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## FUEL COMPOSITION

Field of the Invention

The present invention is in the field of fuel formulations, particularly fuel formulations for flexible fuel vehicles (FFVs).

5 Background of the Invention

Flexible fuel vehicles, also known as flex-fuel vehicles or FFVs, are vehicles which contain an internal combustion engine such as a spark ignition internal combustion engine, and which are capable of operating on gasoline and blends of gasoline with an alcohol such as ethanol or methanol. While the use of ethanol in conventional gasoline cars is usually limited to 10-15% by volume due to technical limitations of the engines, FFVs can operate on a wide range of ethanol-containing formulations from E0 (0% ethanol) up to E85 in the US or E100 in Brazil. E85 is a blend of gasoline and ethanol, typically containing from 51 vol% to 83 vol% ethanol, or 53 vol% to 85 vol% of denatured ethanol. The ethanol can be derived from biological sources for example by the fermentation of sugar-containing feeds using yeast, by biomass gasification followed by alcohol synthesis, or by gasification followed by fermentation using anaerobic bacteria.

The gasoline used in high ethanol containing flex-fuels such as E85 has been conventionally produced by refining crude oil (petroleum). This typically involves separating various fractions of crude oil by distillation. One such fraction is naphtha, which is a volatile liquid fraction distilled between the light gaseous components of crude oil and the heavier kerosene

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fraction. Naphtha contains a mixture of hydrocarbons (linear alkanes, branched alkanes, cycloalkanes and aromatic hydrocarbons) having a boiling point between about 30°C and about 200°C. The density of naphtha is typically 750-785 kg/m<sup>3</sup>. Naphtha has many uses, one of which is as an automotive fuel or automotive fuel blending component.

Whereas the longer chain molecules in gasoil have a high cetane number and can be blended into diesel, naphtha has historically not been used in gasoline fuels, or has only been used in low amounts, because of its poor octane rating. This has been the case despite the fact that naphtha has comparable distillation properties to those of gasoline.

Renewable fuels derived from biological matter ('biofuels') are increasingly being used as a more sustainable alternative to fossil fuels, with an increase in production volumes of renewable naphtha in recent years. It would therefore be advantageous to use renewable naphtha as an alternative blend component to conventional gasoline in an E85 type flex-fuel composition such that the final flex-fuel composition can be a fully renewable fuel, or an almost fully renewable fuel, suitable for use in flexible fuel vehicles.

Attempts have been made to produce fully renewable E85 type fuels containing bioethanol and renewable naphtha. For example, US2013/0131360 relates to a method for producing a naphtha product from a renewable feedstock by converting naturally occurring triglycerides and fatty acids to a composition including naphtha boiling range hydrocarbons. US2013/0131360 also relates to the resultant biorenewable naphtha product, whereby the naphtha is used as chemical feedstock, fuel, fuel

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blend stock, or solvent. Example 3 of US2013/0131360 discloses a bio-renewable naphtha as blendstock for 100% renewable E85 gasoline. Example 5 of US2013/0131360 provides the compositional properties of the bio-renewable naphtha produced in Example 2; from Table 4 it can be seen that the level of 'iso-paraffins' is 59.893 wt% and the level of 'paraffins' is 32.407 wt%. No information is provided on the emissions profile of the final E85 product.

US 10,414,992 B2 relates to a fuel composition comprising a) 70-86% by volume of ethanol and b) 5-20% by volume of a hydrocarbon component comprising hydrocarbons derived from feedstock comprising tall oil material, where said hydrocarbon component has RON of 50-70 and said hydrocarbon component comprises 25-60 mass% of naphthenes.

An article published in Biomass Magazine by Pearson Fuels dated 23 October 2019 reports the replacing of petroleum with renewable naphtha in their E85 flex fuel for the California market (article available at <https://biomassmagazine.com/articles/16560/pearson-fuels-blends-ethanol-renewable-naphtha-into-advanced-e85> (Accessed 24 May 2023)). In addition, an article published on the Advanced Biofuels USA website on 22 July 2022 by Melissa Anderson reports that Pearson Fuels is producing E85 almost entirely from biobased inputs using ethanol and renewable naphtha and being sold in Southern California (article available at <https://advancedbiofuelsusa.info/in-pursuit-of-pure-the-quest-to-make-e85-a-totally-biobased-fuel/> (Accessed 24 May 2023)). Further, an article entitled '2021 California E85 Sales Shatter Previous Record; Momentum Continues in 2022' published on the Advanced Biofuels USA website on

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28 March 2022 reports that Pearson fuels are blending E85 with renewable naphtha, resulting in a nearly 100 percent renewable fuel (article available at [https://advancedbiofuelsusa.info/2021-california-e85-](https://advancedbiofuelsusa.info/2021-california-e85-sales-shatter-previous-record-momentum-continues-in-2022/)  
5 [sales-shatter-previous-record-momentum-continues-in-2022/](https://advancedbiofuelsusa.info/2021-california-e85-sales-shatter-previous-record-momentum-continues-in-2022/) (Accessed 24 May 2023). There is no specific information in these articles about the properties of the renewable naphtha.

Despite the reported availability of renewable E85  
10 flex fuel in certain geographies, it would be desirable to formulate a renewable flex-fuel which provides an improved emissions profile, in particular which provides both reduced CO emissions and reduced NO<sub>x</sub> emissions. There is typically a trade-off between CO emissions and  
15 NO<sub>x</sub> emissions and therefore it is a challenge to formulate a fuel formulation which leads to a reduction in both CO emissions and NO<sub>x</sub> emissions.

At the same time, it would be desirable to be able to formulate a renewable flex-fuel composition which  
20 complies with the relevant flex-fuel specifications, such as, but not limited to, US Federal ASTM5798, US California CCR § 2292.4 and EU EN 15293:2018.

#### Summary of the Invention

According to the present invention there is provided  
25 a fuel composition comprising:

- (i) from 35 vol% to 95 vol% of an alcohol component;  
and
- (ii) from 5 vol% to 65 vol% of a renewable naphtha component, wherein the renewable naphtha component has a  
30 total paraffins content of at least 90 mass%, an iso-paraffins content of at least 60 mass%, an n-paraffins content of less than 30 mass%, and an iso-paraffins to n-paraffins ratio of greater than 3:1.

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According to the present invention there is further provided the use of a fuel composition as defined above for reducing CO emissions and NO<sub>x</sub> emissions, in particular wherein the fuel composition is used to fuel a flexible fuel vehicle.

It has surprisingly been found by the present inventors that by blending a renewable naphtha component having certain physicochemical properties with a renewable alcohol component in specified concentrations, a renewable fuel composition is provided which provides reduced CO and NO<sub>x</sub> emissions, while meeting the requirements of flexible fuel specifications, such as US Federal ASTM5798, US California CCR § 2292.4 and EU EN 15293:2018.

It has also surprisingly been found that the fuel compositions of the present invention maintain a high octane (RON) value despite the low RON values for renewable naphtha.

The liquid fuel compositions of the present invention also provide reduced tank to wheel CO<sub>2</sub> emissions, reduced particulate emissions, and excellent fuel economy, acceleration and power performance.

#### Brief Description of the Drawings

Figure 1 shows the physicochemical properties of the renewable naphthas and the gasoline base fuel used in the Examples.

Figure 2 shows the RON numbers of the renewable naphthas and the gasoline base fuel used in the Examples as well as the RON numbers for the fully formulated fuel compositions tested in the Examples.

Figure 3 shows the two-day test sequence used in the Examples.

#### Detailed Description of the Invention

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A first essential component of the fuel compositions of the present invention is a renewable naphtha. The renewable naphtha is present at a level in the range from 5 vol% to 65 vol%, preferably from 5 vol% to 50 vol%,  
5 more preferably 10 vol% to 40 vol%, even more preferably from 10 vol% to 30 vol%, and especially from 10 vol% to 20 vol%, based on the fuel composition.

In one embodiment of the invention, the renewable naphtha is present at a level in the range from 20 vol%  
10 to 40 vol%, based on the fuel composition.

The person skilled in the art would know what is meant by the term "naphtha". Typically, the term "naphtha" means a mixture of hydrocarbons generally having between 5 and 12 carbon atoms and having a boiling  
15 point in the range of 30 to 200° C. The liquid fuel compositions herein comprise a naphtha which is a renewable naphtha, also known as a renewable naphtha distillate, or biorenewable naphtha.

Renewable naphtha can be obtained from various  
20 processes and from a variety of feedstocks. Preferably, the renewable naphtha for use herein is obtained as a by-product from the production of Hydrogenated Vegetable Oil (HVO) (also known as renewable diesel). This involves the hydrotreatment of fatty acids and derivatives  
25 thereof, such as triglycerides present in fatty acid containing materials such as animal fats and plant material. Plant material may comprise both vegetable based material, such as vegetable oils as well as oils obtained from other plants, such as oils from trees, e.g.  
30 tall oil. Renewable diesel and renewable naphtha distillate may be obtained from the hydrotreatment of fatty acids, and derivatives thereof. The hydrotreatment of fatty acids and derivatives thereof involves

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deoxygenation reactions, such as hydrodeoxygenation (HDO), and may also involve other hydroprocessing reactions, such as isomerisation (for example hydroisomerisation) and cracking (for example hydrocracking). When refining the renewable diesel, a renewable naphtha distillate is also obtained. The renewable naphtha distillate comprises the fraction having an IBP of 30°C, such as an IBP of 30°C or higher and a FBP of 200°C, such as a FBP of 200°C or lower. The hydrocarbons present in that distillation range usually range from those containing 4 or 5 carbon atoms to those containing about 10 or 11 or 12 carbon atoms.

Alternative processes for producing renewable naphtha include (i) the Shell IH<sup>2</sup> (RTM) process, an integrated process of hydropyrolysis and hydroconversion at moderate pressures (250-500 psi) and temperatures ranging from 350 to 450°C, (ii) a renewable gas-to-liquid (GTL) process which involves water electrolysis to produce green hydrogen, catalytic reverse water gas shift reaction, Fischer-Tropsch synthesis and hydroprocessing, and (iii) an ethanol-to-gasoline (ETG) process.

Renewable fuels, such as renewable naphtha distillate, are derived from resources which are naturally replenished on a human timescale, as opposed to fossil fuels, such as petroleum gasoline, which are derived from the refining of crude oil. Suitable feedstocks for producing renewable fuels include edible and non-edible vegetable oils, animal fats, agricultural waste products and residues, municipal solid waste algae oil, purpose grown crops, and woody biomass. By the term renewable naphtha as used herein is meant a naphtha fraction which contains bio-based carbon atoms as determined according to ASTM method D6866-10 entitled

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"Standard Test Methods for Determining the Biobased Content of Solid, Liquid and Gaseous samples using Radiocarbon Analysis". The renewable content may then be determined by isotopic distribution involving  $^{14}\text{C}$ ,  $^{13}\text{C}$  and/or  $^{12}\text{C}$  as described in ASTM D6866.

When the renewable naphtha is obtained from the processing of fatty acid containing materials, such as animal fats and plant material, the renewable naphtha distillate is paraffinic with very little naphthenes and virtually no aromatics or oxygenates.

Renewable naphtha distillate is mainly comprised of paraffins (alkanes), which can be straight chain n-paraffins or branched chain iso-paraffins. The renewable naphtha used herein has a total paraffins content of at least 90 mass%, an iso-paraffins content of at least 60 mass%, an n-paraffins content of at most 30 mass%, and an iso-paraffins to n-paraffins ratio of 3:1 or greater. It has been surprisingly found that by selecting a renewable naphtha having these these amounts of total paraffins, n-paraffins and iso-paraffins, and including them in a fuel blend together with alcohol, preferably an alcohol from renewable sources, an improved fuel composition can be produced which exhibits both reduced CO and NO<sub>x</sub> emissions when used in a spark ignition internal combustion, especially a spark ignition internal combustion engine in a flexible fuel vehicle. This is particularly surprising as there is often a trade-off between CO and NO<sub>x</sub> emissions.

The renewable naphtha may have 90 vol% or more C<sub>5</sub>-C<sub>12</sub> paraffins, such as 95 vol% or more C<sub>5</sub>-C<sub>12</sub> paraffins, or 98 vol% or more C<sub>5</sub>-C<sub>12</sub> paraffins.

When the renewable naphtha distillate has been produced as described above as part of the refining of

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renewable diesel, it may comprise 30 vol% or more C<sub>5</sub>-C<sub>6</sub> paraffins, such as 40 vol% or more C<sub>5</sub>-C<sub>6</sub> paraffins.

5 The renewable naphtha for use herein preferably has an average carbon number of greater than 7.0, more preferably greater than 7.1, even more preferably greater than 7.3 and especially greater than 7.37. The relatively heavy average carbon number of the renewable naphtha used in the present invention has been found to provide surprising reductions in FFV emissions such as PM  
10 and NO<sub>x</sub> compared to gasoline and light renewable naphtha.

In addition to mainly comprising paraffins, the renewable naphtha distillate for use herein also has a low content of naphthenes (cycloalkanes), which are alkanes with at least one non-aromatic ring structure,  
15 where the ring typically has 5 or 6 carbon atoms. The renewable naphtha used herein preferably comprises 5 mass% or less of naphthenes, such as 4 mass% or less of naphthenes, or 3.4 mass% or less of naphthenes.

In addition to mainly comprising paraffins, the renewable naphtha distillate also has a very low content  
20 of aromatics. Aromatic compounds contain a benzene ring or other ring structure that is aromatic. The renewable naphtha used herein preferably has an aromatics content (as measured according to ASTM D6729) of 0.5 mass% or  
25 less, more preferably 0.4 mass% or less.

In addition to mainly comprising paraffins, the renewable naphtha distillate also has a very low content of oxygenates. Oxygenates are organic molecules that contain oxygen as part of their chemical structure, and  
30 are usually employed as gasoline additives to reduce carbon oxides and soot created during the burning of the fuel. Common oxygenates include alcohols, ethers and esters. Renewable naphtha distillate may have 1 vol% or

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less of oxygenates, such as 0.5 vol% or less of oxygenates, or 0.1 vol% or less of oxygenates, although it is preferably essentially free of oxygenates.

5 The renewable naphtha used herein typically has a low octane number, i.e. for example having a RON and/or a MON of from 35 to 70, such as from 35 to 60 or from 35 to 50 or from 35 to 45, or from 38 to 42. It has surprisingly been found that despite the low octane quality of the renewable naphtha, it can be included in  
10 the fuel composition of the present invention at a relatively high level without detrimentally effecting the Research Octane Number (RON) of the final fuel composition. This can be seen from Figure 2.

The renewable naphtha distillate used herein  
15 preferably has a Reid Vapour Pressure (as measured according to ASTM D5191) in the range from 8 to 30 kPa, more preferably in the range from 10 to 28 kPa, even more preferably in the range from 25 to 28 kPa. The low Reid Vapour Pressure of the renewable naphtha distillate used  
20 in the present invention, compared to 50 to 80 kPa for gasoline, has surprisingly been found to reduce FFV emissions such as CO, NO<sub>x</sub>, etc.

The renewable naphtha used herein preferably has a specific gravity at 15°C (as measured according to ASTM  
25 D6729) in the range from 0.660 to 0.715, more preferably from 0.675 to 0.715, even more preferably in the range from 0.680 to 0.705, and especially in the range from 0.691 to 0.702.

The renewable naphtha used herein may have a boiling  
30 range of from 30 to 200°C, such as 90 to 200°C, or 40 to 180°C.

The renewable naphtha component of the present invention can be prepared according to the methods

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provided in WO2018/069137, WO2018/234187,  
WO2009/148909 and EP3397734B1, all of which are  
incorporated herein by reference in their entirety.

5 In a preferred embodiment, especially from the  
viewpoint of providing both reduced CO and NO<sub>x</sub> emissions,  
in particular in a spark ignition combustion engine,  
especially in a flexible fuel vehicle, the renewable  
naphtha has the following properties: (i) a total  
10 paraffins content of at least 90 mass%, an iso-paraffins  
content of at least 60 mass%, an n-paraffins content of  
at most 30 mass%, and an iso-paraffins to n-paraffins  
ratio of 3:1 or greater; (ii) an aromatics content of 0.5  
mass% or less; (iii) a Reid Vapour Pressure in the range  
from 8 to 30 kPa; and (iv) specific gravity at 15°C in  
15 the range from 0.660 to 0.715.

A preferred renewable naphtha component for use  
herein is commercially available heavy naphtha from World  
Energy AltAir Paramount plant in California, USA under  
the tradename AltAir Paramount Renewable Naphtha, Heavy  
20 grade, which utilizes beef tallow and small amounts of  
non-edible vegetable oils as feedstock having the  
physicochemical properties set out in Figure 1.

In addition to the renewable naphtha, the liquid  
fuel composition of the present invention comprises an  
25 alcohol component, preferably of renewable origin, at a  
level of 35 vol% to 95 vol%, preferably from 50 vol% to  
95 vol%, more preferably from 60 to 90 vol%, even more  
preferably from 70 vol% to 90 vol%, and especially from  
80 to 90 vol%, based on the fuel composition. In one  
30 embodiment, the renewable alcohol component is present at  
a level from 51 vol% to 85 vol%, based on the total fuel  
composition. In another embodiment, the renewable  
alcohol component is present at a level from 60 vol% to

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80 vol%, based on the total fuel composition.

Suitable alcohols for use herein include methanol, ethanol, propanol, 2-propanol, butanol, tert-butanol, iso-butanol, 2-butanol and mixtures thereof.

5 A particularly alcohol for use herein is ethanol, especially bioethanol.

When both the alcohol and the naphtha are of renewable origin, the portion of renewable content in the fuel composition is increased. Preferably the fuel  
10 composition comprises at least 95 vol% renewable components, more preferably at least 99 vol% renewable components and especially 100 %vol renewable components.

While it is preferred for the level of renewable components to be as high as possible, it is also possible  
15 for the fuel composition of the present invention to include one or more petroleum-derived gasoline blending components. When present, the petroleum-derived gasoline blending components may be in the form of a gasoline base fuel. Preferably, the fuel composition comprises at most  
20 10% vol petroleum-derived gasoline blending components, more preferably at most 5% vol, even more preferably at most 2% vol. In an especially preferred embodiment the fuel composition is free of petroleum-derived gasoline blending components.

25 The fuel composition according to the present invention preferably has a Research Octane Number (RON) in the range of from 85 to 105. The fuel composition of the present invention preferably has a Motor Octane Number in the range from 75 to 90.

30 Whilst not critical to the present invention, the fuel composition of the present invention may conveniently include one or more optional fuel additives. The concentration and nature of the optional fuel

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additive(s) that may be included in the fuel composition is not critical.

5 The (active matter) concentration of any optional additives present in the fuel composition of the present invention is preferably up to 1% m/m, more preferably in the range from 5 to 2000mg/kg, advantageously in the range of from 300 to 1500 mg/kg, such as from 300 to 1000 mg/kg.

10 Suitable additives for use in fuel compositions herein include corrosion inhibitors, for example based on ammonium salts of organic carboxylic acids, said salts tending to form films, or of heterocyclic aromatics for nonferrous metal corrosion protection; antioxidants or stabilizers, for example based on amines such as  
15 phenyldiamines, e.g., p-phenylenediamine, N,N'-di-sec-butyl-p-phenyldiamine, dicyclohexylamine or derivatives thereof or of phenols such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxy-phenylpropionic acid; anti-static agents; metallocenes such as ferrocene; methyl-  
20 cyclopentadienylmanganese tricarbonyl; lubricity additives, such as certain fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl) fatty amines, hydroxyacetamides or castor oil; and also dyes (markers). Amines may also be added, if appropriate, for example as described in  
25 WO03/076554. Optionally anti-valve seat recession additives may be used such as sodium or potassium salts of polymeric organic acids.

The gasoline compositions herein can also comprise a detergent additive. Suitable detergent additives include  
30 those disclosed in WO2009/50287, incorporated herein by reference.

Preferred detergent additives for use in the gasoline composition herein typically have at least one

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hydrophobic hydrocarbon radical having a number-average molecular weight (Mn) of from 85 to 20 000 and at least one polar moiety selected from:

5 (A1) mono- or polyamino groups having up to 6 nitrogen atoms, of which at least one nitrogen atom has basic properties;

10 (A6) polyoxy-C<sub>2</sub>- to -C<sub>4</sub>-alkylene groups which are terminated by hydroxyl groups, mono- or polyamino groups, in which at least one nitrogen atom has basic properties, or by carbamate groups;

(A8) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or

15 (A9) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

The hydrophobic hydrocarbon radical in the above detergent additives, which ensures the adequate solubility in the base fluid, has a number-average molecular weight (Mn) of from 85 to 20 000, especially from 113 to 10 000, in particular from 300 to 5000. Typical hydrophobic hydrocarbon radicals, especially in conjunction with the polar moieties (A1), (A8) and (A9), include polyalkenes (polyolefins), such as the  
25 polypropenyl, polybutenyl and polyisobutenyl radicals each having Mn of from 300 to 5000, preferably from 500 to 2500, more preferably from 700 to 2300, and especially from 700 to 1000.

30 Non-limiting examples of the above groups of detergent additives include the following:

Additives comprising mono- or polyamino groups (A1) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or conventional (i.e., having

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predominantly internal double bonds) polybutene or polyisobutene having Mn of from 300 to 5000. When polybutene or polyisobutene having predominantly internal double bonds (usually in the beta and gamma position) are used as starting materials in the preparation of the additives, a possible preparative route is by chlorination and subsequent amination or by oxidation of the double bond with air or ozone to give the carbonyl or carboxyl compound and subsequent amination under reductive (hydrogenating) conditions. The amines used here for the amination may be, for example, ammonia, monoamines or polyamines, such as dimethylaminopropylamine, ethylenediamine, diethylene-triamine, triethylenetetramine or tetraethylenepentamine. Corresponding additives based on polypropene are described in particular in WO-A-94/24231.

Further preferred additives comprising monoamino groups (A1) are the hydrogenation products of the reaction products of polyisobutenes having an average degree of polymerization of from 5 to 100, with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO-A-97/03946.

Further preferred additives comprising monoamino groups (A1) are the compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols, as described in particular in DE-A-196 20 262.

Additives comprising polyoxy-C<sub>2</sub>-C<sub>4</sub>-alkylene moieties (A6) are preferably polyethers or polyetheramines which are obtainable by reaction of C<sub>2</sub>- to C<sub>60</sub>-alkanols, C<sub>6</sub>- to C<sub>30</sub>-alkanediols, mono- or di-C<sub>2</sub>-C<sub>30</sub>-alkylamines, C<sub>1</sub>-C<sub>30</sub>-alkylcyclohexanols or C<sub>1</sub>-C<sub>30</sub>-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or

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butylene oxide per hydroxyl group or amino group and, in the case of the polyether-amines, by subsequent reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP-A-310 875, EP-A-356 725, EP-A-700 985 and US-A-4 877 416. In the case of polyethers, such products also have carrier oil properties. Typical examples of these are tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and also the corresponding reaction products with ammonia.

Additives comprising moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups (A8) are preferably corresponding derivatives of polyisobutenylsuccinic anhydride which are obtainable by reacting conventional or highly reactive polyisobutene having Mn of from 300 to 5000 with maleic anhydride by a thermal route or via the chlorinated polyisobutene. Of particular interest are derivatives with aliphatic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. Such additives are described in particular in US-A-4 849 572.

Additives comprising moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines (A9) are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and mono- or polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. The polyisobutenyl-substituted phenols may stem from conventional or highly reactive polyisobutene having Mn of from 300 to 5000. Such "polyisobutene-Mannich bases"

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are described in particular in EP-A-831 141.

Preferably, the detergent additive used in the gasoline compositions of the present invention contains at least one nitrogen-containing detergent, more preferably at least one nitrogen-containing detergent containing a hydrophobic hydrocarbon radical having a number average molecular weight in the range of from 300 to 5000. Preferably, the nitrogen-containing detergent is selected from a group comprising polyalkene monoamines, polyetheramines, polyalkene Mannich amines and polyalkene succinimides. Conveniently, the nitrogen-containing detergent may be a polyalkene monoamine.

In the above, amounts (concentrations, % v/v, mg/kg (ppm), % m/m) of components are of active matter, i.e., exclusive of volatile solvents/diluent materials.

The fuel composition of the present invention can be produced by admixing the renewable naphtha and the alcohol component in suitable amounts.

The fuel composition of the present invention is suitable for use in an internal combustion engine, especially as used in a flexible fuel vehicle.

The fuel composition of the present invention has been found to be particularly useful in reducing CO and NO<sub>x</sub> emissions, particularly when used in a spark ignition internal combustion engine, especially in a flexible fuel vehicle. Preferably, the reduction in CO and NO<sub>x</sub> emissions is as compared to a comparable gasoline-based fuel composition (i.e. containing a conventional gasoline base fuel instead of a renewable naphtha) and having the same ethanol content. The CO and NO<sub>x</sub> emissions can be measured by bag emission method according to U.S. Environmental Protection Agency (EPA) 40 Code of Federal Regulations Title 40, Part 1066 Vehicle-Testing

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Procedures. Hence according to another aspect of the present invention there is provided the use of a fuel composition as described hereinabove for reducing CO emissions and NO<sub>x</sub> emissions, particularly wherein the  
5 fuel composition is used for fuelling an internal combustion engine in a flexible fuel vehicle. The internal combustion engine is preferably a spark ignition internal combustion engine.

According to a further aspect of the present  
10 invention there is provided a method for reducing CO emissions and NO<sub>x</sub> emissions in a spark ignition internal combustion engine within the powertrain of a flexible fuel vehicle, wherein the method comprises combusting a fuel composition in the spark ignition internal  
15 combustion engine and measuring the reduction in CO emissions and NO<sub>x</sub> emissions produced by the spark ignition internal combustion engine.

The use and methods of the present invention can preferably provide at least 5% reduction in both CO  
20 emissions and NO<sub>x</sub> emissions, more preferably at least a 10% reduction in both CO and NO<sub>x</sub> emissions, even more preferably at least a 15% reduction in both CO and NO<sub>x</sub> emissions, compared to an analogous fuel composition which contains a petroleum-derived gasoline base fuel  
25 instead of a renewable naphtha and which contains the same level and type of ethanol.

The invention is further described by reference to the following non-limiting examples.

#### Examples

30 Several fuel blends were prepared having the compositions detailed below. Each fuel blend contained the same denatured ethanol, in the stated amount. In addition, each fuel blend contained either a naphtha

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component or a regular unleaded gasoline. No additive packages were used in any of the fuel blends.

Reference Fuel 1 (Ref-1) contained 20 vol% regular unleaded gasoline having the physicochemical properties shown in Figure 1 and 80 vol% denatured ethanol.

Reference Fuel 2 (Ref-2) contained 40 vol% of the regular unleaded gasoline used in Ref-1 and 60 vol% of denatured ethanol.

Reference Fuel 3 (Ref-3) contained 15 vol% of the regular unleaded gasoline used in Ref-1 and 85 vol% of denatured alcohol.

Fuel A-E80 contained 20 vol% AltAir Paramount Renewable Naphtha, Full-range grade, a renewable naphtha sourced from AltAir Paramount Refinery of World Energy LLC., California, USA having the physicochemical properties shown in Figure 1, and 80% denatured ethanol.

Fuel A-E60 contained 40 vol% Full-Range grade AltAir naphtha (as used in A-E80), and 60 vol% denatured ethanol.

Fuel B-E80 contained 20 vol% of Neste Renewable Naphtha/Eni bio-naphtha blend sourced from Shell Rotterdam Botlek Tank Terminal, The Netherlands having the physicochemical properties shown in Figure 1, and 80 vol% denatured ethanol.

Fuel C-E85 contained 15 vol% gas-to-liquid (GTL) naphtha, sourced from the Shell Pearl plant, Qatar having the physicochemical properties shown in Figure 1, and 85 vol% denatured ethanol.

Fuel C-E80 contained 20 vol% GTL naphtha (as used in C-E85) and 80 vol% denatured ethanol.

Fuel C-E60 contained 40 vol% GTL naphtha (as used in C-E85) and 60 vol% denatured ethanol.

Fuel D-E80 contained 20 vol% Ekobenz Ethanol-to-

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Gasoline (ETG), a renewable motor fuel produced by an ethanol-to-gasoline process, supplied by Ekobenz, Poland, having the physicochemical properties shown in Figure 1, and 80 vol% denatured ethanol. The ETG process for making such an ETG product is described in particular in EP2940103A1)

Fuel D-E60 contained 40 vol% Ekobenz ETG motor fuel (as used in D-E80) and 60 vol% denatured ethanol.

Fuel E-E80 contained 20 vol% AltAir Paramount Renewable Naphtha Heavy grade, a renewable naphtha supplied by World Energy AltAir Paramount plant in California, USA having the physicochemical properties shown in Figure 1 and 80 vol% denatured ethanol.

Fuel E-E60 contained 40 vol% heavy AltAir naphtha (as used in E-E80) and 60 vol% denatured ethanol.

The detailed hydrocarbon analyses (DHAs) (as per ASTM D6729 and D6730 test methods) of the various naphthas and the gasoline used in the fuel blends are shown in Figure 1. In Figure 1, graph (a) shows the normal paraffin and iso-paraffin content, graph (b) shows the naphthene content, (c) shows the average carbon number, graph (d) shows the specific gravity, graph (e) shows the aromatics content, and graph (f) shows the RON of the neat bio-naphtha samples.

The RON of the neat bio-naphthas and the gasoline were calculated from detailed hydrocarbon analysis, but the RON of all high ethanol blends were measured using ASTM D2699 test method. These RON values can be seen in Figure 2. In view of the low RON numbers of the bionaphtha, it is surprising that the RON values of the final fuel compositions are high.

In order to test the performance of the fuels above, vehicle tests were carried out using a 2021 Ford Transit

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Connect flexible fuel vehicle equipped with a 2.0 liter Gasoline Direct Injection (GDI) I-4 engine with Auto Start Stop Technology, 8-speed SelectShift (RTM) automatic transmission, 162 hp @6,500 rpm and 144 lb. ft. of torque @4,500 rpm. Further details of the vehicle spec are provided in Table 1 below.

Table 1: Vehicle Specification

|                                        |                                                        |
|----------------------------------------|--------------------------------------------------------|
| Engine                                 | 2.0L GDI I-4 engine                                    |
| Block/head material                    | Aluminium block, aluminium heads                       |
| Displacement                           | 2.0 liters (122 cubic inches)                          |
| Bore x stroke                          | 3.44 x 3.27 inches (87.5 x 83.1 mm)                    |
| Compression ratio                      | 12:1                                                   |
| Valvetrain                             | Ti-VCT DOHC 4 valves per cylinder                      |
| Intake Valve diameter/lift @zero lash  | 1.378 in (35 mm)/0.346 in (8.8 mm)                     |
| Exhaust Valve diameter/lift @zero lash | 1.142 in (29 mm)/0.346 in (8.8 mm)                     |
| Piston Materials                       | Aluminium                                              |
| Connecting rods materials              | Powdered Steel                                         |
| Ignition System                        | Coil on plug                                           |
| Fuel delivery                          | Sequential electronic direct injection                 |
| Recommended fuel                       | Regular Unleaded or E85                                |
| Engine control system                  | Multicore Powertrain Control Module                    |
| Intake manifold                        | Nylon (PA6 GF30)                                       |
| Oil grade                              | SAE 5W-20                                              |
| Oil Capacity including oil filter      | 4.80 qt (4.54 L)                                       |
| Oil Capacity without oil filter        | 4.40 qt (4.16 L)                                       |
| Coolant capacity                       | 8.06 qt (7.63 L)                                       |
| SAE Horsepower                         | 162 hp @6,500 rpm                                      |
| SAE Torque                             | 144 ft.-lbs.@4,500 rpm                                 |
| Red line                               | 6,500 rpm                                              |
| Maximum engine speed                   | 6,800 rpm max continuous<br>7,000 rpm max intermittent |
| Build location                         | Dearborn Engine Plant (North America)                  |

Each candidate fuel was tested against a reference

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fuel following the two-day test sequence shown in Figure 3. World harmonized Light duty vehicles Test Procedure (WLTP) (an Industry standard test procedure) was selected and during each WLTP drive cycle, emissions (CO, CO<sub>2</sub>, total hydrocarbon (THC), NO<sub>x</sub> and Particulate Matter (PM)) and fuel economy was measured. The first step for each day entailed a cold-start WLTP in which the emissions and fuel economy of the candidate fuel were measured. Then A-B-A-B-A-B test sequence, where A is a reference fuel and B is a candidate fuel, of the hot-start WLTP was conducted. On day 2 of the test sequence, the three runs of performance checks which includes acceleration, steady-state power check, and coastdowns (only for the last run). The acceleration time was measured from 10 to 60 miles/hour (mph) at wide-open throttle. The steady-state power checks entail measurement of peak power engine RPM, which was then converted to power in horsepower. Coastdown times are measured from 70 to 30 mph to ensure no drifts in dynamometer.

Table 2 provides the results for the CO emissions, NO<sub>x</sub> emissions, cold-start and hot-start PM emissions, fuel economy, acceleration and power for the fuel compositions containing AltAir heavy naphtha (E-E60 and E-E80) as well as for the gasoline-based reference flex fuels (E80 and E60). All metrics in Table 2 (and Table 3) were measured according to the Code of US Federal Regulations, Title 40, Part 1066 - Vehicle Testing Procedures. All results in Table 2 and Table 3 are averaged over the number of test runs.

Table 2

| Metric                                                                         | Ref.E9<br>0 | Ref.<br>E60 | E90<br>With<br>AltAir<br>Full-<br>Range<br>(A-E90) | E60<br>With<br>AltAir<br>Full-<br>Range<br>(A-E60) | E90<br>with<br>GIL<br>naphtha<br>(C-E90) | E60<br>with<br>GIL<br>naphtha<br>(C-E60) | E90<br>With<br>Ekobenz<br>ETG<br>(D-E90) | E60<br>with<br>Ekobenz<br>ETG (D-<br>E60) | E90<br>with<br>AltAir<br>Heavy<br>(E-E90) | E60 with<br>AltAir<br>Heavy<br>(E-E60) |
|--------------------------------------------------------------------------------|-------------|-------------|----------------------------------------------------|----------------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|-------------------------------------------|-------------------------------------------|----------------------------------------|
| Averaged CO<br>emissions<br>(g/mile)                                           | 0.659       | 0.464       | 0.800                                              | 0.388                                              | 0.504                                    | 0.449                                    | 0.553                                    | 0.218                                     | 0.443                                     | 0.362                                  |
| Averaged<br>NO <sub>x</sub><br>emissions<br>(g/mile)                           | 0.0132      | 0.0132      | 0.0137                                             | 0.0121                                             | 0.0104                                   | 0.0139                                   | 0.0121                                   | 0.0138                                    | 0.00828                                   | 0.0081                                 |
| Averaged<br>CO <sub>2</sub><br>emissions<br>(g/mile)                           | 272         | 275         | 281                                                | 273                                                | 264                                      | 270                                      | 271                                      | 275                                       | 267                                       | 265                                    |
| Averaged<br>Cold start<br>particulate<br>matter (PM)<br>emissions<br>(mg/mile) | 5.62        | 15.6        | 2.22                                               | 2.51                                               | 3.66                                     | 2.66                                     | 6.79                                     | 50.1                                      | 4.48                                      | 3.25                                   |
| Averaged<br>Hot-start<br>particulate<br>matter (PM)<br>emissions<br>(mg/mile)  | 2.28        | 6.6         | 2.47                                               | 2.02                                               | 1.49                                     | 2.13                                     | 1.13                                     | 42.2                                      | 1.79                                      | 2.29                                   |

|                                                          |        |        |        |        |        |        |        |        |        |        |        |
|----------------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Averaged<br>Total<br>Hydrocarbon<br>emission,<br>g/mile) | 0.0194 | 0.0134 | 0.0190 | 0.0155 | 0.0201 | 0.0218 | 0.0155 | 0.0151 | 0.0143 | 0.0201 | 0.0161 |
| Averaged<br>Fuel<br>Economy<br>(mile/gal)                | 23.0   | 24.6   | 22.2   | 24.0   | 22.8   | 22.6   | 24.9   | 23.1   | 24.4   | 23.1   | 25.1   |
| Averaged<br>10-60 mph<br>acceleration<br>time<br>(sec)   | 9.5    | 9.4    | 9.6    | 9.5    | 9.5    | 9.6    | 9.3    | 9.5    | 9.6    | 9.4    | 9.3    |
| Averaged<br>Steady-<br>state power<br>(hp)               | 115    | 116    | 115    | 116    | 116    | 114    | 118    | 114    | 116    | 115    | 116    |

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5       The key findings of all of the experiments are  
summarized in Table 3 below which shows comparisons  
between candidate fuels and reference fuels from the same  
two-day test sequence.

      The key to Table 3 is as follows:

      'Yes' means that the candidate fuel is better than the  
reference in both E60 and E80

10       'O' means that the candidate fuel is the same as the  
reference in both E60 and E80

      'x' means that the candidate fuel is worse than the  
reference in both E60 and E80

Table 3

| Metric                                                          | E80 and E60 with AltAir Full Range (A-E80 and A-E60) | E80 with Neste/Eni (B-E80) | E80 and E60 with GTL naphtha (C-E80 and C-E60) | E80 and E60 with Ekobenz ETG (D-E80 and D-E60) | E80 and E60 with AltAir Heavy (E-E80 and E-E60) |
|-----------------------------------------------------------------|------------------------------------------------------|----------------------------|------------------------------------------------|------------------------------------------------|-------------------------------------------------|
| Averaged CO emissions (g/mile)                                  | Yes                                                  | o                          | Yes                                            | Yes                                            | Yes                                             |
| Averaged NO <sub>x</sub> emissions (g/mile)                     | o                                                    | o                          | 0                                              | o                                              | Yes                                             |
| Averaged CO <sub>2</sub> emissions (g/mile)                     | o                                                    | Yes                        | Yes                                            | o                                              | Yes                                             |
| Averaged Cold start particulate matter (PM) emissions (mg/mile) | Yes                                                  | Yes                        | Yes                                            | x                                              | Yes                                             |
| Averaged Hot-start particulate matter (PM) emissions (mg/mile)  | o                                                    | o                          | Yes                                            | x                                              | Yes                                             |
| Averaged Total hydrocarbon emission, g/mile                     | o                                                    | o                          | o                                              | o                                              | o                                               |

|                                            |   |   |   |   |     |
|--------------------------------------------|---|---|---|---|-----|
| Averaged Fuel Economy (mile/gal)           | x | x | o | o | Yes |
| Averaged 10-60 mph acceleration time (sec) | o | o | o | o | o   |
| Averaged Steady-state power (hp)           | o | o | o | o | o   |

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From Table 3 it can be seen that E80 and E60 with AltAir Heavy naphtha (E-E80 and E-E60) provide the best overall results since these candidates are better than the reference for six out of the nine parameters measured (namely CO emissions, NO<sub>x</sub> emissions, CO<sub>2</sub> emissions, cold start and warm start particulate matter emissions (PM) and fuel economy) and are the same as the reference for the remaining three parameters (namely THC emissions, 10-60 mph acceleration and steady-state power).

By contrast, the E80 and E60 with AltAir Full Range naphtha (A-E80 and A-E60) were better than the reference for only two out of the nine parameters measured (namely CO emissions and cold-start PM); the E80 with Neste/ENI Naphtha (B-E80) was better than the reference for only two out of the nine parameters measured (namely CO<sub>2</sub> emissions and cold-start particulate matter; the E80 and E60 with GTL naphtha were better than the reference for only four out of the nine parameters measured (namely CO emissions, CO<sub>2</sub> emissions, cold-start particulate matter and hot-start particulate matter; the E80 and E60 with Ekobenz ETG naphtha (D-E80 and D-E60) were better than the reference for only one out of the nine parameters measured (namely CO emissions).

The E80 and E60 with AltAir Heavy naphtha (E-E80 and E-E60) were the only fuel blends which were better than the reference for both NO<sub>x</sub> emissions and CO emissions. This is particularly surprising as there is typically a trade-off between NO<sub>x</sub> emissions and CO emissions.

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C L A I M S

1. A fuel composition comprising:

(i) from 35 vol% to 95 vol% of a renewable alcohol component; and

5 (ii) from 5 vol% to 65 vol% of a renewable naphtha component, wherein the renewable naphtha component has a total iso-paraffins and n-paraffins content of at least 90 mass%, an iso-paraffins content of at least 60 mass%, an n-paraffins content of less than 30 mass%, and an iso-paraffins to n-paraffins ratio of greater than 3:1.

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2. A fuel composition according to Claim 1 wherein the renewable naphtha component has a specific gravity in the range from 0.660 to 0.715.

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3. A fuel composition according to Claim 1 or 2 wherein the renewable naphtha component has an aromatics content of 0.5 mass% or less.

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4. A fuel composition according to any of Claims 1 to 3 wherein the renewable naphtha component has an average carbon number of greater than 7.37.

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5. A fuel composition according to any of Claims 1 to 4 wherein the renewable naphtha component comprises less than 5 mass% naphthenes.

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6. A fuel composition according to any of Claims 1 to 5 wherein the renewable naphtha component has an RVP in the range from 8 to 30 kPa.

7. A fuel composition according to any of Claims 1 to 6 wherein the fuel composition comprises from 80 vol% to 90 vol% of the renewable alcohol component.
- 5        8. A fuel composition according to any of Claims 1 to 7 wherein the fuel composition comprises from 10 vol% to 20 vol% of the renewable naphtha component.
9. A fuel composition according to any of Claims 1 to 8  
10 wherein the renewable alcohol component is ethanol.
10. Use of a fuel composition according to any of Claims 1 to 9 for reducing CO emissions and NO<sub>x</sub> emissions.
- 15        11. Use according to Claim 10 wherein the fuel composition is used in spark ignition internal combustion engine of a flexible fuel vehicle.
12. Method for reducing CO emissions and NO<sub>x</sub> emissions in  
20 a spark ignition internal combustion engine within the powertrain of a flexible fuel vehicle, wherein the method comprises combusting a fuel composition in the spark ignition internal combustion engine and measuring the reduction in CO emissions and NO<sub>x</sub> emissions produced by the spark ignition  
25 internal combustion engine.