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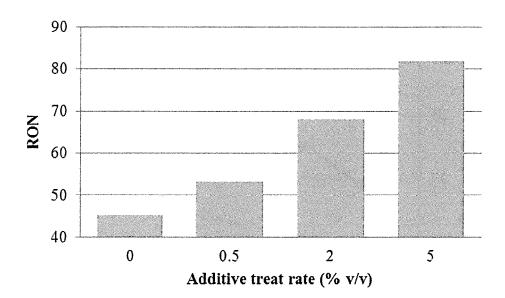
# (54) LOW GREENHOUSE GAS FUEL COMPOSITIONS

(57) A fuel composition for a spark-ignition internal combustion engine comprises naphtha in an amount of at least 5 % by volume, and an octane-boosting additive having the formula:

The well-to-wheel greenhouse gas emissions associated with the fuel composition are significantly lower than those associated with a conventional gasoline fuel of comparable performance.

$$R_{7}$$
 $R_{6}$ 
 $R_{5}$ 
 $R_{4}$ 
 $R_{12}$ 
 $R_{8}$ 
 $R_{9}$ 
 $R_{1}$ 
 $R_{2}$ 

Fig. 1



## Description

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#### Field of the Invention

**[0001]** This invention relates to fuel compositions for use in a spark-ignition internal combustion engine. In particular, the invention relates to fuel compositions which may meet standard fuel specifications yet have a relative low well-to-wheel greenhouse gas emissions rating. The invention further relates to methods for preparing such fuels.

## **Background of the Invention**

**[0002]** Spark-ignition internal combustion engines are widely used for power, both domestically and in industry. For instance, spark-ignition internal combustion engines are commonly used to power vehicles, such as passenger cars, in the automotive industry.

**[0003]** Every fuel has a certain level of well-to-wheel greenhouse gas emissions associated therewith. Well-to-wheel emissions are made up of a combination of well-to-tank emissions (*i.e.* those relating to the extraction, transportation, refining, *etc.* of the fuel and any additives contained therein) and tank-to-wheel emissions (*i.e.* those relating to the combustion efficiency of the fuel, the chemical composition of the fuel itself, *etc.*). Thus, well-to-wheel emissions are a useful measure of the overall environmental impact of different fuels.

**[0004]** Spark-ignition internal combustion engines are typically powered using gasoline, which may be obtained as a crude oil refinery stream. Ideally, refinery streams other than gasoline would also be used as a fuel for a spark-ignition internal combustion engine.

**[0005]** One such refinery stream is naphtha. Naphtha contains a mixture of hydrocarbons having an initial boiling point of at least 35 °C and a final boiling point of up to 210 °C at atmospheric pressure. Typically the majority of naphtha is made up from straight-chain, moderately branched and cyclic aliphatic hydrocarbons, with between five to twelve carbon atoms per molecule. Though naphtha was originally obtained from crude oil, nowadays it is often produced synthetically using Fischer-Tropsch processes or as a byproduct in the production of biodiesel and bio-jet fuels.

**[0006]** Naphtha would be an effective fuel since it has a high energy density by mass. Thus, in principle, naphtha that has not been subjected to extensive refining represents a fuel component having relatively low well-to-wheel greenhouse gas emissions. However, virgin naphtha typically exhibits a very low octane rating, in particular its research octane number (RON). This has severely limited the extent to which virgin naphtha may be used in a fuel for a spark-ignition internal combustion engine.

**[0007]** To produce naphtha with a higher octane rating, virgin naphtha may be reformed. However, this processing can be energy-intensive and usually reduces the ratio of hydrogen to carbon in the naphtha, resulting in increased  $CO_2$  emissions on combustion. Furthermore, many refineries do not have suitable facilities for reforming naphtha, leading to the import and export of virgin and reformed naphtha streams, depending on the local facilities.

**[0008]** Although naphtha has previously been used in fuels for internal combustion engines, these fuels significantly have failed to meet the octane requirements of conventional specifications. Thus, they have typically required changes to the engine or the vehicle fuel system, or are not considered to be drop-in fuels since they don't meet the requirements of existing fuel distribution, logistics and retail infrastructure.

**[0009]** There is therefore a need for liquid fuels which can be used as a replacement for a conventional gasoline fuel in a spark-ignition internal combustion engine. In particular, there is a need for liquid fuels which can be used as dropin fuels in a spark-ignition internal combustion engine, which do not compromise the performance of the fuel and which, crucially, may be less energy intensive in their production and use than conventional gasoline fuels.

**[0010]** Fuels for a spark-ignition internal combustion engine (generally gasoline fuels) typically contain a number of additives to improve the properties of the fuel.

**[0011]** One class of fuel additives is octane improving additives. These additives increase the octane number of the fuel which is desirable for combatting problems associated with pre-ignition, such as knocking. Additisation of a fuel with an octane improver may be carried out by refineries or other suppliers, e.g. fuel terminals or bulk fuel blenders, so that the fuel meets applicable fuel specifications when the base fuel octane number is otherwise too low.

**[0012]** Organometallic compounds, comprising e.g. iron, lead or manganese, are well-known octane improvers, with tetraethyl lead (TEL) having been extensively used as a highly effective octane improver. However, TEL and other organometallic compounds are generally now only used in fuels in small amounts, if at all, as they can be toxic, damaging to the engine and damaging to the environment.

**[0013]** Octane improvers which are not based on metals include oxygenates (e.g. ethers and alcohols) and aromatic amines. However, these additives also suffer from various drawbacks. For instance, N-methyl aniline (NMA), an aromatic amine, must be used at a relatively high treat rate (1.5 to 2 % weight additive / weight base fuel) to have a significant effect on the octane number of even a conventional gasoline fuel. NMA can also be toxic and can cause sludge formation in engines. Oxygenates give a reduction in energy density in the fuel and, as with NMA, have to be added at high treat

rates, potentially causing compatibility problems with fuel storage, fuel lines, seals and other engine components.

**[0014]** The lack of suitable octane-boosting additives has meant that naphtha has not successfully been utilised as a low greenhouse gas fuel component.

[0015] Recently, a new class of octane-boosting additive has been discovered which are derivatives of benzo[1,4] oxazines and 1,5-benzoxazepine. These octane-boosting additives have shown great promise in conventional gasoline fuels due to their non-metallic nature, their low oxygenate content, and their efficacy at low treat rates (see WO 2017/137518). However, it was not previously anticipated that the octane-boosters could be used to enhance the octane number of a naphtha-containing fuels to a level whereby the fuel would meet the requirements of modern fuel specifications.

**[0016]** Accordingly, there remains a need for fuels for spark-ignition internal combustion engines which mitigate at least some of the problems highlighted above, for instance because they have a relative low well-to-wheel greenhouse gas emissions rating.

## **Summary of the Invention**

**[0017]** Surprisingly, it has now been found that the new class of octane-boosting additives are highly effective at enhancing the RON value of a fuel which contains a significant amount of naphtha. In particular, it has been found that the octane-boosting additives may be used to bring a naphtha-containing fuel up to a standard which meets the requirements of conventional fuel standards, where other methods of boosting the naphtha will contravene such specifications, harm engines and/or worsen the toxicology of the fuel. The well-to-wheel greenhouse gas emissions associated with a fuel of the present invention may be significantly lower than that of conventional fuels.

[0018] Accordingly, the present invention provides the use of an octane-boosting additive having the formula:

where: R<sub>1</sub> is hydrogen;

 $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_{11}$  and  $R_{12}$  are each independently selected from hydrogen, alkyl, alkoxy, alkoxy-alkyl, secondary amine and tertiary amine groups;

 $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each independently selected from hydrogen, alkyl, alkoxy, alkoxy-alkyl, secondary amine and tertiary amine groups;

X is selected from -O- or -NR $_{10}$ -, where R $_{10}$  is selected from hydrogen and alkyl groups; and n is 0 to 2,

and naphtha for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine. The present invention also provides for the use of naphtha for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine which comprises an octane-boosting additive as defined above.

**[0019]** Also provided is a method for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine, said method comprising blending an octane-boosting additive as defined above and naphtha with the fuel. A method is also provided for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine which comprises an octane-boosting additive as defined above, said method comprising blending naphtha with the fuel.

**[0020]** A fuel composition for a spark-ignition internal combustion engine is also provided, the fuel composition comprising naphtha in an amount of at least 5 % by volume, and an octane-boosting additive as defined above.

**[0021]** The present invention further provides a method for quantifying the environmental impact of a fuel, said method comprising: blending a fuel of the present invention; and comparing the environmental impact of the blended fuel with that of a reference fuel to arrive at a metric of environmental impact.

## **Brief Description of the Figures**

[0022]

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**Figure 1** shows the effect on the observed RON of increasing amount of an octane-boosting additive described herein in bio-naphtha.

**Figure 2** shows the effect on the observed RON of increasing the volume proportion of the octane-boosting additive in fuel compositions of the present invention.

**Figure 3** is a graph showing the volume of mineral naphtha or bio-naphtha that may be used in octane-boosted fuels while maintaining a RON of either 95 or 98.

**Figure 4** is a graph depicting the environmental impact of a 95 RON fuel which contains 0.5 % by volume of octane-boosting additive and 25 % by volume of bio-naphtha.

## Detailed Description of the Invention

#### Fuel composition

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**[0023]** The octane-boosting additives described herein are used in a fuel composition for a spark-ignition internal combustion engine. It will be appreciated that the octane-boosting additives may be used in engines other than spark-ignition internal combustion engines, provided that the fuel in which the additive is used is suitable for use in a spark-ignition internal combustion engine. Gasoline fuels (including those containing oxygenates) are typically used in spark-ignition internal combustion engines. Commensurately, the fuel composition according to the present invention may be a gasoline fuel composition.

**[0024]** The fuel composition may comprise a major amount (*i.e.* greater than 50 % by weight) of liquid fuel ("base fuel") and a minor amount (*i.e.* less than 50 % by weight) of octane-boosting additive described herein. It will be appreciated that the naphtha component of the fuel composition forms part of the liquid fuel.

**[0025]** Naphthas are mixtures of hydrocarbons that have an initial boiling point of at least 35 °C and a final boiling point of up to 210 °C, the boiling points being determined at atmospheric pressure. Naphtha is largely made up from straight-chain, moderately branched and cyclic aliphatic hydrocarbons, with between five to twelve carbon atoms per molecule. Aromatic compounds may also be present depending on the nature of the crude oil.

**[0026]** The naphtha that is used in the fuel compositions of the present invention may be selected from petroleum naphtha, bio-naphtha, synthetic naphtha and combinations thereof.

[0027] Petroleum naphtha, bio-naphtha and synthetic naphtha are all well-known sources of naphtha. Petroleum naphtha, also known as mineral naphtha, is an intermediate hydrocarbon stream that is obtained during the initial processing of crude oil. Bio-naphtha is a naphtha stream derived from the processing of biomass. Synthetic naphtha is typically synthesized using a Fischer-Tropsch process, in which hydrogen and carbon monoxide react to form hydrocarbons in the presence of a metal catalyst; this naphtha may be referred to as Fischer-Tropsch naphtha. Petroleum naphtha typically comprises a higher proportion by mass of aromatic hydrocarbons and sulfur than bio-naphtha or Fischer-Tropsch naphtha, which are typically substantially free of sulfur and comprise low proportions by mass of aromatic hydrocarbons.

**[0028]** Petroleum naphtha and bio-naphtha, if unreformed, typically have a RON of between 40 and 80. Reformed naphtha and synthetic naphthas such as Fischer-Tropsch naphtha, may sometimes have higher RON values, for instance up to 60, up to 90 or in some cases even up to 100. Hence the present invention relates predominantly to enhancing the octane number, and hence anti-knocking performance, of fuel compositions comprising petroleum naphtha or bionaphtha since these exhibit lower RON values. Thus, in preferred embodiments, the naphtha is selected from petroleum naphtha, bio-naphtha and combinations thereof.

**[0029]** The naphtha that is used in the fuel composition may have a RON of up to 80, preferably up to 75 and more preferably up to 70. For instance, the naphtha may have a RON of at least 35, preferably at least 40, and more preferably at least 45. Thus, the naphtha may have a RON of from 35 to 80, preferably from 40 to 75, and more preferably from 45 to 70. It will be appreciated that a naphtha having suitable a RON may be obtained by blending naphthas having higher and lower RONs that those mentioned above.

**[0030]** The fuel compositions of the present invention comprise naphtha blended in an amount of at least 5 % by volume. Unless otherwise stated, % by volume is used herein to indicate % volume / volume.

[0031] The amount of naphtha that is included in the fuel will depend on a number of different factors, such as the properties of the naphtha, and the target properties for the finished fuel. The fuel compositions may comprise naphtha blended in an amount of at least 10 % by volume, preferably at least 15 % by volume, and more preferably at least 20 % by volume. The fuel compositions may comprise naphtha blended in an amount of up to 50 % by volume, preferably up to 40 % by volume, and more preferably up to 35 % by volume. Thus, the fuel compositions may comprise naphtha blended in an amount of from 10 to 50 % by volume, preferably from 15 to 40 % by volume, and more preferably from 20 to 35 % by volume.

[0032] It will be appreciated that, when more than one naphtha stream is used, these values refer to the total amount of naphtha that may be present in the fuel composition.

**[0033]** The fuel composition preferably comprises liquid fuel other than naphtha. Examples of liquid fuels include hydrocarbon fuels (other than naphtha), oxygenates and combinations thereof. In preferred embodiments, the fuel composition comprises a hydrocarbon fuel other than naphtha and an oxygenate.

**[0034]** Hydrocarbon fuels (other than naphtha) that may be used in a spark-ignition internal combustion engine may be selected from those derived from mineral sources, renewable sources such as biomass (e.g. biomass-to-liquid sources which may be used to produce bio-gasoline), gas-to-liquid sources, coal-to-liquid sources, and combinations thereof. Preferred hydrocarbon fuels include mineral-derived fuels such as gasoline base fuels due to cost, but could be hydrocarbons derived from renewable resources where such are available economically.

**[0035]** The RON of the hydrocarbon fuel will depend on the target specification of the fuel which varies from region to region. The hydrocarbon fuel may have a RON of at least 80, preferably at least 85, and more preferably at least 90. The hydrocarbon fuel may have a RON of up to 105, preferably up to 100, and more preferably up to 95. Thus, the hydrocarbon fuel may have a RON of from 80 to 105, preferably from 85 to 100, and more preferably from 90 to 95.

**[0036]** The fuel composition may comprise the hydrocarbon fuel in an amount of at least 50 %, preferably at least 55 %, and more preferably at least 60 % by volume. The fuel composition may comprise the hydrocarbon fuel in an amount of up to 92 %, preferably up to 80 %, and more preferably up to 85 % by volume. Thus, the fuel composition may comprise the hydrocarbon fuel in an amount of from 50 % to 92 %, preferably from 55 % to 90 %, and more preferably from 60 % to 85 %, by volume.

**[0037]** It will be appreciated that, when more than one hydrocarbon fuel other than naphtha is used, these values refer to the total amount of hydrocarbon fuel that may be present in the fuel composition.

**[0038]** The oxygenate that may optionally be used in the fuel composition may be selected from alcohols, ethers and combinations thereof. The oxygenates are preferably bio-oxygenates, *i.e.* oxygenates that are fully or partially derived from renewable biological sources. Examples of bio-oxygenates are bioalcohols and bioethers, *i.e.* ethers prepared using a bioalcohol. By using a bio-oxygenate, the well-to-wheel greenhouse emissions associated with the fuel composition are further lowered.

**[0039]** Preferred oxygenates are mono-alcohols or mono-ethers with a final boiling point of up to 225 °C. Suitable mono alcohols may contain less than six, more preferably less than five, carbon atoms, e.g. methanol, ethanol, n-propanol, n-butanol, isobutanol, tert-butanol. Suitable ethers may contain at least five carbon atoms, e.g. methyl tert-butyl ether and ethyl tert-butyl ether. Mixtures of oxygenates may, of course, be used.

**[0040]** Preferably, the oxygenate is methanol, ethanol, butanol, methyl tert-butyl ether or ethyl tert-butyl ether, more preferably ethanol or ethyl tert-butyl ether. The ethyl tert-butyl ether may be fully bio-sourced. The ethanol may comply with EN 15376:2014.

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**[0041]** The oxygenate may be introduced into fuel composition in amount so that the fuel composition meets particular automotive industry standards. For instance, the fuel composition may have a maximum oxygen content of 2.7 % by mass. The fuel composition may have maximum amounts of oxygenates as specified in BS EN 228:2012. For instance, the E5 specification requires methanol: 3.0 % by volume, ethanol: 5.0 % by volume, isopropanol: 10.0 % by volume, iso-butyl alcohol: 10.0 % by volume, tert-butanol: 7.0 % by volume, ethers (e.g. having 5 or more carbon atoms): 10 % by volume and other oxygenates (subject to suitable final boiling point): 10.0 % by volume.

[0042] The fuel composition may comprises the oxygenate in an amount of up to 85 %. The fuel composition may comprise the oxygenate in an amount of at least 1 %, preferably at least 3 %, and more preferably at least 5 % by volume. The fuel composition may comprise the oxygenate in an amount of up to 30 %, preferably up to 20 %, and more preferably up to 15 % by volume. Thus, the fuel composition may comprise the oxygenate in an amount of from 1 % to 30 %, preferably from 3 % to 20 %, and more preferably from 5 % to 15 %, by volume. For instance, the fuel composition may contain ethanol in an amount of about 5 % by volume (*i.e.* an E5 fuel), about 10 % by volume (*i.e.* an E10 fuel) or about 15 % by volume (*i.e.* an E15 fuel). A fuel which is free from ethanol is referred to as an E0 fuel.

[0043] It will be appreciated that, when more than one oxygenate is used, these values refer to the total amount of oxygenate that may be present in the fuel composition.

**[0044]** The fuel compositions of the present invention also comprise an octane-boosting additive. Preferred octane-boosting additives are discussed in greater detail below.

[0045] The amount of octane-boosting additive that is included in the fuel will depend on the octane number and volume of the naphtha, as well as the target octane number for the finished fuel. The fuel composition may comprise the octane-boosting additive in in an amount of at least 0.1 %, preferably at least 0.25 %, and more preferably at least 0.5 % by volume. The fuel composition may comprise the octane-boosting additive in an amount of up to 10 %, preferably up to 5 %, and more preferably up to 1 % by volume. Thus, the fuel composition may comprise the octane-boosting additive in an amount of from 0.1 to 10 %, preferably from 0.25 to 5 %, and more preferably from 0.5 to 1 % by volume.

**[0046]** It will be appreciated that, when more than one octane-boosting additive described herein is used, these values refer to the total amount of octane-boosting additive described herein in the fuel.

**[0047]** The fuel compositions may comprise at least one other further fuel additive. Examples of such other additives that may be present in the fuel composition include detergents, friction modifiers/anti-wear additives, corrosion inhibitors,

combustion modifiers, anti-oxidants, valve seat recession additives, dehazers/demulsifiers, dyes, markers, odorants, anti-static agents, anti-microbial agents, and lubricity improvers.

[0048] Further octane improvers may also be used in the fuel composition, i.e. octane improvers which are not octaneboosting additives described herein.

[0049] Examples of suitable detergents include polyisobutylene amines (PIB amines) and polyether amines.

[0050] Examples of suitable friction modifiers and anti-wear additives include those that are ash-producing additives or ashless additives. Examples of friction modifiers and anti-wear additives include esters (e.g. glycerol mono-oleate) and fatty acids (e.g. oleic acid and stearic acid).

[0051] Examples of suitable corrosion inhibitors include ammonium salts of organic carboxylic acids, amines and heterocyclic aromatics, e.g. alkylamines, imidazolines and tolyltriazoles.

[0052] Examples of suitable anti-oxidants include phenolic anti-oxidants (e.g. 2,4-di-tert-butylphenol and 3,5-di-tertbutyl-4-hydroxyphenylpropionic acid) and aminic anti-oxidants (e.g. para-phenylenediamine, dicyclohexylamine and derivatives thereof).

[0053] Examples of suitable valve seat recession additives include inorganic salts of potassium or phosphorus.

15 [0054] Examples of suitable further octane improvers include non-metallic octane improvers include N-methyl aniline and nitrogen-based ashless octane improvers

[0055] Examples of suitable dehazers/demulsifiers include phenolic resins, esters, polyamines, sulfonates or alcohols which are grafted onto polyethylene or polypropylene glycols.

[0056] Examples of suitable markers and dyes include azo or anthraquinone derivatives.

[0057] Examples of suitable anti-static agents include fuel soluble chromium metals, polymeric sulfur and nitrogen compounds, quaternary ammonium salts or complex organic alcohols. However, the fuel composition is preferably substantially free from all polymeric sulfur and all metallic additives, including chromium based compounds.

[0058] In some embodiments, the fuel composition comprises solvent, e.g. which has been used to ensure that the additives are in a form in which they can be stored or combined with the liquid fuel. Examples of suitable solvents include polyethers and aromatic and/or aliphatic hydrocarbons, e.g. Solvesso (Trade mark), xylenes and kerosene.

[0059] Representative typical and more typical independent amounts of additives (if present) and solvent in the fuel composition are given in Table 1 below. For the additives, the concentrations are expressed by weight (of the base fuel) of active additive compounds, i.e. independent of any solvent or diluent. Where more than one additive of each type is present in the fuel composition, the total amount of each type of additive is expressed in the table below.

> **Fuel Composition** Typical amount More typical amount (ppm, by weight) (ppm, by weight) 1000 to 100000 2000 to 50000 Octane-boosting additives Detergents 10 to 2000 50 to 300 Friction modifiers and anti-wear additives 10 to 500 25 to 150 Corrosion inhibitors 0.1 to 100 0.5 to 40 Anti-oxidants 1 to 100 10 to 50 Further octane improvers 0 to 20000 50 to 10000 Dehazers and demulsifiers 0.05 to 30 0.1 to 10 0.1 to 5 0.5 to 2 Anti-static agents Other additive components 0 to 500 0 to 200 10 to 3000 50 to 1000 Solvent

[0060] In some embodiments, the fuel composition comprises or consists of additives and solvents in the typical or more typical amounts recited in the table above.

[0061] The fuel composition of the present invention may have a RON of at least 87, preferably at least 90, and more preferably at least 95. Although a significant effect is observed in all fuels in which the octane-boosting additive is used, the effects are more pronounced in low to mid-range fuels. Accordingly, the fuel composition of the present invention may have a RON of up to 105, preferably up to 102, and more preferably up to 100. Thus, the fuel composition of the present invention may have a RON of from 87 to 105, preferably from 90 to 102, and more preferably from 95 to 100. [0062] The renewable content of the fuel compositions of the present invention is preferably at least 10 %, more

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preferably at least 15 %, and more preferably at least 20 % by volume. The renewable content of the fuel compositions may be up to 50 %, preferably up to 45 %, such as up to 40 % by volume. Thus, the renewable content of the fuel compositions may be from 10 to 50 %, preferably from 15 to 45 %, and more preferably from 20 to 40 % by volume. The renewable content may be achieved where a combination of bio-oxygenates and bio-naphtha are used, or by the use of one of these components alone.

[0063] The fuel composition may meet particular automotive industry standards.

**[0064]** For instance, the fuel composition may meet the requirements of EN 228, *e.g.* as set out in BS EN 228:2012. In other embodiments, the fuel composition may meet the requirements of ASTM D 4814, *e.g.* as set out in ASTM D 4814-19. It will be appreciated that the fuel compositions may meet both requirements, and/or other fuel standards.

**[0065]** The fuel composition may exhibit one or more (such as all) of the following, e.g., as defined according to BS EN 228:2012: a minimum research octane number of 95.0, a minimum motor octane number of 85.0 a maximum lead content of 5.0 mg/1, a density of 720.0 to 775.0 kg/m³, an oxidation stability of at least 360 minutes, a maximum existent gum content (solvent washed) of 5 mg/100 ml, a class 1 copper strip corrosion (3 h at 50 °C), clear and bright appearance, a maximum olefin content of 18.0 % by weight, a maximum aromatics content of 35.0 % by weight, and a maximum benzene content of 1.00 % by volume.

**[0066]** The fuel composition may have a sulfur content of up to 50.0 ppm by weight, e.g. up to 10.0 ppm by weight. **[0067]** Examples of suitable fuel compositions include leaded and unleaded fuel compositions. Preferred fuel compositions are unleaded fuel compositions and, as such, are free from tetraethyl lead. Other, lead-free organometallic octane boosters, such as methylcyclopentadienyl manganese tricarbonyl (MMT), or ferrocene may be used in the fuel composition, but preferably the fuel composition is free of all organometallic compounds.

**[0068]** Fuel compositions of the present invention may be produced by a process which comprises blending, in one or more steps, naphtha with an octane-boosting additive described herein. In embodiments in which the fuel composition comprises one or more further liquid fuels (*i.e.* base fuels) and/or fuel additives, these may also be blended, in one or more steps, with the fuel.

**[0069]** In some embodiments, the octane-boosting additive may be combined with the naphtha in the form of a refinery additive composition or as a marketing additive composition. Thus, the octane-boosting additive may be combined with one or more other components (e.g. additives and/or solvents) of the fuel composition as a marketing additive, e.g. at a terminal or distribution point. The octane-boosting additive may also be added to the naphtha on its own at a terminal or distribution point. The octane-boosting additive may also be combined with one or more other components (e.g. additives and/or solvents) of the fuel composition for sale in a bottle, e.g. for addition to fuel at a later time.

[0070] The octane-boosting additive and any other additives of the fuel composition may be incorporated into the fuel composition as one or more additive concentrates and/or additive part packs, optionally comprising solvent or diluent.

[0071] The octane-boosting additive may also be added to the fuel within a vehicle in which the fuel is used, either by addition of the additive to the fuel stream or by addition of the additive directly into the combustion chamber.

**[0072]** It will also be appreciated that the octane-boosting additive may be added to the fuel in the form of a precursor compound which, under the combustion conditions encountered in an engine, breaks down to form an octane-boosting additive as defined herein.

# Octane-boosting additive

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[0073] The octane-boosting additives used in the present invention have the following formula:

where: R<sub>1</sub> is hydrogen;

 $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_{11}$  and  $R_{12}$  are each independently selected from hydrogen, alkyl, alkoxy, alkoxy-alkyl, secondary amine and tertiary amine groups;

 $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each independently selected from hydrogen, alkyl, alkoxy, alkoxy-alkyl, secondary amine and tertiary amine groups;

X is selected from -O- or -NR $_{10}$ -, where R $_{10}$  is selected from hydrogen and alkyl groups; and n is 0 to 2.

**[0074]** In some embodiments,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_{11}$  and  $R_{12}$  are each independently selected from hydrogen and alkyl groups, and preferably from hydrogen, methyl, ethyl, propyl and butyl groups. More preferably,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_{11}$  and  $R_{12}$  are each independently selected from hydrogen, methyl and ethyl, and even more preferably from hydrogen and methyl.

**[0075]** In some embodiments,  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each independently selected from hydrogen, alkyl and alkoxy groups, and preferably from hydrogen, methyl, ethyl, propyl, butyl, methoxy, ethoxy and propoxy groups. More preferably,  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each independently selected from hydrogen, methyl, ethyl and methoxy, and even more preferably from hydrogen, methyl and methoxy.

**[0076]** Advantageously, at least one of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$ , and preferably at least one of  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$ , is selected from a group other than hydrogen. More preferably, at least one of  $R_7$  and  $R_8$  is selected from a group other than hydrogen. Alternatively stated, the octane-boosting additive may be substituted in at least one of the positions represented by  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_8$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$ , preferably in at least one of the positions represented by  $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$ , and more preferably in at least one of the positions represented by  $R_7$  and  $R_8$ . It is believed that the presence of at least one group other than hydrogen may improve the solubility of the octane-boosting additives in a fuel.

**[0077]** Also advantageously, no more than five, preferably no more than three, and more preferably no more than two, of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are selected from a group other than hydrogen. Preferably, one or two of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are selected from a group other than hydrogen. In some embodiments, only one of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  is selected from a group other than hydrogen.

**[0078]** It is also preferred that at least one of  $R_2$  and  $R_3$  is hydrogen, and more preferred that both of  $R_2$  and  $R_3$  are hydrogen.

**[0079]** In preferred embodiments, at least one of  $R_4$ ,  $R_5$ ,  $R_7$  and  $R_8$  is selected from methyl, ethyl, propyl and butyl groups and the remainder of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are hydrogen. More preferably, at least one of  $R_7$  and  $R_8$  are selected from methyl, ethyl, propyl and butyl groups and the remainder of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are hydrogen.

**[0080]** In further preferred embodiments, at least one of  $R_4$ ,  $R_5$ ,  $R_7$  and  $R_8$  is a methyl group and the remainder of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are hydrogen. More preferably, at least one of  $R_7$  and  $R_8$  is a methyl group and the remainder of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are hydrogen.

**[0081]** Preferably, X is -O- or -NR<sub>10</sub>-, where  $R_{10}$  is selected from hydrogen, methyl, ethyl, propyl and butyl groups, and preferably from hydrogen, methyl and ethyl groups. More preferably,  $R_{10}$  is hydrogen. In preferred embodiments, X is -O-.

[0082] n may be 0 to 2, though it is preferred that n is 0.

[0083] Octane-boosting additives that may be used in the present invention include:

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and

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[0084] Preferred octane-boosting additives include:

**[0085]** A mixture of additives may be used in the fuel composition. For instance, the fuel composition may preferably comprise a mixture of:

$$\begin{array}{c|c}
O \\
N \\
H
\end{array}$$
 and 
$$\begin{array}{c}
O \\
N \\
H
\end{array}$$

**[0086]** It will be appreciated that references to alkyl groups include different isomers of the alkyl group. For instance, references to propyl groups embrace n-propyl and i-propyl groups, and references to butyl embrace n-butyl, isobutyl, sec-butyl and tert-butyl groups.

#### Uses and methods

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**[0087]** One of the key benefits of the present invention is that a relatively low environmental impact may be associated with the fuel compositions. Thus, the octane-boosting additives and naphtha may be used for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine. Also provided is a method for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine. The method comprises blending an octane-boosting additive described herein and naphtha with the fuel.

[0088] It will be appreciated that the reduction in environmental impact in these instances is relative to the same fuel but in which the octane-boosting additive and naphtha are replaced with mineral-derived hydrocarbon base fuels other than naphtha (*i.e.* conventional gasoline base fuels). Thus, where the fuel of the present invention has a particular oxygenate content, then the reduction in environmental impact is relative to a fuel having the same oxygenate content, e.g. if the fuel of the present invention is an E10 fuel, then the reduction in environmental impact is relative to an E10 fuel. Preferably, the use and method are for reducing the environmental impact of a fuel having a specific RON, *i.e.* the octane-boosting additive and naphtha are used to reduce environmental impact while maintaining (e.g.  $\pm$ 0.25) the RON of a fuel and preferably keeping its measured oxygen level within specifications such as BS EN 228:2012 or ASTM D 4814-19.

**[0089]** Further provided is the use of naphtha for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine which comprises an octane-boosting additive as described herein, as well as a method for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine which comprises an octane-boosting additive as defined herein, said method comprising blending naphtha with the fuel.

**[0090]** It will be appreciated that the reduction in environmental impact in these instances is relative to the same fuel but in which the naphtha is replaced with mineral-derived hydrocarbon base fuels other than naphtha (*i.e.* conventional gasoline base fuels). As before, where the fuel of the present invention has a particular oxygenate content, then the reduction in environmental impact is relative to a fuel having the same oxygenate content.

[0091] The environmental impact of a fuel is preferably reduced by reducing the well-to-wheel greenhouse gas emissions associated with the fuel.

**[0092]** Well-to-wheel analysis is known in the art as a useful measure of the environmental impact of a component through its entire preparation (well-to-tank) and subsequent use in a vehicle (tank-to-wheel). In the present case, the well-to-wheel analysis relates to greenhouse gas emissions, and may be expressed in terms carbon dioxide equivalents (CO<sub>2</sub>e).

[0093] Values for the well-to-tank greenhouse gas emissions associated with naphtha (of different types) and other gasoline base fuels may be obtained directly from the UK Governments Department for Business, Energy & Industrial Strategy document "2018 Government GHG Conversion Factors for Company Reporting". The well-to-tank greenhouse gas emissions associated with the octane-boosting additives described herein are taken to be 150 gCO<sub>2</sub>e/MJ. Although this figure is relatively high compared with other fuel components, the lower additive treat rate means that the overall CO<sub>2</sub>e associated with the use of the additive is, relatively speaking, very low.

[0094] The tank-to-wheel impact of a fuel may be determined using known methods, such as modelling. For the purposes of the present invention, the tank-to-wheel impact of fuels is based on the combustion efficiency (fuels having the same RON number are assume to exhibit the same efficiency) and is also predicated on the amounts and ratio of hydrogen and carbon in the fuel (higher amounts of hydrogen give a more specific energy efficient fuel, and therefore a high H:C produces comparative less  $CO_2$ ).

[0095] The environmental impact of a fuel for a spark-ignition internal combustion engine may alternatively, or additionally, be reduced by lowering the particulate emissions produced by the fuel. The use of naphtha in a fuel reduces the aromatics content, and hence the particulate emissions associated with said fuel. Particulate emissions may be measured according to the method specified by the regulatory authorities in a region, for instance according to Commission Regulation (EU) 2017/1151 of 1 June 2017 (see section 4.2).

**[0096]** The present invention also provides a method for quantifying the environmental impact of a fuel, said method comprising: blending a fuel of the present invention; and comparing the environmental impact of the blended fuel with that of a reference fuel to arrive at a metric of environmental impact.

**[0097]** The environmental impact associated with the blended fuel may be determined as mentioned above, *i.e.* by looking at the well-to-wheel greenhouse gas emissions associated with the fuel or, though less preferred, the particulate emissions produced by the blended fuel. Of course, the metric of environmental impact will depend on the nature of the environmental impact that is measured, *e.g.* well-to-wheel emissions will take the units gCO<sub>2</sub>e/MJ of energy produced by the fuel.

**[0098]** The reference fuel may be the same as the blended fuel, but in which the octane-boosting additive and naphtha are replaced with mineral-derived hydrocarbon base fuels other than naphtha (*i.e.* conventional gasoline base fuels). As before, where the blended fuel has a particular oxygenate content, then the reference fuel may also have the same oxygenate content, e.g. if the blended fuel is an E10 fuel, then the reference fuel is also an E10 fuel. Preferably, the blended and reference fuels will have the same RON (e.g.  $\pm 0.25$ ) and their measured oxygen levels will preferably remain within the same specifications such as BS EN 228:2012 or ASTM D 4814-19.

**[0099]** However, in preferred embodiments, the reference fuel is a standard reference fuel, *e.g.* a fuel that is used as a regional benchmark for environmental impact. For instance, the reference fuel may be a fossil fuel specified in the EU Renewable Energy Directive (RED) II, e.g. having a well-to-wheel greenhouse gas emissions figure of 94 gCO<sub>2</sub>/MJ

**[0100]** Preferably, the method comprises monitoring the amount of blended fuel produced over a period of time. The period of time may be day, a month or, most preferably, a year. By monitoring the amount of blended fuel produced, the total reduction in environmental impact over a particular period of time may be determined.

**[0101]** The method of the present invention may further comprise converting the total reduction in environmental impact relative to a reference fuel over a period of into an asset, *e.g.* a tradable asset such as a carbon credit.

**[0102]** The naphtha-containing fuel compositions disclosed herein may be used in a spark-ignition internal combustion engine. Examples of spark-ignition internal combustion engines include direct injection spark-ignition engines and port fuel injection spark-ignition engines. The spark-ignition internal combustion engine may be used in automotive applications, *e.g.* in a vehicle such as a passenger car.

**[0103]** Examples of suitable direct injection spark-ignition internal combustion engines include boosted direct injection spark-ignition internal combustion engines, *e.g.* turbocharged boosted direct injection engines and supercharged boosted direct injection engines. Suitable engines include 2.0L boosted direct injection spark-ignition internal combustion engines. Suitable direct injection engines include those that have side mounted direct injectors and/or centrally mounted direct injectors.

**[0104]** Examples of suitable port fuel injection spark-ignition internal combustion engines include any suitable port fuel injection spark-ignition internal combustion engine including *e.g.* a BMW 318i engine, a Ford 2.3L Ranger engine and an MB M111 engine.

**[0105]** The octane-boosting additives disclosed herein may be used to increase the octane number of a fuel comprising naphtha for a spark-ignition internal combustion engine. Thus, the additives disclosed herein are used as octane-boosting additives in the fuel. In some embodiments, the octane-boosting additives increase the RON and/or the MON of the fuel. In preferred embodiments, the octane-boosting additives increase the RON of the fuel, and more preferably the RON and MON of the fuel. RON and MON values, as described herein, may be tested according to ASTM D2699-19 and ASTM D2700-19, respectively.

**[0106]** Since the octane-boosting additives described herein may increase the octane number of a naphtha-containing fuel, they may also be used to address abnormal combustion that may arise as a result of a lower than desirable octane number in spark-ignition internal combustion engine. Thus, the octane-boosting additives may be used for improving the auto-ignition characteristics of a naphtha-containing fuel, e.g. by reducing the propensity of a fuel for at least one of auto-ignition, pre-ignition, knock, mega-knock and super-knock, when used in a spark-ignition internal combustion engine. **[0107]** Also contemplated is a method for increasing the octane number of a naphtha-containing fuel for a spark-ignition internal combustion engine, as well as a method for improving the auto-ignition characteristics of such a fuel, e.g. by reducing the propensity of the fuel for at least one of auto-ignition, pre-ignition, knock, mega-knock and super-knock, when used in a spark-ignition internal combustion engine. These methods comprise the step of blending an octane-boosting additive described herein with naphtha (and any other further components of the fuel).

**[0108]** The methods described herein may further comprise delivering the blended fuel to a spark-ignition internal combustion engine and/or operating the spark-ignition internal combustion engine.

[0109] The invention will now be described with reference to the following non-limiting examples.

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## **Examples**

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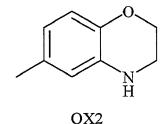
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#### Example 1: Effect of octane-boosting additive on bio-naphtha

**[0110]** The effect of an octane-boosting additive on the fuel characteristics of a bio-naphtha was measured. Specifically, fuel compositions were prepared by blending commercially available bio-naphtha (Neste MY Renewable Naphtha, obtained from Neste Oyj of Espoo, Finland) with the following octane-boosting additive:



**[0111]** The octane-boosting additive was used in the fuel compositions in amounts of 0.5%, 2.0% and 5.0% by volume, with the remainder of the fuel made up from the bio-naphtha.

**[0112]** The fuel characteristics of the fuel compositions and the corresponding untreated bio-naphthas were tested to determine the RON and MON (according to EN ISO 5164:2014 and EN ISO 5163:2014, respectively), and the density (according to EN ISO 12185:1996/COR 1:2001) and of the fuel. The appearance of the fuels was also assessed visually. The results are shown in the following table:

	Addi	tive trea	t rate (%	% v/v)
	0	0.5	2	5
RON	45.2	53.2	68.0	81.8
MON	45.4	50.6	66.0	-
Density (kg/m³)	0.68	0.68	0.69	0.70
Visual appearance	All fue	ls were o	clear and	d bright

[0113] A graph showing the effect of additive treat rate on RON is also shown in Figure 1.

**[0114]** It can be seen that the octane-boosting additives described herein dramatically increase both the RON and MON of fuel compositions, even though they consist purely of naphtha.

# Example 2: Preparation of EN228 compliant E10 bio-naphtha-containing fuel composition

**[0115]** A fuel composition containing significant amounts of bio-naphtha was prepared which, unlike earlier naphthacontaining fuels, meets the requirements of BS EN 228:2012 for E10 gasoline fuels.

**[0116]** Specifically, fuel compositions were prepared by blending 15 % v/v of the bio-naphtha and optionally 0.75 % v/v of the octane-boosting additive from Example 1 (*i.e.* the octane-boosting additive was used in an amount of 5 % by weight relate to the bio-naphtha) with 10 % v/v ethanol. The remainder of the fuel was composed of an E0 95 RON unoxygenated gasoline.

**[0117]** The fuel characteristics of the additised fuel composition and the corresponding untreated fuel composition were tested as described in Example 1. The results are shown in the following table:

	Additive trea	it rate (% v/v)
	0.75	0
RON	96.9	93. 7
MON	85.8	84.5
Density (kg/m³)	0.73	0.73
Visual appearance	All fuels were clear and bright	

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**[0118]** It can be seen that, by using the octane-boosting additives described herein, the RON of the fuel composition is increased to a RON of significantly greater than 95, a key indicator of fuel quality. This demonstrates that bio-naphtha may be used in a gasoline composition in significant amounts, *e.g.* amounts of 25 % v/v, while still meeting the requirements of fuel specifications such as EN228 E10 (95 RON).

**[0119]** The RON of the composition was also predicted based on the known effect of OX2 in conventional gasolines to determine whether the effect observed in a fuel containing a significant amount of naphtha was in line with that observed in conventional gasoline fuels. The predicted RON value was 95.0, *i.e.* significantly lower than that obtained in real life, thereby demonstrating that the extent of the octane-boosting effect in the fuels of the present invention is surprising.

Example 3: Effect of octane boosting additive on mineral naphtha

**[0120]** Four fuel composition blends comprising mineral naphtha and an octane-boosting additive (OX2) were designed to meet an EN228 E10 specification. The fuel characteristics of the compositions were predicted based on the known effect of OX2 in conventional gasolines, and also tested as described in Example 1.

**[0121]** As in Example 2, the RON of the fuels was notably higher than the RON predicted based on the known effect of OX2 in conventional gasolines. The predictive model was therefore adjusted so that it was based on real measurements of the enhanced octane-boosting effect observed in fuels containing added naphtha.

[0122] The results are shown in the following table:

	Fuel 1	Fuel 2	Fuel 3	Fuel 4
	%	(v/v) of c	omponer	its
E0 95 RON unoxygenated gasoline	68.5	74.5	65	54
Ethanol	10	10	10	10
Mineral naphtha 65 RON	21	0	0	35
Mineral naphtha 74 RON	0	15	24	0
OX2 fuel additive	0.5	0.5	1.0	1.0
	F	uel char	acteristic	S
Density (kg/m³)	0.73	0.73	0.73	0.74
Predicted RON	96.3	98.1	98.5	94.9
Measured RON	96.1	98.2	98.2	95.2
Accuracy of RON prediction	-0.2	0.1	-0.3	0.3

**[0123]** It can be seen that, by using an octane-boosting additive as described herein, fuel compositions comprising as much as 35 % v/v of petroleum naphtha may be blended which meet the EN228 E10 (95 RON) fuel specification. Moreover, the adjusted model predicted the RON of Fuels 1 to 4 to within an accuracy of  $\pm$  0.3.

# Example 4: Provision of high mineral naphtha fuel compositions

**[0124]** A series of high naphtha fuel compositions containing varying amounts of an octane-boosting additive described herein (OX2) were prepared. Each base fuel, except the base fuel having a RON of 82, contained a mixture of two mineral naphthas: a 65 RON naphtha and a 74 RON naphtha. The base fuels were blends of actual refinery streams, prepared according to recipes used in refining to meet the fuel specifications. The RON of the resulting fuel compositions was tested. The results are shown in Figure 2 and in the following table:

	Naphtha (%v/v)					
65 RON	16.6	31.7	44	29.6	23.2	17.1
74 RON	44	19	0	4.4	6.3	9
Total	60.6	50.7	44	34	29.5	26.1

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(continued)

		RON					
	0	72.9	75.3	82	84.3	85.2	86.5
OX-02 (% v/v)	0.5	78.2	80	86	87.8	89.4	90
OX-02 (76 V/V)	1	82.1	83.5	89	90.5	91.6	92.5
	2	86.8	87.8	93.2	94.7	95.1	95.8

**[0125]** It can be seen that the RON of all of fuel compositions was significantly enhanced by the use of the octane-boosting additive, even at relatively low treat rates, thereby allowing more naphtha to be used.

## Example 6: Reduction in well-to-wheel greenhouse gas emissions of naphtha-containing fuels

**[0126]** Naphtha-containing fuels were designed using either mineral or bio-naphtha. Each fuel included 10 % by volume of bioethanol. The octane boosting additive OX2 was included in the fuels in an amount of 0.33, 0.5, 0.75 or 1 % by volume. The volume of naphtha required for the fuel to meet a target RON of 95 or 98 was then predicted using a model based on real measurements of the enhanced octane-boosting effect of OX2 in naphtha-containing fuels.

**[0127]** A graph of the results is shown in Figure 3. It can be seen that, as a higher volume of octane booster is used, the amount of naphtha that may be included in the fuel without compromising the RON rating also increases.

**[0128]** The well-to-wheel greenhouse gas emissions associated with the fuels were calculated. A 2 % combustion benefit in GHG emissions was assumed for 98 RON fuels (see Han et al., Energy Systems Division, Argonne National Laboratory (2015), ANL/ESD-15/10: "Well-to-Wheels Greenhouse Gas Emissions Analysis of High-Octane Fuels with Various Market Shares and Ethanol Blending Levels" citing Speth et al., 2014 (6561-6568), Environ Sci Technol.: "Economic and environmental benefits of higher-octane gasoline"). The well-to-wheel emissions were compared with an E0 95 RON fuel, *i.e.* a fuel having 0 % volume of renewable components. The results are shown in the following table:

RON	% components		% well-to-wheel CO <sub>2</sub> saving vs E0		
KON	OX2	Naphtha	Mineral naphtha	Bio-naphtha	
	0.33	18	5.8	20.6	
0.5	0.5	25	6.1	26.8	
95	0.75	30	6.3	31.1	
	1	34	6.4	34.6	
	0.33	6	6.8	11.6	
00	0.5	10	6.9	15	
98	0.75	14	7	18.3	
	1	16	6.9	19.8	

**[0129]** It can be seen that considerable well-to-wheel greenhouse gas emissions savings are observed when naphtha is used in the fuel, and that this increases with the volume of naphtha. Significant improvements are observed even where the naphtha is a mineral naphtha.

**[0130]** Figure 4 contains graph relating to the 95 RON fuel which contains 0.5 % by volume of octane-boosting additive and 25 % by volume of bio-naphtha (see the first bar on the graph).

**[0131]** The second bar on the graph in Figure 4 indicates the proportion of the well-to-wheel greenhouse gas emissions that are produced by each of the components in the fuel. It can be seen that the bio-naphtha contributes a disproportionately small level of emissions.

**[0132]** The third bar on the graph in Figure 4 is a comparison of the fuel to a conventional fossil fuel gasoline having a well-to-wheel greenhouse gas emissions figure of 94  $gCO_2/MJ$  - this fossil fuel comparator figure is that specified in the EU Renewable Energy Directive (RED) II. An improvement of approximately 27 % relative to the comparator fossil fuel is observed, which is equivalent to removing 27 % cars off the road, if all cars were powered by the conventional fossil fuel gasoline.

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## Example 7: Reduction in well-to-wheel greenhouse gas emissions of high performance fuels

**[0133]** A variety of high-performance naphtha-containing fuels were designed having a RON of 102. The fuels were additised using the octane-boosting additive OX2, and the amount of naphtha increased so as to maintain the RON. The amount of oxygenates was maintained at the same level in the additised and corresponding unadditised fuel.

**[0134]** The well-to-wheel greenhouse gas emissions associated with the additised fuel and its unadditised counterpart were modelled using the method described in Example 6 (though a 5 % combustion benefit in GHG emissions was assumed for the 102 RON fuels), and the difference in % well-to-wheel emissions between the additised and unadditised fuels determined. The results are shown in the following table:

Additised	fuel comp	osition % volume	A 9/ well to wheel CO poving vs woodditiond		
Oxygenate	OX2	Naphtha (∆ vs unadditised fuel)	$ \Delta$ % well-to-wheel CO $_2$ saving vs unadditised fuel		
Ethanol 20 %	0.33 %	Mineral 4% (+4 %)	~+1.3 %		
Ethyl tert-butyl ether 22 %	0.5 %	Mineral 25 % (+ 5 %)	~+1.8 %		
Ethanol 10 %	0.75 %	Mineral 22 % (+7 %)	~+2.1%		
Butanol 16 %	1 %	Mineral 23 % (+8 %)	~+2.3 %		
Ethyl tert-butyl ether 22 %	0.5 %	Bio 36 % (+5 %)	~+5.9 %		

**[0135]** Notable improvements are observed across the fuels in which a range of oxygenates and different types of naphtha are used.

**[0136]** The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

**[0137]** Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern. **[0138]** While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope and spirit of this invention.

## Claims

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1. Use of an octane-boosting additive having the formula:

where: R<sub>1</sub> is hydrogen;

 $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_{11}$  and  $R_{12}$  are each independently selected from hydrogen, alkyl, alkoxy, alkoxy-alkyl, secondary amine and tertiary amine groups;

 $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each independently selected from hydrogen, alkyl, alkoxy, alkoxy-alkyl, secondary amine and tertiary amine groups;

X is selected from -O- or -NR $_{10}$ -, where R $_{10}$  is selected from hydrogen and alkyl groups; and n is 0 to 2,

and naphtha for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine.

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- 2. A method for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine, said method comprising blending an octane-boosting additive as defined in claim 1 and naphtha with the fuel.
- **3.** A use according to claim 1 or a method according to claim 2, wherein the octane-boosting additive and naphtha reduce the environmental impact while maintaining the RON of the fuel.
  - **4.** Use of naphtha for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine which comprises an octane-boosting additive as defined in claim 1.
- 5. A method for reducing the environmental impact of a fuel for a spark-ignition internal combustion engine which comprises an octane-boosting additive as defined in claim 1, said method comprising blending naphtha with the fuel.
  - **6.** A method for quantifying the environmental impact of a fuel, said method comprising:
- blending a fuel composition for a spark-ignition internal combustion engine, the fuel composition comprising naphtha in an amount of at least 5 % by volume, and an octane-boosting additive as defined in claim 1; and comparing the environmental impact of the blended fuel with that of a reference fuel to arrive at a metric of environmental impact.
- 7. The method of claim 6, wherein the method comprises monitoring the amount of blended fuel produced over a period of time, such as a year, and preferably determining the total reduction in environmental impact over said period of time.
  - **8.** A use according to any of claims 1, 3 and 4, or a method according to any of claims 2, 3, 5 to 7, wherein the environmental impact of the fuel is reduced by reducing at least one of the well-to-wheel greenhouse gas emissions and the particulate emissions associated with the fuel.
    - **9.** A use according to any of claims 1, 3, 4 and 8, or a method according to any of claims 2, 3 and 5 to 8, wherein the fuel, when combined with the octane-boosting additive, forms a fuel composition comprising the naphtha in an amount of at least 5 % by volume.
    - **10.** A fuel composition for a spark-ignition internal combustion engine, the fuel composition comprising naphtha in an amount of at least 5 % by volume, and an octane-boosting additive as defined in claim 1.
- **11.** A use according to any of claims 1, 3, 4, 8 and 9, a method according to any of claims 2, 3 and 5 to 9, or a fuel composition according to claim 10, wherein the naphtha is selected from petroleum naphtha, bio-naphtha, synthetic naphtha and combinations thereof, and preferably from petroleum naphtha, bio-naphtha and combinations thereof.
- **12.** A use according to any of claims 1, 3, 4, 8, 9 and 11, a method according to any of claims 2, 3, 5 to 9 and 11, or a fuel composition according to claim 10 or claim 11, wherein the fuel composition comprises naphtha in an amount of from 10 to 50 %, preferably from 15 to 40 %, and more preferably from 20 to 35 % by volume.
  - **13.** A use according to any of claims 1, 3, 4, 8, 9, 11 and 12, a method according to any of claims 2, 3, 5 to 9, 11 and 12, or a fuel composition according to any of claims 10 to 12, wherein the fuel composition comprises a liquid fuel other than naphtha, the liquid fuel preferably being selected from hydrocarbon fuels, oxygenates and combinations thereof.
  - 14. A use according to any of claims 1, 3, 4, 8, 9 and 11 to 13, a method according to any of claims 2, 3, 5 to 9 and 11

to 13, or a fuel composition according to any of claims 10 to 13, wherein fuel composition comprises the octane-boosting additive in an amount of from 0.1 to 10 %, preferably from 0.25 to 5 %, and more preferably from 0.5 to 1 % by volume.

**15.** A use according to any of claims 1, 3, 4, 8, 9 and 11 to 14, a method according to any of claims 2, 3, 5 to 9 and 11 to 14, or a fuel composition according to any of claims 10 to 14, wherein:

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- $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_{11}$  and  $R_{12}$  are each independently selected from hydrogen and alkyl groups, preferably from hydrogen, methyl, ethyl, propyl and butyl groups, more preferably from hydrogen, methyl and ethyl, and even more preferably from hydrogen and methyl; and/or
- $R_6$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each independently selected from hydrogen, alkyl and alkoxy groups, preferably from hydrogen, methyl, ethyl, propyl, butyl, methoxy, ethoxy and propoxy groups, more preferably from hydrogen, methyl, ethyl and methoxy, and even more preferably from hydrogen, methyl and methoxy;
- and preferably wherein at least one of  $R_4$ ,  $R_5$ ,  $R_7$  and  $R_8$  is selected from methyl, ethyl, propyl and butyl groups and the remainder of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are hydrogen, and preferably wherein at least one of  $R_7$  and  $R_8$  are selected from methyl, ethyl, propyl and butyl groups and the remainder of  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{11}$  and  $R_{12}$  are hydrogen.
- **16.** A use according to any of claims 1, 3, 4, 8, 9 and 11 to 15, a method according to any of claims 2, 3, 5 to 9 and 11 to 15, or a fuel composition according to any of claims 10 to 15, wherein:
  - X is -O- or -NR $_{10}$ -, where R $_{10}$  is selected from hydrogen, methyl, ethyl, propyl and butyl groups, preferably from hydrogen, methyl and ethyl groups, and even more preferably is hydrogen, and preferably wherein X is -O-; and/or n is 0 or 1, and preferably is 0.

Fig. 1

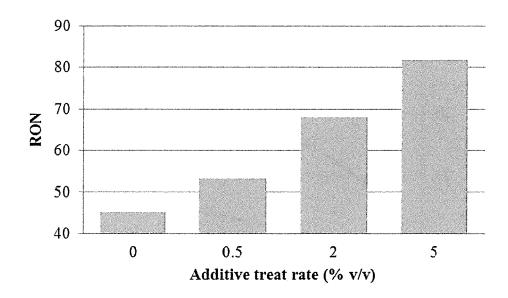


Fig. 2

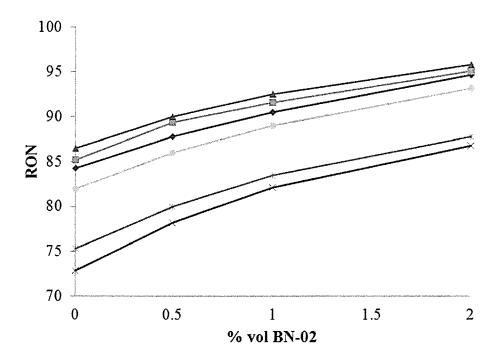
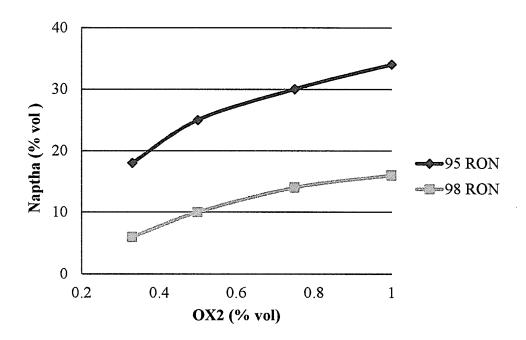
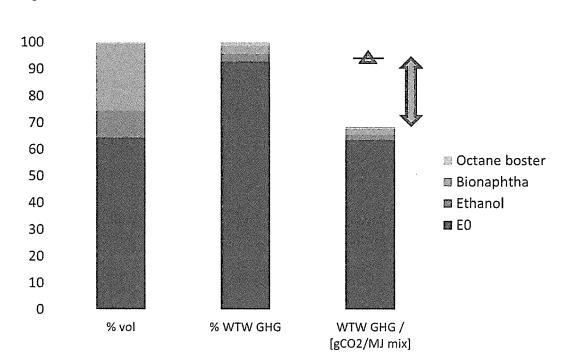


Fig. 3









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		ERED TO BE RELEVANT			
Category	Citation of document with in of relevant passa	dication, where appropriate, ges	Relev to cla		
Y	ET AL) 13 December * paragraphs [0004] [0013], [0043], [			INV. C10L1/233 C10L10/02 C10L10/10 C10L1/232	
Y	gasoline containing ignition engine at FUEL, IPC SCIENCE A GUILDFORD, GB, vol. 194, 17 Januar pages 436-447, XP02 ISSN: 0016-2361, DO 10.1016/J.FUEL.2017 * page 437, left-ha-right-hand column *	I: .01.042 nd column, paragraph 2 , paragraph 1; table 2	1-16		
	<pre>* paragraphs [03.2] * abstract *</pre>	, [0004] *		TECHNICAL FIE SEARCHED	LDS (IPC)
X,D Y	W0 2017/137518 A1 ( 17 August 2017 (201 * page 1, lines 4-8 * page 3, line 25 - * page 7, line 24 - * page 15, lines 4- * page 17, lines 15	* page 4, line 18 * page 9, line 29 * 10 *	1-11 13-16 1-16	.ć	
X	W0 2019/034582 A1 ( 21 February 2019 (2 * page 3, lines 6-1 * page 4, line 23 - * page 9, lines 16- * page 12, line 26	019-02-21) 6 * page 5, line 17 * 21 * - page 15, line 7 * 	1-11	·	
	The present search report has be Place of search	peen drawn up for all claims  Date of completion of the search	<u> </u>	Examiner	
	Munich	15 July 2020		Bork, Ana-Mari	a
X : part Y : part docu A : tech	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone cularly relevant if combined with anoth unent of the same category inological background	L : document cited fo	cument, but e n the appli or other rea	ut published on, or lication easons	
	-written disclosure mediate document	& : member of the sa document	ame pateni	nt family, corresponding	

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# **EUROPEAN SEARCH REPORT**

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	DOCUMENTS CONSIDE			
Category	Citation of document with ind of relevant passag		Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2019/034584 A1 (B 21 February 2019 (20 * examples *	P OIL INT [GB]) 19-02-21)	1-11, 13-16	
Х	WO 2019/034581 A1 (B 21 February 2019 (20 * examples *	P OIL INT [GB]) 19-02-21)	1-11, 13-16	
A	WO 2017/036485 A1 (S METWALLY [EG]) 9 Mar * the whole document	ch 2017 (2017-03-09	1-16	TECHNICAL FIELDS SEARCHED (IPC)
	The present search report has be	en drawn up for all claims		
	Place of search	Date of completion of the sea	rch	Examiner
	Munich	15 July 2020	Bor	rk, Ana-Maria
X : part Y : part docu A : tech O : non	ATEGORY OF CITED DOCUMENTS ticularly relevant if taken alone ticularly relevant if combined with anothe ument of the same category nological backgroundwritten disclosure rmediate document	E : earlier pate after the fill r D : document L : document	cited in the application cited for other reasons	shed on, or

page 2 of 2

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 19 21 2636

5

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

15-07-2020

10	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
15	US 2018355265 A	13-12-2018	BR 112018010277 A2 EP 3397734 A1 US 2018355265 A1 WO 2017093203 A1	27-11-2018 07-11-2018 13-12-2018 08-06-2017
20	WO 2017137518 A	1 17-08-2017	AU 2017217780 A1 BR 112018016445 A2 CA 3013833 A1 CN 108884400 A EA 201891778 A1 EP 3205701 A1 EP 3414305 A1	16-08-2018 26-12-2018 17-08-2017 23-11-2018 29-03-2019 16-08-2017 19-12-2018
25			JP 2019508546 A KR 20180107204 A PH 12018501699 A1 SG 11201806675S A US 2019048277 A1 WO 2017137518 A1	28-03-2019 01-10-2018 10-06-2019 27-09-2018 14-02-2019 17-08-2017
30	WO 2019034582 A	1 21-02-2019	CN 111278955 A EP 3668953 A1 WO 2019034582 A1	12-06-2020 24-06-2020 21-02-2019
35	WO 2019034584 A	1 21-02-2019	CN 111133080 A EP 3668954 A1 WO 2019034584 A1	08-05-2020 24-06-2020 21-02-2019
	WO 2019034581 A	1 21-02-2019	EP 3668952 A1 WO 2019034581 A1	24-06-2020 21-02-2019
40	WO 2017036485 A	1 09-03-2017	NONE	
45				
50				
55	FOHM P0459			

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## REFERENCES CITED IN THE DESCRIPTION

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## Patent documents cited in the description

• WO 2017137518 A **[0015]** 

## Non-patent literature cited in the description

- Commission Regulation (EU) 2017/1151, 01 June 2017 [0095]
- HAN et al. Energy Systems Division. Argonne National Laboratory, 2015 [0128]
- SPETH et al. Well-to-Wheels Greenhouse Gas Emissions Analysis of High-Octane Fuels with Various Market Shares and Ethanol Blending Levels, 2014, 6561-6568 [0128]
- Economic and environmental benefits of higher-octane gasoline [0128]