

In a further aspect, the present invention provides a use of:
(i) a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and
(ii) an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;

for decreasing the regeneration temperature and/or required regeneration frequency of a particulate filter located in an exhaust system of a combustion system.

In a further aspect, the present invention provides a use of an additive composition as herein defined for decreasing the regeneration temperature and/or required regeneration frequency of a particulate filter located in an exhaust system of a combustion system.

In a further aspect, the present invention provides a use of a fuel composition as herein defined for decreasing the regeneration temperature and/or required regeneration frequency of a particulate filter located in an exhaust system of a combustion system.

Soot content

The Bacharach soot number is a qualitative measure for evaluating the completeness of combustion, based on the optical absorption of visible light by particles that have been deposited on a filter. The Bacharach soot number is part of the required testing procedure for judging the combustion quality of oil burners in countries such as Switzerland.

A well defined amount of undiluted flue gas is sucked through a white filter, leaving behind a discoloured spot. The colour of the spot is compared with a calibrated gray scale reaching from 0 (white) to 9 (black). This number is assessed electronically by measuring the reflectance of visible light shone on the loaded filter. The discolouring of the sample filter is attributed to the presence of black shoot.

Preferably, the fuel composition provides a 0.5 reduction in the Bacharach soot number compared with the Bacharach soot number observed with the fuel alone. Preferably, the fuel composition provides a 0.8 reduction in the Bacharach soot number; preferably a 1.0 reduction in the Bacharach soot number; preferably a 1.2 reduction in the Bacharach soot number: preferably a 1.5 reduction in the Bacharach soot number; preferably a 1.8 reduction in the Bacharach soot number; preferably a 2.0 reduction in the Bacharach soot number compared with the Bacharach soot number observed with the fuel alone.

Preferably, the fuel composition provides a Bacharach soot number of less than 1.0; preferably, less than 0.9; preferably, less than 0.8; preferably, less than 0.7; preferably,

less than 0.6; preferably, less than 0.5.

In one aspect, the soot content is measured by ASTM test method D-2156.

Ash content

Preferably, the fuel composition provides an ash content of 0.010 wt % or less. Preferably, the fuel composition provides an ash content of 0.009 wt % or less; 0.008 wt % or less; 0.007 wt % or less; 0.006 wt % or less; 0.005 wt % or less; 0.004 wt % or less; 0.003 wt % or less; 0.002 wt % or less; 0.001 wt % or less.

Ash content may be measured according to the standard method DIN EN 6245.

The present invention will now be described in further detail in the following examples.

Examples

For the trials, 25 litres heating oil was mixed with 0.2 litres of trial additive in each case. Different recipes were tested. The task during the combustion trials using an oil-fired hot water boiler fitted with yellow flame burners was to establish whether the recipes had a soot-reducing effect. For this purpose, the initial smoke spot number with the additive-free heating oil was set to approximately 4 by altering the burner to where measurable smoke is produced. Then, the additives were tested using this burner in order to measure the additive effect. The soot number was measured by evacuation (extraction suction with a manual smoke tester of a defined partial gas volume through a filter pad. This filter pad will be judged optically (by comparison) after the measurement. The soot number average value is a result of 10 individual measurements.

Test equipment	
Steel heating boiler	Ruhr Brenner, Model B 4T/14021kW, Year of Manufacture 1996
Heat output	Set at 20 kW
Oil burner	Ruhr Brenner, Model RH-4, 12-45 kW, Year of Manufacture 1996
Jet	Danfoss Typ H, 0.50 US gallons per hour (1.87 kg/h), 60°H

°H is the index angle/spraying index, hollow cone.

Smoke tester Brigon Smoke Tester

For the trial, one container with heating oil containing additive and one container without additive were placed next to the steel heating boiler. The burner pump was set to single-line mode, which obviates return of oil to the containers and therefore heating by the burner pump.

The change from additive-free oil to oil with additive was achieved by switching over a three-way valve immediately in front of the burner. Because of the three-way valve and the single-line circuit is it ensured that incorrect measurements caused by additive residues in the pipeline cannot occur. The respective soot measurements were pulled through a Bacharach soot pump and evaluated by means of visual inspection and measurement with a soot number test device.

Implementation

The steel hot water boiler was brought up to operating temperature with additive-free heating oil. A smoke spot number of approximately 4 was set by throttling the air feed to the burner.

The duration of the trial was approximately 0.75 hours, and then the smoke spot number was measured.

Results:

Example No.	Amount of Ferrocene (ppm)	Amount of Camphor (ppm)	Reduction in Bacharach Soot No.
Comparative Ex.1	7	0	0.80
Comparative Ex.2	0	40	0.36
1	1	40	0.76
2	3	40	0.80
3	5	40	0.90
4	6	40	1.00
5	7	40	2.21
6	7	20	0.80

Table 1

Over the entire trial series the additive with 7 ppm ferrocene/40 ppm camphor yields the best results, namely a reduction of the smoke spot number more than 2 points on the scale, from smoke spot number 4 to smoke spot number of less than 2. By comparison a concentration of 15 to 20 ppm of ferrocene would be required to obtain a comparable reduction in the smoke spot number in the absence of any camphor. However, the formation of ash caused by using 15 to 20 ppm of ferrocene would be approximately 40 times higher.

Using the same measurement procedure, a trial was carried out using a variety of organic compounds (ii) with ferrocene. The results are shown in table 2 below.

Example No.	Metal Compound (i)/ amount	Organic compound (ii) / 40.0 ppm	Reduction in Bacharach Soot No.
7	Ferrocene / 0.5 ppm	Propylene carbonate	0.30
8	Ferrocene / 0.5 ppm	camphene	0.40
9	Ferrocene / 0.5 ppm	isobornylacetate	0.80
10	Ferrocene / 0.5 ppm	adamatane	0.60

Table 2

These results indicated that a range of organic compounds (ii) could be effective.

Using the same measurement procedure, a trial was carried out using different metal compounds (i) with camphor. The results are shown in table 3 below.

Example No.	Metal Compound (i)/ 7.0 ppm	Amount of camphor (ppm)	Reduction in Bacharach Soot No.
11	Iron tallate	40	0.30
12	Methylcyclopentadienyl manganese tricarbonyl	40	0.25

Table 3

Further aspects of the invention are described in the following numbered paragraphs. In these numbered paragraphs by camphor is meant a group of compounds consisting of double-ring-form, monoterpenic hydrocarbons such as camphene or phenzene, or analog aldehydes or monoterpenic ketones, for example phenzione. 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one is preferred.

(1) Liquid hydrocarbon mixture (HC mixture) burning so as to produce a low level of soot, with at least 0.1 ppm ferrocene or an equivalent volume in relation to iron of another organic iron compound soluble in HC added, along with 10 ppm camphor

(2) HC mixture according to paragraph (1) with a content of around 7 ppm ferrocene and around 40 ppm camphor.

(3) HC mixture according to one of the previous numbered paragraphs, characterised in that the HC is composed at least mostly of hydrocarbon of mineral origin.

(4) HC mixture according to one of the previous numbered paragraphs, characterised in that the HC mixture is a crude oil middle distillate.

(5) HC mixture according to one of the previous numbered paragraphs, characterised in that the HC mixture is heating oil, in particular HEL (extra light heating oil).

(6) Additive concentrate for manufacture of an HC mixture containing additive according to numbered paragraph (1), with a content of 0.1-25 ppm ferrocene or in relation to iron an equivalent volume of another organic iron compound soluble in HC, and 10 to 80 ppm camphor.

(7) Additive concentrate according to numbered paragraph (6), characterised in that the ratio by weight of ferrocene to camphor is around 7 to 40.

(8) Additive concentrate according to numbered paragraphs (6) or (7), characterised in that in terms of volume, mainly aromates or iso-paraffins are contained as solvent.

(9) Use of an additive concentrate according to numbered paragraphs (6) to (8) for manufacture of an HC mixture containing additive according to numbered paragraph (1).

(10) Liquid hydrocarbon mixture (HC mixture) burning so as to produce a low level of soot, with at least 0.1 ppm ferrocene or an equivalent volume in relation to iron of another organic iron compound soluble in HC added, along with at least 10 ppm camphor.

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims

CLAIMS

1. A fuel composition comprising:
(i) at least 0.1 ppm of a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof;
(ii) at least 1 ppm of an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and
(iii) a fuel selected from biofuel, diesel, marine fuel, heating oil, middle distillate oil and heavy fuel oil and including such fuels containing renewable or bio-derived components and commonly termed biofuel; wherein the fuel composition comprises 9 ppm or less of metal compound (i).

2. A fuel composition according to claim 1, which is provided by diluting an additive concentrate composition with a fuel in a ratio of additive concentrate composition to fuel of from 1: 100 to 1:10,000; wherein the additive concentrate composition comprises less than 10 wt% C_1 to C_5 alcohols.

3. A fuel composition according to claim 1 or claim 2 which is provided by diluting an additive concentrate composition with a fuel in a ratio of additive concentrate composition to fuel of from 1:500 to 1:8000.

4. A fuel composition according to claim 2 or claim 3 wherein the additive concentrate composition comprises less than 0.5 wt% C_1 to C_5 alcohol compounds.

5. A fuel composition according to any preceding claim wherein metal compound (i) is selected from an iron compound, methylcyclopentadienyl manganese tricarbonyl, manganese (II) 2-ethyl-hexanoate, manganese naphthenate, calcium 2-ethylhexanoate, calcium naphthenate, calcium sulfonate, cerium (III) 2-ethylhexanoate, cerium sulfonate and mixtures thereof.

6. A fuel composition according to any preceding claim wherein fuel (iii) is selected from biofuel, diesel, marine fuel, heating oil, middle distillate oil and heavy fuel oil.

7. The fuel composition of any one of the preceding claims, wherein the fuel composition comprises the metal compound (i) in an amount sufficient to provide at least 0.03 ppm of the metal.

8. The fuel composition of any one of the preceding claims, wherein the fuel composition comprises the metal compound (i) in an amount to provide 2.70 ppm or less of the metal.

9. The fuel composition of any one of the preceding claims, which comprises 50 ppm or less of the organic compound (ii).

10. The fuel composition of any one of the preceding claims, which comprises from 20 ppm to about 50 ppm of the organic compound (ii).

11. The fuel composition of any of the preceding claims wherein the metal compound (i) is selected from an iron compound and mixtures thereof.

12. The fuel composition of claim 11 wherein the iron compound is an iron complex selected from bis-cyclopentadienyl iron, substituted bis-cyclopentadienyl iron, iron tallate and mixtures thereof.

13. The fuel composition of any of the preceding claims, wherein the metal compound (i) is bis-cyclopentadienyl iron.

14. The fuel composition of claim 11 wherein the iron compound is a substituted bis-cyclopentadienyl iron selected from adamantyl bis-cyclopentadienyl iron, bis(dicyclopentadienyl-iron)dicarbonyle and mixtures thereof.

15. The fuel composition of any of the preceding claims, wherein the organic compound (ii) is a bicyclic monoterpene or substituted bicyclic monoterpene selected from camphor, camphene, isobornyl acetate, dipropyleneglycol-isobornyl ether and mixtures thereof.

16. The fuel composition of any of the preceding claims, wherein the organic compound (ii) is camphor.

17. The fuel composition of any of the preceding claims, wherein the ratio of metal compound (i) to organic compound (ii) is from 9:1 to 1:700.

18. The fuel composition of any of the preceding claims, wherein the ratio of metal provided by the metal compound (i) to organic compound (ii) is from 6:10 to 3:1000.

19. A method for combustion of a fuel composition in a combustion system with an exhaust, comprising providing the fuel composition comprising:

(i) at least 0.1 ppm of a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof;

(ii) at least 1 ppm of an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof; and

(iii) a fuel; and

combusting the same such that soot content and ash content of the exhaust is reduced; wherein the fuel composition comprises 9 ppm or less of metal compound (i).

20. Use of:

(i) at least 0.1 ppm of a metal compound selected from an iron compound, a manganese compound, a calcium compound, a cerium compound and mixtures thereof; and

(ii) at least 1 ppm of an organic compound selected from a bicyclic monoterpene, substituted bicyclic monoterpene, adamantane, propylene carbonate and mixtures thereof;

in a fuel composition comprising 9 ppm or less of metal compound (i) for reducing the soot content and the ash content of an exhaust of a combustion system for fuel.