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(54) Title: IMPROVEMENTS IN OR RELATING TO FUEL COMPOSITIONS

(57) Abstract: The invention provides use of a fuel composition comprising a gasoline base fuel and at least one additional component selected from the group consisting of (i) a diesel fuel ignition improver in a concentration of 0.05 to 1% v/v based on the fuel composition, (ii) a Fischer-Tropsch derived gas oil in a concentration of 1 to 20% v/v based on the fuel composition and (iii) a Fischer-Tropsch derived naphtha fuel in a concentration of 1 to 20% v/v based on the fuel composition for improved auto-ignition performance in a homogeneous charge compression ignition engine; fuel compositions perse; and a method of operating a HCCI internal combustion engine.



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Improvements in or relating to fuel compositions

This invention relates to use of fuel compositions in homogeneous charge compression ignition (HCCI) engines, to fuel compositions per se, and to a method of operating a HCCI internal combustion engine.

5 EP-A-879871 (Ethyl Corporation) discloses a fuel composition comprising unleaded gasoline containing a major amount of hydrocarbons in the gasoline boiling range and from 1 to 1000 ppm of (0.001 to 0.1%v) of at least one organic nitrogen-containing compound selected
10 from:

- (a) organic nitrates selected from alkyl, alkenyl, cycloalkyl and aryl nitrates having up to 12 carbon atoms and nitrate esters of alkoxy substituted aliphatic alcohols;
 - 15 (b) organic nitro compounds selected from nitrotoluenes and dinitrotoluenes; and
 - (c) mixtures thereof; together with use of such compositions in a spark-ignition internal combustion engine, e.g. for improving ignition properties, for
20 reducing misfire, for preventing partial combustion and/or for improving cycle-to-cycle variation.
- Preferably about 10 to about 30 ppm (0.001 to 0.03% v), more preferably about 50 to 100 ppm (0.005 to 0.01% v) of nitrogen-containing compound is used. In the examples,
25 100 ppm (0.01% v) of 2-ethylhexylnitrate is used.

GB-A-1,152,380 (Esso) discloses a gasoline composition comprising a major proportion by weight of gasoline boiling between 20°C and 250°C and 0.0001% to 0.25% by weight (1 to 2,500 ppmw) of a nitric acid ester

of a C₃ or C₄ alcohol, e.g. isopropyl nitrate. The ester is preferably in a concentration between 0.001% and 0.1% by weight (10 to 1000 ppmw). Reduced severity of vibration (improved engine smoothness) is described in relation to spark-ignition engines in Ford Anglia (trade mark), Triumph Herald (trade mark) and Vauxhall Victor 101 (trade mark) motor vehicles.

US Patent 2,324,779 (ass. to Standard Oil, Delaware) discloses a motor fuel for spark-ignition engines comprising a gasoline base fuel blended with a defined concentration of a lead alkyl antiknock agent and 0.005% to 0.2% by weight (50 to 2000 ppmw) of an alkyl nitrate containing from 3 to 6 carbon atoms per molecule (e.g. amyl nitrate), as ignition accelerator. Other ignition accelerators are mentioned, e.g. organic peroxides, nitrogen derivatives and organic sulphides of similar molecular weight, preferably having boiling points in the range 100°C to 300°C.

Downs et al. "Octane and Cetane Numbers of Gasolines", Journal of the Institute of Petroleum, Vol. 52, No. 515, November 196, Pages 331 to 346, XP-002075889, describes various fuel modifications, in the context of the military need for multi-fuel compression ignition engines to be able to operate satisfactorily on a wide range of fuels including automotive gasolines. Cetane and octane values are given for unleaded and unleaded gasolines containing 0.25% v to 1% v (2,500 to 10,000 ppmv) of isopropyl nitrate, isoamyl nitrate and cyclohexyl nitrate (Tables V and VI, Page 335), and reference is made to unleaded and leaded gasoline containing 5% v (50,000 ppmv) of lubricating oil or DERV (Table X, Page 337).

US Patent 6,056,793 (Suppes, ass. University of Kansas Center for Research) discloses a compression-ignition fuel composition which comprises from about 30 to about 95% w (preferably about 60 to about 95% w) of a light synthetic crude (syncrude), preferably from Fischer-Tropsch synthesis or related processes, and from about 5 to about 75 mass % (preferably about 40 to about 5% w) of a blending stock that improves one or more properties such as pour point temperature, viscosity, and emissions generated during combustion in a diesel engine. The blending stock has an average molecular weight lower than the average molecular weight of the light syncrude, and is preferably selected from hydrocarbons, oxygenates and combinations thereof. A cetane improver may be added (Col. 5 lines 1 to 44), preferably in an amount from about 0.01 to about 0.5% w (100 to 5,000 ppmw). Table 1 illustrates fuels containaing 75% w syncrude and 25% w gasoline, and 75% w syncrude and 25% w of a 1:1 w/w mixture of ethanol/diethyl ether. Other tables show fuels with other specifications, but where gasoline is present, it is either 25% w or 30% w gasoline with, respectively, 75% w or 70% light syncrude.

The HCCI internal combustion engine is a hybrid of the well known spark ignition (SI, petrol) and compression ignition (CI, diesel) engines. A homogeneous, typically highly dilute, fuel/air mixture is created in the inlet system, as in a SI engine, but during the compression stroke the mixture auto-ignites as in a CI engine. Potentially HCCI engines can offer the efficiency of a diesel engine but with cleaner operation (eg, lower emissions of particulates and nitrogen oxides) and lower cyclic variations.

Various working HCCI engines have been described in the literature (see editor's keynote address (page 1) in "A new generation of engine combustion processes for the future?", Ed. P. Duret, *Editions Technip*, Paris, 2002, ISBN 2-7108-0812-9). These include the ATAC (Active Thermo - Atmospheric Combustion) [Onishi, S. et al, SAE Paper # 790501, SAE (Society of Automotive Engineers) 1979]; TS (Toyota - Soken); FDCCP (Fluid Dynamically Controlled Combustion Process); AR (Activated Radicals) [Ishibashi, Y. and Asai, M., SAE Paper # 960742, SAE 1996]; PCCI (Pre-mixed Charge Compression Ignition) [Ayoma, T. et al, SAE Paper # 960081, SAE 1996] and CAI (Controlled Auto-Ignition) [Oakley, A. et al, SAE Paper # 2001-01-1030, SAE 2001] engines. PCCI engines are also described in US 2002/0026926 A1 (Loye et al.) (published 7 March 2002).

HCCI combustion processes are also currently used in certain commercially available 2-stroke engines but 4-stroke engines exploiting the advantages of the HCCI technology do not yet appear to be feasible over a wide operating range.

One of the main problems with HCCI engines is that at low loads it can be difficult to ensure that auto-ignition always occurs. Olsson, Jan-Ola et al [SAE Paper # 2001-01-1031, SAE 2001] describe blending of the easily ignited fuel n-heptane with a gasoline base fuel (iso-octane) to promote auto-ignition in a HCCI engine. The n-heptane and iso-octane are metered separately into the engine under an electronic closed loop control system, so that the overall fuel formulation may be tailored in response to load conditions. This strategy may be used to extend the operating regime of a HCCI engine.

However, it is now well established that the conventional measures of auto-ignition quality in gasoline fuels - RON (Research Octane Number) and MON (Motor Octane Number) - are not relevant to auto-ignition in HCCI combustion using such fuels (see Montagne, X. et al in "A new generation of engine combustion processes for the future?", Ed. P. Duret, *Editions Technip*, Paris, 2002, ISBN 2-7108-0812-9 (page 177)). It has further been reported that the efficiency of HCCI combustion can be adversely affected in blends of gasoline with diesel fuels by poor combustion due to poor fuel vapourisation (see Oakley et al (*supra*) and Christensen, M. et al, SAE Paper # 1999-01-3679, SAE 1999). Thus it is by no means straightforward to identify gasoline fuel additives which might be used as alternatives to the n-heptane tested by Olsson et al, to improve the auto-ignition properties of the fuel and thus extend the operating regime of a HCCI engine running on it.

It has now surprisingly been found that certain fuel compositions comprising a gasoline base fuel together with one or more additional components selected from the group consisting of (i) a diesel fuel ignition improver, (ii) a Fischer-Tropsch derived gas oil and (iii) a Fischer-Tropsch derived naphtha fuel can exhibit improved auto-ignition capability and thus improve performance in a homogeneous charge compression ignition (HCCI) engine particularly at lower loads. A HCCI engine running on such a fuel composition can therefore function at a lower load, at any given speed, than when running on the gasoline base fuel alone; this factor may thus be used to extend the operating range of the engine.

According to the present invention there is provided use of a fuel composition comprising a gasoline base fuel

and at least one additional component selected from the group consisting of (i) a diesel fuel ignition improver in a concentration of 0.05 to 1% v/v based on the fuel composition, (ii) a Fischer-Tropsch derived gas oil in a concentration of 1 to 20% v/v based on the fuel composition and (iii) a Fischer-Tropsch derived naphtha fuel in a concentration of 1 to 20% v/v based on the fuel composition, for improved auto-ignition performance in a homogeneous charge compression ignition engine.

The present invention further provides a fuel composition, particularly a fuel composition for use in a HCCI engine, comprising a gasoline base fuel and at least one additional component selected from the group consisting of (i) a diesel fuel ignition improver in a concentration of 0.05 to 1% v/v based on the fuel composition, (ii) a Fischer-Tropsch derived gas oil in a concentration of 1 to 20% v/v based on the fuel composition and (iii) a Fischer-Tropsch derived naphtha fuel in a concentration of 1 to 20% v/v based on the fuel composition, wherein at least one of (ii) and (iii) is present in the fuel composition.

By "for use in a HCCI engine" is meant that the fuel composition is suitable for such use, whether or not it is actually intended for such use. The term "HCCI engine" is intended to encompass any engine which is operating or is operable in the HCCI mode, whether or not it is also capable of operating in another mode such as spark ignition or diesel compression ignition. In engines capable of operating in more than one such mode, the present invention can extend the operating regime over which HCCI operation is possible and/or feasible (in particular without undue mis-firing).

The gasoline base fuel comprises a liquid hydrocarbon fuel and would normally be suitable for use in an internal combustion engine of the spark ignition (petrol) type. Gasolines typically contain mixtures of hydrocarbons boiling in the range from 25 to 230 °C (EN-ISO 3405), the optimal ranges and distillation curves typically varying according to climate and season of the year. The hydrocarbons in a gasoline fuel may conveniently be derived in known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons, hydro-cracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

The research octane number (RON) of the gasoline base fuel may suitably be from 80 to 100, preferably from 90 to 100, more preferably from 94 to 100 (EN 25164). Its motor octane number (MON) may suitably be from 80 to 100, preferably from 84 to 100 (EN 25163).

It may have an olefin content of for instance from 0 to 20 % v/v (ASTM D1319), an oxygen content of for instance from 0 to 5 % w/w (EN 1601), an aromatics content of for instance from 0 to 50 % v/v (ASTM D1319) and in particular a benzene content of at most 1 % v/v.

The base fuel, and suitably also the overall fuel composition, preferably has a low or ultra low sulphur content, for instance at most 1000 ppmw (parts per million by weight), preferably no more than 500 ppmw, most preferably no more than 100 or 50 or even 10 ppmw. It also preferably has a low total lead content, such as at most 0.005 g/l, most preferably being lead free - having no lead compounds added thereto.

Oxygenates may be incorporated in the gasoline base fuel; these include alcohols (such as methanol, ethanol,

iso-propanol, tert-butanol and iso-butanol) and ethers (preferably ethers containing 5 or more carbon atoms per molecule, eg, methyl tert-butyl ether). Such ethers may be used in amounts up to 15 % v/v of the base fuel, but
5 if methanol is used, it can generally only be in an amount up to 3 % v/v and stabilisers may be required. Stabilisers may also be needed for ethanol, which may generally be used up to 5 % v/v. Iso-propanol may generally be used up to 10 % v/v, tert-butanol up to 7 %
10 v/v and iso-butanol up to 10 % v/v.

Oxygenates may in particular be desirable additives in unleaded gasoline fuels, since they are of use as octane boosters.

Particularly preferred gasoline base fuels
15 incorporate from 0 to 10 % v/v of at least one oxygenate selected from methanol, ethanol, iso-propanol and iso-butanol.

A gasoline base fuel may include one or more additives such as anti-oxidants, corrosion inhibitors,
20 ashless detergents, dehazers, dyes and synthetic or mineral oil carrier fluids. Examples of suitable such additives are described generally in US Patent No. 5,855,629. They can be added directly to the gasoline or can be blended before addition with one or more diluents,
25 to form an additive concentrate.

The gasoline base fuel preferably comprises a major proportion (by which is meant preferably 99 % w/w or more of the overall base fuel, more preferably 99.5 % w/w or more, most preferably 99.8 % w/w or more, even up to 100
30 % w/w) of liquid hydrocarbon gasoline fuel (which optionally incorporates one or more oxygenates), and a minor proportion of any additives present. The (active matter) concentration of any additives present in the

base fuel is thus preferably up to 1 % w/w, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to 150 ppmw.

5 The diesel fuel ignition improver (i) is an ignition improving agent suitable for use in a diesel fuel composition. It may comprise one or more reagents selected from the group consisting of:

 a) organic nitrates of the general formula R^1-O-NO_2 , or nitrites of the general formula R^1-O-NO , where R^1 is a hydrocarbyl group such as in particular an alkyl, cycloalkyl, alkenyl or aromatic group, or an ether containing group, preferably having from 1 to 10, more preferably from 1 to 6, carbon atoms;

15 b) organic peroxides and hydroperoxides, of the general formula $R^2-O-O-R^3$, where R^2 and R^3 are each independently either hydrogen or a hydrocarbyl group such as in particular an alkyl, cycloalkyl, alkenyl or aromatic group, preferably having from 1 to 10, more preferably from 1 to 6, carbon atoms; and

20 c) organic peracids and peresters, of the general formula $R^4-C(O)-O-O-R^5$, where R^4 and R^5 are each independently either hydrogen or a hydrocarbyl group such as in particular an alkyl, cycloalkyl, alkenyl or aromatic group, preferably having from 1 to 10, more preferably from 1 to 6, carbon atoms.

 Examples of ignition improvers of type (a) include (cyclo)alkyl nitrates such as isopropyl nitrate, 2-ethyl hexyl nitrate (2EHN) and cyclohexyl nitrate, and ethyl nitrates such as methoxy ethyl nitrate. Examples of type 30 (b) include di-tert-butyl peroxide.

Other diesel ignition improvers are disclosed in US-4,208,190 at column 2, line 27 to column 3, line 21.

The diesel ignition improver (i) is preferably a (cyclo)alkyl nitrate, more preferably 2-ethyl hexyl
5 nitrate.

Ignition improvers of this type are widely used as cetane improvers in diesel fuels, where auto-ignition can be a significant problem. They have not however been used as additives for gasoline fuels, where octane rather
10 than cetane numbers are important.

Diesel fuel ignition improvers are commercially available for instance as HITEC™ 4103 (ex Ethyl Corporation).

In the use and the fuel composition of the
15 invention, component (i) may be present in a concentration of 0.05 to 1 % v/v, preferably from 0.05 to 1 % v/v, more preferably from 0.1 to 0.7 % v/v, such as from 0.2 to 0.5 % v/v.

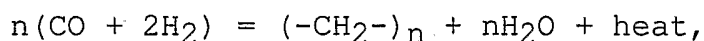
The Fischer-Tropsch derived gas oil (ii) is a liquid
20 hydrocarbon middle distillate gas oil with boiling points within the typical diesel fuel range, ie, from about 150 to 370 °C. It is a reaction product of a Fischer-Tropsch methane condensation process, such as for example the process known as Shell Middle Distillate Synthesis (van
25 der Burgt et al, "The Shell Middle Distillate Synthesis Process", paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985; see also the November 1989 publication of the same title from Shell International Petroleum Company Ltd, London, UK).

30 Fischer-Tropsch derived gas oils are low in undesirable fuel components such as sulphur, nitrogen and aromatics and tend to lead to lower vehicle emissions. They are typically used in diesel fuel compositions, in the form

of blends with other diesel base fuels such as petroleum derived gas oils, but not in gasoline fuel compositions.

The Fischer-Tropsch derived component (ii) should therefore be suitable for use as a diesel fuel, and its components (or the majority, for instance 95 % w/w or greater, thereof) should have boiling points within the typical diesel fuel ("gas oil") range, ie, from about 150 to 400 °C. It will suitably have a 90 % w/w distillation temperature of from 300 to 400 °C.

By "Fischer-Tropsch derived" is meant that a fuel is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons:



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

A gas oil product may be obtained directly from this reaction, or indirectly for instance by fractionation of a Fischer-Tropsch synthesis product or from a hydrotreated Fischer-Tropsch synthesis product.

Hydrotreatment can involve hydrocracking to adjust the boiling range (see, eg, GB-2 077 289 B and EP-A-0 147 873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0 583 836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no

isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and

5 isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired gas oil fraction(s) may subsequently be isolated for instance by distillation.

Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-

10 decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in US-A-4,125,566 and US-A-4,478,955.

Typical catalysts for the Fischer-Tropsch synthesis

15 of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0 583 836 (pages 3 and 4).

20 An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al (*supra*). This process produces middle distillate range products by conversion of a natural gas

25 (primarily methane) derived synthesis gas into a heavy long-chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. A version of the SMDS process,

30 utilising a fixed-bed reactor for the catalytic conversion step, is currently in use in Bintulu, Malaysia and its products have been used in petroleum derived gas oil blends in commercially available automotive fuels.

Gas oils prepared by the SMDS process are commercially available for instance from the Shell Group of companies. Further examples of Fischer-Tropsch derived gas oils are described in EP-A-0 583 836, EP-A-1
5 101 813, WO-97/14768, WO-97/14769, WO-00/20534, WO-00/20535, WO-01/11116, WO-01/11117, WO-01/83406, WO-01/83641, WO-01/83647, WO-01/83648 and US-A-6,204,426.

The Fischer-Tropsch derived gas oil (ii) will typically consist of at least 90 % w/w, preferably at
10 least 95 % w/w, of paraffinic components, preferably iso- and linear paraffins. The weight ratio of iso-paraffins to normal paraffins will typically be greater than 0.3 and may typically be up to 12; preferably it is from 2 to 6. The actual value for this ratio will be determined,
15 in part, by the hydroconversion process used to prepare the gas oil from the Fischer-Tropsch synthesis product. Some cyclic paraffins may also be present.

By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived gas oil has essentially no, or
20 undetectable levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed. Further, the process as usually operated produces no or virtually no aromatic components.
25 The aromatics content of a Fischer-Tropsch gas oil, as determined by ASTM D 4629, will typically be below 1 % w/w, preferably below 0.5 % w/w and more preferably below 0.1 % w/w.

The Fischer-Tropsch derived gas oil (ii) will
30 typically have a density from 0.76 to 0.79 g/cm³ at 15 °C; a cetane number (ASTM D976) greater than 70, suitably from 74 to 82; a kinematic viscosity from 2.5 to 4.0, preferably from 2.9 to 3.7, centistokes at 40 °C; and a

sulphur content of 5 ppmw (parts per million by weight) or less.

Preferably it is a product prepared by a Fischer-Tropsch methane condensation reaction using a
5 hydrogen/carbon monoxide ratio of less than 2.5, preferably less than 1.75, more preferably from 0.4 to 1.5, and ideally using a cobalt containing catalyst. Suitably it will have been obtained from a hydrocracked Fischer-Tropsch synthesis product (for instance as
10 described in GB-2 077 289 B and/or EP-A-0 147 873), or more preferably a product from a two-stage hydroconversion process such as that described in EP-A-0 583 836 (see above). In the latter case, preferred features of the hydroconversion process may be as
15 disclosed at pages 4 to 6, and in the examples, of EP-A-0 583 836.

In the use or the fuel composition of the invention, component (ii) may be present in a concentration of 1 to 20 % v/v, preferably from 1 to 15 % v/v, more preferably
20 from 2 to 12 % v/v, such as from 5 to 10 % v/v.

The Fischer-Tropsch derived naphtha fuel (iii) is a liquid hydrocarbon middle distillate fuel with a final boiling point of typically up to 220 °C or preferably of 180 °C or less, and which is a reaction product of a
25 Fischer-Tropsch methane condensation process, such as for example the Shell Middle Distillate Synthesis described above. Its initial boiling point is preferably higher than 25 °C, more preferably higher than 35 °C. Its components (or the majority, for instance 95 % w/w or
30 greater, thereof) are typically hydrocarbons having 5 or more carbon atoms; they are usually paraffinic.

The distillation properties of the naphtha fuel are comparable to those of gasoline. Despite this, naphtha

fuel components of this type have not previously been used directly in gasoline fuel compositions because their octane numbers are too low, and have been incorporated instead into diesel fuel blends for instance for winter
5 fuels.

As with the corresponding gas oils, Fischer-Tropsch derived naphtha fuels tend to be low in undesirable fuel components such as sulphur, nitrogen and aromatics. In the fuel composition of the present invention, the
10 naphtha fuel component (iii) preferably has a density of from 0.67 to 0.73 g/cm³ at 15 °C and/or a sulphur content of 5 ppmw or less. It preferably contains 95 % w/w or greater of iso- and normal paraffins, preferably from 20 to 98 % w/w or greater of normal paraffins.

15 In the fuel composition of the invention, component (iii) may be present in a concentration of 1 to 20 % v/v, preferably from 1 to 15 % v/v, more preferably from 2 to 12 % v/v, such as from 5 to 10 % v/v. It is preferably the product of a SMDS process, preferred features of
20 which may be as described above in connection with component (ii).

When both Fischer-Tropsch derived gas oil (ii) and Fischer-Tropsch derived naphtha (iii) are each present, the total concentration of (ii) and (iii) together is
25 preferably up to 20% v/v. Thus in a preferred fuel composition of the invention, the concentration of the Fischer-Tropsch derived gas oil (ii) and/or the Fischer-Tropsch derived naphtha fuel (iii) is up to 20% v/v.

Any of the additional components (i) to (iii) may
30 be pre-mixed with the gasoline base fuel, eg, prior to loading into the fuel tank of an automobile to be run on the fuel composition of the invention. Alternatively, and often preferably, they may be mixed with the base

fuel *in situ* immediately prior to, or on, introduction of the fuel composition into an HCCI engine. By way of example, the additional component(s) may be mixed with the base fuel on board an automobile, for instance from
5 separate storage vessels such as in the manner described by Olsson et al (*supra*) - such mixing may occur on introduction of the base fuel and additional component(s) into a combustion chamber of the engine, for instance by metering separate streams of the base fuel and additional
10 component(s) directly into the fuel inlet system or combustion chamber via separate inlets. Alternatively the two components may be metered into a separate mixing chamber upstream of the fuel inlet system and/or combustion chamber.

15 An engine management system may be used to control switching between fuel supplies as loads change, for instance in response to accelerator pedal movement, allowing the engine to run on a fuel according to the invention at lower loads and thus extending its HCCI
20 operating regime. In the case of *in situ* mixing, the engine management system may be used to control metering of gasoline fuel and additional component(s), from separate tanks, into a combustion chamber of the engine or into an upstream mixing chamber, in appropriate
25 proportions. Here the tank(s) carrying the additional component(s) may be much smaller in capacity than that for the gasoline base fuel. In the case where a fuel according to the invention is stored in pre-mixed form, switching may then be between this and a conventional
30 gasoline fuel also carried on board.

A further aspect of the present invention provides a method of operating a HCCI internal combustion engine, and/or an automobile or other machine which is driven by

such an engine, which method involves introducing into a combustion chamber of the engine a fuel composition as defined in relation to the use according to the invention. If desired, the fuel composition may be prepared, i.e. the gasoline base fuel and the additional components may be mixed, *in situ*, e.g. on board a machine to be driven by the engine, immediately before or on introduction of the fuel composition into a combustion chamber of the HCCI engine.

According to another aspect of the invention there is provided a HCCI internal combustion engine in combination with a source of a fuel composition as defined in relation to the use according to the invention, and/or with sources of (a) a gasoline base fuel and (b) one or more of the additional components (i) to (iii). In particular there is provided an automobile or other machine incorporating such an engine in combination with the relevant fuel source(s). Again, the term "HCCI internal combustion engine" is intended to encompass any internal combustion engine which either is, or is capable of, operating in HCCI mode.

The engine and fuel source(s) are preferably provided in combination with control means by which a fuel composition in accordance with the invention may be supplied, in appropriate quantities and with appropriate proportions of gasoline base fuel and additional component(s), to a combustion chamber of the engine, ideally at times when HCCI operation of the engine might benefit from a fuel composition according to the invention.

Where the system incorporates separate sources of a gasoline base fuel and one or more of the additional components (i) to (iii), the capacity of any "secondary"

vessel for storage of the additional component(s) is preferably 50 % or less of, more preferably 20 % or less of, still more preferably 10 % or 5 % or 2 % or less of that of the vessel in which the base fuel is stored. A
5 suitable capacity for a secondary storage vessel for a component of type (i), for instance, might be from 0.5 to 5 litres, preferably from 0.5 to 3 litres, such as about 1 litre.

The present invention further provides the use of
10 one or more of the additional components (i) to (iii) above in a gasoline fuel composition for use in a HCCI internal combustion engine, preferably for the purpose of improving the auto-ignition properties of the fuel composition.

15 By "gasoline fuel composition" in this context is meant a fuel composition which comprises a gasoline base fuel, typically a major proportion (eg, 80 % v/v or more, preferably 90 % v/v or more, most preferably 95 % or 98 % or 99 % or 99.5 % v/v or more) of the gasoline base fuel.

20 "Use" of the additional component(s) in a fuel composition means incorporating the component(s) into the composition, typically as a blend (ie, a physical mixture). This may be done before the composition is introduced into an engine or, as described above, may
25 involve some form of *in situ* mixing of a gasoline base fuel and the additional component(s) immediately prior to, or on, introduction of the fuel composition into a combustion chamber of the engine, for instance from separate storage vessels on board a machine to be driven
30 by the engine.

An improvement in the auto-ignition properties of the fuel composition, and preferably therefore of its low load performance in a HCCI engine, should be as compared

to the gasoline base fuel alone, and/or to the same composition but minus the additional component(s) (i) to (iii). It will typically be manifested by auto-ignition occurring earlier in the engine cycle when the engine is running on the fuel composition containing the additional component(s), at any given air:fuel ratio, compression ratio, inlet charge temperature and engine speed. Instead or in addition, it may be manifested by a lower value of BT_{min} and/or a higher value of λ_{min} (the minimum values of brake torque and air:fuel ratio respectively at which auto-ignition can be sustained) for any given set of operating conditions such as compression ratio, inlet charge temperature and engine speed. The performance of the engine at lower loads may thereby be greatly improved.

Such aspects of fuel and engine performance may be assessed for instance by running an engine, such as a single cylinder HCCI engine, on the fuel composition(s) in question and measuring the crank angle at which auto-ignition occurs at any given air:fuel ratio, for example as described in the examples below.

Improved auto-ignition may mean that for any given inlet charge temperature, the engine may be run (without mis-firing) with a lower compression ratio than if it were running on the gasoline base fuel and/or on a fuel composition which did not contain any of the components (i) to (iii). It may mean that for any given compression ratio, the inlet charge temperature does not need to be so high in order to maintain HCCI combustion without mis-firing.

In general, therefore, use of the additional component(s) as described above can extend the lower HCCI operating limits of an engine by allowing a leaner fuel

mixture (ie, a higher air:fuel ratio) to be used to give a lower torque at any given speed. Thus if the engine is adapted to operate in two or more ignition modes, the operating range over which it can be run in HCCI mode can be extended by running it on a gasoline fuel composition containing the additional component(s).

The present invention also provides a process for the preparation of a fuel composition of the invention, which process involves blending a gasoline base fuel with one or more of the additional components (i) to (iii) defined above. Again the blending is ideally carried out with the aim of improving the auto-ignition properties of the fuel composition in a HCCI internal combustion engine. It may be carried out *in situ*, ie, immediately before, or on, introducing the fuel composition into a combustion chamber of an engine.

Preferred features of all aspects of the invention, in particular regarding the nature of the gasoline base fuel and the nature and quantities of the additional component(s) (i) to (iii), may be as described earlier above.

The present invention will be further understood from the following examples, which illustrate the effects of components (i) to (iii) on the performance of a gasoline fuel in a HCCI engine.

General

The following tests used a single-cylinder HCCI engine (compression ratio 10.3, bore 80.6 mm, stroke 88.0 mm, connecting rod length 140.7 mm, crank throw 44 mm, displacement volume 449 cm³) having a pent-roof combustion chamber, four valves and two straight intake ports, mounted on a dynamometer. Valve timings were as listed in Table 1.

Table 1

Inlet valve open (IVO)	450 CAD ATDC*
Inlet valve close (IVC)	560 CAD ATDC
Exhaust valve open (EVO)	150 CAD ATDC
Exhaust valve close (EVC)	260 CAD ATDC

*CAD = crank angle degree; ATDC = after top dead centre
Fuel was injected into the ports using an electronic
injector system, the timing and quantity of injection
being independently variable. Fuel was injected at the
5 top dead centre (TDC) of the compression stroke to enable
full vapourisation. The inlet air was at room
temperature, ie, around 16 °C. The normalised air:fuel
ratio, λ , was measured by analysing the oxygen content of
the exhaust gases using an NTK MO1000™ analyser (when the
10 mixture strength is stoichiometric, $\lambda = 1$, whereas for a
fuel lean mixture, $\lambda > 1$). In-cylinder pressure was
measured using a Kistler™ pressure transducer.

The tests involved supplying the engine with either
an unleaded liquid hydrocarbon gasoline base fuel A,
15 having the properties listed in Table 2 :

Table 2

Density @ 15 °C (g/cm ³) (ISO 3675:93)	0.733
Research octane number (RON) (EN 25164)	95.2
Motor octane number (MON) (EN 25163)	87.1
Distillation (% evap) (ISO 3405:88) :	
IBP (° C)	38
FBP (° C)	169
E70	26
E100	49.5
E120	71
C	6.76
H	12.59
O	0
Iso- + n-paraffins (% v/v)	61.6
Olefins (% v/v)	3.51
Aromatics (% v/v)	31.9
Oxygenates (% v/v)	0

or a blend of the base fuel with one of the additives I, II or III detailed below.

The engine was run at a fixed speed of 1500 rpm, full throttle opening, and the coolant and oil
 5 temperatures were fixed at 85 °C and 100 °C respectively.

The engine was firstly warmed up with the base gasoline fuel A, using spark ignition, until the coolant and oil temperatures stabilised at their fixed values. The fuelling level was adjusted until λ reached 1.0.
 10 Ignition was then switched off and the engine started running in HCCI mode.

The pressure signal was recorded using a storage oscilloscope, from which was determined the crank angle CA_i at which auto-ignition occurred in HCCI combustion.
 15 CA_i for the base fuel A was assumed to be zero and CA_i for the fuel blends was therefore expressed in terms of crank angles before this arbitrary zero.

The fuel flow rate was slowly reduced and the engine was run at a leaner condition of $\lambda=1.1$ to repeat the

measurements. The fuel flow rate was further slowly reduced until the engine began to misfire and eventually stopped because auto-ignition could no longer be sustained. The value of λ and of the brake torque just before this happened were recorded and represent the limiting conditions denoted by $\lambda_{\min}$ and $BT_{\min}$ respectively. A lower value for $BT_{\min}$ indicated improved performance.

At each change of fuel, the engine was flushed through with the new fuel for one minute with the fuel pump running and the return fuel drained from the engine. This minimised cross contamination between tests.

Examples 1

In these examples, the performance of the base fuel A was compared with that of blends of fuel A with additive I, which is the diesel ignition improver 2-ethyl hexyl nitrate (2EHN). Fuel blend B contained 99.8 % v/v of the base fuel and 0.2 % v/v 2EHN. Blend C contained 99.5 % v/v of the base fuel and 0.5 % v/v 2EHN.

The base fuel was also compared with a fuel blend D containing 90 % v/v of fuel A with 10 % v/v n-heptane, as used in the HCCI dual fuel system disclosed by Olsson et al (*supra*).

The results are shown in Table 3.

Table 3

		CA_i^* $\Lambda = 1$	CA_i $\lambda = 1.1$	Λ_{min}	BT_{min} (Nm)
Fuel A	Base gasoline	0.0	0.0	1.15	5.1
Fuel blend B	99.8 %v fuel A + 0.2 %v 2EHN	7.7	9.5	1.27	3.95
Fuel blend C	99.5 %v fuel A + 0.5 %v 2EHN	9.0	10.3	1.38	2.8
Fuel blend D	90 %v fuel A + 10 %v n-heptane	10.8	9.0	1.25	3.95

* CA_i is crank angle degrees before the time of auto-ignition for base fuel A

It can be seen that for both EHN-containing fuel blends B and C, auto-ignition occurs much earlier in the engine cycle compared to the base fuel A.

The blends B and C also have significantly lower values of BT_{min} and higher values of Λ_{min} compared to the base fuel A. Thus the additive 2EHN appears to extend the lower HCCI operating limit by allowing a leaner fuel mixture to be run to give a lower torque at a given speed.

Moreover the improvement at a 2EHN treat rate of 0.2 % v/v compares favourably with that observed using n-heptane at a treat rate (10 % v/v) which is 50 times greater - see data for blends B and D in Table 3. Thus 2EHN is nearly 50 times as effective as n-heptane in improving auto-ignition performance. This means a significant reduction in the tank capacity necessary for the additive to be carried in a separate tank on board a vehicle, for *in situ* mixing with a gasoline base fuel.

Examples 2

In these examples, the performance of the base fuel A was compared with that of blends of fuel A with additive II, which is a Fischer-Tropsch derived gas oil made by the Shell Middle Distillate Synthesis (SMDS) as described above. Fuel blend E contained 90 % v/v of the base fuel and 10 % v/v of the SMDS gas oil. Blend F contained 95 % v/v of the base fuel and 5 % v/v gas oil.

The gas oil II had been obtained from a Fischer-Tropsch (SMDS) synthesis product via a two-stage hydroconversion process analogous to that described in EP-A-0 583 836. Its properties are listed in Table 4, and the test results in Table 5.

Table 4

Density @ 15 °C (g/cm ³)	0.7842
Distillation :	
IBP (°C)	212.5
10 %	248
20 %	264
30 %	277.5
40 %	290.5
50 %	300.5
60 %	309
70 %	316
80 %	327
90 %	332
95 %	339
FBP	344
Kinematic viscosity @ 40 °C (centistokes)	3.467

Table 5

		CA_i $\lambda = 1$	CA_i $\lambda = 1.1$	λ_{min}	BT_{min} (Nm)
Fuel A	Base gasoline	0.0	0.0	1.15	5.1
Fuel blend E	90 %v fuel A + 10 %v SMDS gas oil	9.9	10.4	1.23	4.2
Fuel blend F	95 %v fuel A + 5 %v SMDS gas oil	1.4	1.6	1.17	4.6

Again for both fuel blends E and F, auto-ignition occurs earlier in the engine cycle compared to the base fuel A. The blends also give significantly lower values of BT_{min} and higher values of λ_{min} compared to the base gasoline.

- 5 Thus the SMDS gas oil additive extends the lower HCCI operating limit by allowing a leaner fuel mixture to be run to give a lower torque at a given speed.

Examples 3

- Here the performance of the base fuel A was compared with that of blends of fuel A with additive III, which is a Fischer-Tropsch derived naphtha made by the Shell Middle Distillate Synthesis (SMDS) as described above. This naphtha fuel had a density @ 15 °C of 0.690 g/cm³, an initial boiling point of 43 °C and a final boiling point of 166 °C. Fuel blend G contained 90 % v/v of the base fuel and 10 % v/v of the SMDS naphtha. Blend H contained 95 % v/v of the base fuel and 5 % v/v SMDS naphtha.

The results are shown in Table 6.

Table 6

		CA_i $\lambda = 1$	CA_i $\lambda = 1.1$	λ_{min}	BT_{min} (Nm)
Fuel A	Base gasoline	0.0	0.0	1.15	5.1
Fuel blend G	90 %v fuel A + 10 %v SMDS naphtha	3.8	2.5	1.19	4.5
Fuel blend H	95 %v fuel A + 5 %v SMDS naphtha	2.7	2.2	1.17	4.65

For both naphtha-containing blends auto-ignition occurs earlier in the engine cycle than for the base fuel A.

The blends also have significantly lower values of BT_{min} and higher values of λ_{min} compared to the base fuel A.

- 5 Thus the SMDS naphtha additive again appears to extend the lower HCCI operating limits of the engine.

C L A I M S

1. Use of a fuel composition comprising a gasoline base fuel and at least one additional component selected from the group consisting of (i) a diesel fuel ignition improver in a concentration of 0.05 to 1% v/v based on
5 the fuel composition, (ii) a Fischer-Tropsch derived gas oil in a concentration of 1 to 20% v/v based on the fuel composition and (iii) a Fischer-Tropsch derived naphtha fuel in a concentration of 1 to 20% v/v based on the fuel composition , for improved auto-ignition performance in a
10 homogeneous charge compression ignition engine.
2. Use according to claim 1, wherein the diesel fuel ignition improver (i) comprises one or more reagents selected from the group consisting of:
- a) organic nitrates of the general formula R^1-O-NO_2 , or nitrites of the general formula R^1-O-NO ,
15 where R^1 is a hydrocarbyl group optionally containing an ether group;
 - b) organic peroxides and hydroperoxides, of the general formula $R^2-O-O-R^3$, where R^2 and R^3 are each
20 independently either hydrogen or a hydrocarbyl group; and
 - c) organic peracids and peresters, of the general formula $R^4-C(O)-O-O-R^5$, where R^4 and R^5 are each
25 independently either hydrogen or a hydrocarbyl group.
3. Use according to claim 2, wherein the diesel fuel ignition improver (i) comprises an alkyl or cycloalkyl nitrate.

4. Use according to claim 3, wherein the diesel fuel ignition improver (i) is 2-ethyl hexyl nitrate.

5. A fuel composition according to any one of the preceding claims, wherein the Fischer-Tropsch derived gas oil (ii) and/or the Fischer-Tropsch derived naphtha fuel (iii) is present at a concentration of up to 20 % v/v.

6. Use according to any one of claims 1 to 5, wherein the gasoline base fuel and the additional component(s) are mixed *in situ* immediately prior to, or on, introduction of the fuel composition into a combustion chamber of a HCCI engine.

7. A fuel composition as defined in any one of Claims 1 to 4 comprising a gasoline base fuel and at least one additional component selected from the group consisting of (i) a diesel fuel ignition improver in a concentration of 0.05 to 1% v/v based on the fuel composition, (ii) a Fischer-Tropsch derived gas oil in a concentration of 1 to 20% v/v based on the fuel composition and (iii) a Fischer-Tropsch derived naphtha fuel in a concentration of 1 to 20% v/v based on the fuel composition, wherein at least one of (ii) and (iii) is present in the fuel composition.

8. A fuel composition according to Claim 7 wherein the concentration of the Fischer-Tropsch derived gas oil (ii) and/or the Fischer-Tropsch derived naphtha fuel (iii) is up to 20% v/v.

9. A method of operating a HCCI internal combustion engine, which method involves introducing into a combustion chamber of the engine a fuel composition as defined in any one of claims 1 to 5, 7 and 8.

10. A method according to claim 9, wherein the gasoline base fuel and the additional component(s) are mixed *in situ* immediately prior to, or on, introduction of the

fuel composition into a combustion chamber of a HCCI engine.

AMENDED CLAIMS

[received by the International Bureau on 4 December 2003 (04.12.03);
original claim 5 amended; remaining claims unchanged (1 page)]

4. Use according to claim 3, wherein the diesel fuel ignition improver (i) is 2-ethyl hexyl nitrate.

5. Use according to any one of the preceding claims, wherein the Fischer-Tropsch derived gas oil (ii) and/or
5 the Fischer-Tropsch derived naphtha fuel (iii) is present at a concentration of up to 20 % v/v.

6. Use according to any one of claims 1 to 5, wherein the gasoline base fuel and the additional component(s) are mixed *in situ* immediately prior to, or on,
10 introduction of the fuel composition into a combustion chamber of a HCCI engine.

7. A fuel composition as defined in any one of Claims 1 to 4 comprising a gasoline base fuel and at least one additional component selected from the group consisting
15 of (i) a diesel fuel ignition improver in a concentration of 0.05 to 1% v/v based on the fuel composition, (ii) a Fischer-Tropsch derived gas oil in a concentration of 1 to 20% v/v based on the fuel composition and (iii) a Fischer-Tropsch derived naphtha fuel in a concentration
20 of 1 to 20% v/v based on the fuel composition, wherein at least one of (ii) and (iii) is present in the fuel composition.

8. A fuel composition according to Claim 7 wherein the concentration of the Fischer-Tropsch derived gas oil (ii) and/or the Fischer-Tropsch derived naphtha fuel (iii) is
25 up to 20% v/v.

9. A method of operating a HCCI internal combustion engine, which method involves introducing into a combustion chamber of the engine a fuel composition as
30 defined in any one of claims 1 to 5, 7 and 8.

10. A method according to claim 9, wherein the gasoline base fuel and the additional component(s) are mixed *in situ* immediately prior to, or on, introduction of the

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06278

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/08 C10L1/16 C10L1/22 C10L1/18

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)

IPC 7 C10L

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STANGLMAIER ET AL.: "HCCI Operation of a Dual-Fuel Natural Gas Engine for Improved Fuel Efficiency and Ultra-Low NOx Emissions at Low to Moderate Engine Loads" SAE TECHNICAL PAPER SERIES, SOCIETY OF AUTOMOTIVE ENGINEERS, no. 2001-01-1897, 7 May 2001 (2001-05-07), pages 1-7, XP002259503 Warrendale, PA (USA) ISSN: 0148-7191 page 2, right-hand column -page 3, left-hand column	1-10
X	US 4 111 792 A (GARWOOD WILLIAM E ET AL) 5 September 1978 (1978-09-05) abstract; claims 1,9,10 --- -/--	5,7,8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International Application No

PCT/EP 03/06278

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