

USE OF A DETERGENT ADDITIVE

Field of the Invention

The present invention relates to the use of a detergent additive in a fuel composition for reducing microbial growth.

5 Background of the Invention

Fuel tanks and distribution systems provide an environment where microorganisms can flourish. There are three main types of spoilage and corrosive hydrocarbon-utilising microorganisms in fuel systems, namely
10 bacteria, yeasts and moulds, the latter two often named as fungi. Microbes are ubiquitous and can infect fuel at any point in the distribution chain, surviving and proliferating in water/aqueous phase associated with the fuel and drawing their nutrients across the fuel/water
15 interface (most nutrients diffuse into the cell in aqueous solution). Microbes require elements such as carbon, hydrogen, sulphur, nitrogen and phosphorus in substantial amounts, trace amounts of other elements and some form of oxygen. The rate and type of microbial
20 proliferation is dependent on factors such as water phase pH, oxygen availability, ambient temperature, nutrient availability, etc. Optimum growth is achieved in the temperature range 15°C to 40°C and a neutral/slightly acidic pH. Most of these conditions are met in fuel
25 tanks and distribution systems thereby providing an ideal environment for microbial growth. Water as one key contributor exacerbates the situation and can never be completely eradicated due to condensation effects, leaking tank roofs, poor housekeeping, etc. A fuel
30 storage system is therefore never sterile and at best,

the aim is to restrict microbial growth to an acceptable level by the adoption of good housekeeping practices.

There are several undesirable consequences of microbial growth in fuel systems. One such consequence
5 is Microbially Induced Corrosion (MIC) which is corrosion that is caused by or promoted by microorganisms.

Microbial cells can exist in planktonic (single cells floating/swimming in the fuel) or sessile forms (attached to a surface). A biofilm forms when a
10 collection of microorganisms (mainly bacteria) adhere irreversibly to a surface and begin to excrete slimy, extracellular biopolymers. Biofilms enhance microbial interactions, giving more access to nutrients, environmental stability, protection from viruses and
15 biocides. These microbial communities can attach to the sidewalls and bottoms of fuel storage tanks causing Microbially Induced Corrosion (MIC).

MIC is one of the most serious consequences of microbial growth. Aerobes produce organic acids and
20 deplete oxygen supplies, creating an oxygen-deficient zone around them. Oxygen gradients develop causing the formation of anodic corrosion pits. Sulphate Reducing Bacteria (SRB) can increase this corrosion by producing H_2S , HS and S_2 , all of which are very aggressive to
25 steel.

Other consequences of microbial growth in fuel systems are blocked filters, valves and pipelines, increased pump wear and production of biosurfactants that can cause stable water hazes and coalesce disarming. In
30 particular, fungi are implicated in filter blocking in vehicle fuel systems. Fuel filter plugging is often caused by mould growth, which manifests itself as a mat of hyphae (long filaments of fungi) at the fuel/water

interface. Loss of product quality, foul odour, cloudiness and discolouration and injector fouling can also be undesirable consequences of microbial growth.

5 Biofuels (e.g. FAMES) can play a role in fossil fuel replacement to meet reduction targets of greenhouse gas emissions. Globally, many countries have established or are developing biofuel mandates, with some countries (e.g. Indonesia) introducing B30 (30% biofuel), which is well above the current EU mandated levels of B7 (7%
10 biofuel). However, it is well established that biodiesel and its blends, particularly at the EU mandated levels, are more susceptible to microbial growth than conventional hydrocarbon diesel. The reasons cited for this are that FAME is easier for microorganisms to digest
15 and more hydroscopic than conventional diesel leading to greater free water entrainment.

Gas-to-liquid (GTL) technology converts CH₄/methane currently from natural gas - the cleanest-burning fossil fuel - into high-quality liquid fuel products that would
20 otherwise be made from crude oil. GTL fuel can help to reduce local emissions in conventional diesel vehicles. GTL fuel also has other applications, e.g. as a synthetic marine fuel in inland water way vessels in conventional marine diesel engines. It is known that GTL fuel is more
25 biodegradable than conventional diesel due to its negligible aromatic content and simple structure (it is fully saturated) but may be more susceptible to microbial growth than conventional diesel. Fuel handling and storage conditions with respect to microbial growth could
30 be considered as even more severe for inland water way vessels than for road applications due to the potential presence of water inside the tank, during fuelling and on board bunker ships.

Attempts have been made in the past to solve microbial spoilage incidents in fuels and fuel systems. Chemical treatments such as biocides and biostats are currently used to control and eliminate microbial growth
5 in fuel systems in conjunction with physical control methods such as good housekeeping, settling, filtration, centrifugation and heat treatment.

Unfortunately, chemical treatments by their nature are toxic and their handling presents serious health,
10 safety and environmental issues. The commonly used isothiazolinone chemistry, for example, is a skin sensitiser. Further, it is necessary to dispose of waste biomass after chemical treatment which can be time consuming and expensive.

15 It would therefore be desirable to provide alternative ways of reducing microbial growth in fuels and fuel systems.

Summary of the Invention

According to the present invention there is provided
20 the use of a detergent additive in a fuel composition for reducing microbial growth.

According to another aspect of the present invention there is provided a method for reducing microbial growth in a fuel composition, which method comprises a step of
25 introducing a detergent additive into said fuel composition.

It has been found that use of a detergent additive as described herein can reduce the microbial growth in a fuel composition to which the detergent additive is
30 added. Hence, the invention can lead to a reduction in microbial spoilage incidents in a wide range of fuel compositions.

Brief Description of the Drawings

Figure 1 is a graphical representation of the experimental data generated in Example 1.

Figure 2 is a graphical representation of the experimental data set out in Table 5 below, and in particular shows the average dry biomass weight (g) after 4 weeks and after 12 weeks of fuels tested in Example 2 below, with and without additive.

Figure 3 is a graphical representation of the experimental data set out in Table 5 below, and in particular shows the average dry biomass weight (g) for all fuel formulations tested in Example 2 below with and without Performance Additive Package 2, Performance Additive Package 3, Detergent Additive 1 and Detergent Additive 2.

Detailed Description of the Invention

As used herein there is provided the use of a detergent additive in a fuel composition for reducing microbial growth in said fuel composition.

In the context of this aspect of the invention, the term "reducing microbial growth" embraces any degree of reduction in microbial growth. Microbial growth may be measured by any suitable method such as the biomass method described in the Examples below. The reduction in microbial growth may be of the order of 10% or more, preferably 20% or more, more preferably 50% or more, and especially 70% or more compared to the microbial growth in an analogous fuel composition which does not contain a detergent additive, in particular during the time period where the fuel composition is stored in a fuel tank, for example a time period of up to 12 weeks. As used herein, the term "reducing microbial growth" also encompasses the prevention of microbes growing in the first place.

The present invention is relevant for a wide range

of fuel applications such as diesel fuels, heating oils, aviation fuels, marine fuels, and mixtures thereof. Preferred fuel applications include diesel fuels and aviation fuels.

5 A first essential component herein is a detergent additive, by which is meant an agent (suitably a surfactant) which can act to remove, and/or to prevent the build-up of, combustion related deposits within an engine, in particular in the fuel injection system such
10 as in the injector nozzles. Such materials are sometimes referred to as dispersant additives.

 Detergent-containing diesel fuel additives are known and commercially available. Examples of suitable detergent additives include, but are not necessarily
15 limited to, polyolefin substituted succinimides or succinimides of polyamines, aliphatic amines, Mannich bases or amines, polyolefin maleic anhydrides, and quaternary ammonium salts, and mixtures thereof. A preferred detergent additive for use herein is a
20 nitrogen-containing detergent. In one embodiment, the detergent additive for use herein is a polyolefin substituted succinimide, such as a polyisobutylene succinimide. In another embodiment, the detergent additive for use herein is a quaternary ammonium salt.

25 Many of the detergents mentioned above are nitrogen-containing detergents. With nitrogen being an essential nutrient for microbes, it is particularly surprising that the nitrogen-containing detergents mentioned above have been found to reduce microbial growth when included in a
30 fuel composition.

 Fuel additives can encourage water entrainment in fuel due to their surfactant nature, particularly at higher treat rates, and also act as food sources;

additives containing the essential nutrient nitrogen are particularly important. Therefore, it would be reasonable to assume that fuels blended with performance additives, especially nitrogen-containing performance additives, such as nitrogen-containing detergents, are more conducive to microbial attack. It has been surprisingly found by the present inventors that detergent additives, such as nitrogen-containing detergents, have surprisingly been found to inhibit microbial growth in a fuel composition. In particular, it has been found that detergent additives, such as nitrogen-containing detergents, have surprisingly been found to inhibit microbial growth in a fuel composition, wherein the microbes are fungal species. This is particularly advantageous as filamentous fungi are implicated in filter blocking problems.

The detergent additive is preferably present in the fuel composition at a level from 5 ppmw to 10000ppmw, preferably 5 ppmw to 1000ppmw, more preferably in the range 5 to 500 ppmw, even more preferably in the range from 10 to 200 ppmw active matter detergent based on the overall fuel composition.

In one embodiment of the present invention the detergent additive is a component of a detergent additive package together with one or more other additive components. Examples of other suitable additive components are provided in more detail hereinbelow.

The diesel fuel compositions described herein may comprise a diesel base fuel in addition to the detergent additive.

The diesel base fuel may be any petroleum derived diesel suitable for use in an internal combustion engine, such as a petroleum derived low sulphur diesel comprising

<50 ppm of sulphur, for example, an ultra-low sulphur diesel (ULSD) or a zero sulphur diesel (ZSD). Preferably, the low sulphur diesel comprises <10 ppm of sulphur.

5 The petroleum derived low sulphur diesel preferred for use in the present invention meets the EN590 specification. It will typically have a density from 0.81 to 0.865, preferably 0.82 to 0.85, more preferably 0.825 to 0.845 g/cm³ at 15°C; a cetane number (ASTM D613)
10 of at least 51; and a kinematic viscosity (ASTM D445) from 1.5 to 4.5, preferably 2.0 to 4.0, more preferably from 2.2 to 3.7 mm²/s at 40°C.

In one embodiment, the diesel base fuel is a conventional petroleum-derived diesel.

15 A further preferred component of the fuel composition herein is a biodiesel fuel. Biodiesel fuels are fuels which derive from biological materials.

The biodiesel component is preferably present in the fuel composition herein at a level of 5% v/v or greater up
20 to a level of 50% v/v, preferably from 5% v/v to 30% v/v, for example at levels of 7%v/v, 10%v/v, 20%v/v and 30%v/v.

In one embodiment of the present invention, the fuel composition herein is free of biodiesel component (i.e. a so-called 'B0' fuel).

25 A preferred biodiesel component for use herein is a fatty acid alkyl ester (FAAE). It is known to include fatty acid alkyl esters (FAAEs), in particular fatty acid methyl esters (FAMES), in diesel fuel compositions. Examples of suitable FAAEs include rapeseed methyl ester
30 (RME), palm oil methyl ester (POME), and soy methyl ester (SME). FAAEs are typically derivable from biological sources and are typically included to reduce the environmental impact of the fuel production and

consumption process or to improve lubricity.

FAAEs, of which the most commonly used in the context of diesel fuels are the methyl esters, are already known as renewable diesel fuels (so-called 'biodiesel' fuels).
5 They contain long chain carboxylic acid molecules (generally from 10 to 22 carbon atoms long), each having an alcohol molecule attached to one end. Organically derived oils such as vegetable oils (including recycled vegetable oils) and animal fats (including fish oils) can
10 be subjected to a transesterification process with an alcohol (typically a C₁ to C₅ alcohol) to form the corresponding fatty esters, typically mono-alkylated. This process, which is suitably either acid- or base-catalysed, such as with the base KOH, converts the
15 triglycerides contained in the oils into fatty acid components of the oils from their glycerol backbone. FAAEs can also be prepared from used cooking oils, and can be prepared by standard esterification from fatty acids.

In the present invention, the FAAE may be any
20 alkylated fatty acid or mixture of fatty acids. Its fatty acid component(s) are preferably derived from a biological source, more preferably a vegetable source. They may be saturated or unsaturated; if the latter, they may have one or more, preferably up to 6, double bonds. They may be
25 linear or branched, cyclic or polycyclic. Suitably, they will have from 6 to 30, preferably 10 to 30, more suitably from 10 to 22 or from 12 to 24 or from 16 to 18, carbon atoms including the acid group(s) -CO₂H. A FAAE will typically comprise a mixture of different fatty acid
30 esters of different fatty acid esters of different chain lengths, depending on its source.

A preferred FAAE for use in the present invention is selected from a natural fatty oil, for instance tall oil,

rapeseed oil, palm oil or soy oil.

The FAAE is preferably a C₁ to C₅ alkyl ester, more preferably a methyl, ethyl, propyl, (suitably iso-propyl) or butyl ester, yet more preferably a methyl or ethyl ester and in particular a methyl ester. In one embodiment herein, the FAAE is selected from methyl ester of palm oil (POME) and methyl ester of rapeseed oil (RME, and mixtures thereof.

In general, it may be either natural or synthetic, refined or unrefined ('crude').

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

The FAAE suitably complies with specifications applying to the rest of the fuel composition, and/or to the base fuel to which it is added, bearing in mind the intended use to which the composition is to be put (for example, in which geographical area and at what time of year). In particular, the FAAE preferably has a flash point (IP 34) of greater than 101°C; a kinematic viscosity at 40°C (IP 71) of 1.9 to 6.0 mm²/s, preferably 3.5 to 5.0 mm²/s; a density of 845 to 910 kg/m³, preferably from 860 to 900 kg/m³, at 15°C (IP 365, EN ISO 12185 or EN ISO 3675); a water content (IP 386) of less than 500 ppm; a T₉₅ (the temperature at which 95% of the fuel has evaporated, measured according to IP 123) of less than 360°C; an acid number (IP 139) of less than 0.8mgKOH/g, preferably less than 0.5mgKOH/g; and an iodine number (IP 84) of less than 125, preferably less than 120 or less than 115, grams of iodine (I₂) per 110g of fuel. It also preferably contains (e.g. by gas chromatography (GC)) less than 0.2% w/w of free methanol, less than 0.02% w/w of free glycerol and greater than 96.5% w/w esters. In general it may be preferred for the FAAE to conform to the

European specification EN14214 for fatty methyl esters for use as diesel fuels.

Two or more FAAEs may be added to the fuel composition in accordance with the present invention,
5 either separately or as a pre-prepared blend.

The FAAE can be incorporated into the fuel composition typically as a blend (i.e. a physical mixture) and optionally with one or more other fuel components (such as diesel base fuels) and optionally with one or
10 more fuel additives. The FAAE is conveniently incorporated into the fuel composition before the composition is introduced into the engine which is to be run on the fuel composition.

The fuel composition herein can comprise a paraffinic gasoil, in addition to or instead of the diesel base fuel
15 mentioned above. A suitable paraffinic gasoil for use in the present invention can be derived from any suitable source as long as it is suitable for use in a fuel composition, especially a diesel fuel composition.

20 Suitable paraffinic gasoils include, for example, Fischer-Tropsch derived gasoils, and gasoils derived from hydrogenated vegetable oil (HVO), and mixtures thereof.

A preferred paraffinic gasoil for use herein is a Fischer-Tropsch derived gasoil fuel. The paraffinic
25 nature of Fischer-Tropsch derived gasoil means that diesel fuel compositions containing it will have high cetane numbers compared to conventional diesel.

While Fischer-Tropsch derived gasoil is a preferred paraffinic gasoil for use herein, the term "paraffinic
30 gasoil" as used herein also includes those paraffinic gasoils derived from the hydrotreating of vegetable oils (HVO). The HVO process is based on an oil refining technology. In the process, hydrogen is used to remove

oxygen from the triglyceride vegetable oil molecules and to split the triglyceride into three separate chains thus creating paraffinic hydrocarbons.

When present, the paraffinic gasoil (i.e. the Fischer-Tropsch derived gasoil, the hydrogenated vegetable oil derived gasoil) will preferably consist of at least 95% w/w, more preferably at least 98% w/w, even more preferably at least 99.5% w/w, and most preferably up to 100% w/w of paraffinic components, preferably iso- and normal paraffins, preferably comprising 80% w/w or greater of iso-paraffins.

By "Fischer-Tropsch derived" is meant that a fuel or base oil is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The term "non-Fischer-Tropsch derived" may be interpreted accordingly. A Fischer-Tropsch derived fuel may also be referred to as a GTL (gas-to-liquid) fuel.

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

$$n(\text{CO} + 2\text{H}_2) = (-\text{CH}_2-)_n + n\text{H}_2\text{O} + \text{heat},$$

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

The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane. More recently techniques to derive carbon monoxide and hydrogen from other sources, including more sustainable ones are being explored and used. For example, starting with carbon dioxide and

water, the water can be electrolysed to give free hydrogen, typically using electricity from a sustainable source. This hydrogen can react with the carbon dioxide in the 'reverse water shift reaction' to give a source of carbon monoxide. This carbon monoxide can then be reacted with the remaining hydrogen in the typical Fischer-Tropsch synthesis process. Because of the use of electrolysis, some of these production processes are referred to as 'Power-to-liquids'

Gas oil, kerosene fuel and base oil products may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of Fischer-Tropsch synthesis products or from hydrotreated Fischer-Tropsch synthesis products. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, e. g. GB2077289 and EP0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP0583836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel or oil. Desired diesel fuel fraction(s) may subsequently be isolated for instance by distillation.

Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydrotreating, may be employed to modify the properties of Fischer-Tropsch

condensation products, as described for instance in US-A-4125566 and US-A-4478955.

5 Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP0583836.

10 An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al (vide supra). This process (also sometimes referred to as the Shell "Gas-to-Liquids" or "GTL" technology) produces diesel range products by conversion
15 of a natural gas (primarily methane) derived synthesis gas into a heavy long-chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as gasoils and kerosene. Versions of the SMDS process, utilising fixed-
20 bed reactors for the catalytic conversion step, are currently in use in Bintulu, Malaysia, and in Pearl GTL, Ras Laffan, Qatar. Kerosenes and (gas)oils prepared by the SMDS process are commercially available for instance from the Royal Dutch/Shell Group of Companies.

25 By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived gasoil has essentially no, or undetectable levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from
30 the synthesis gas feed. Further, the process as usually operated produces no or virtually no aromatic components.

For example, the aromatics content of a Fischer-Tropsch gasoil, as determined for instance by ASTM D4629,

will typically be below 1% w/w, preferably below 0.5% w/w and more preferably below 0.1% w/w.

Generally speaking, Fischer-Tropsch derived fuels have relatively low levels of polar components, in particular polar surfactants, for instance compared to petroleum derived fuels. It is believed that this can contribute to improved antifoaming and dehazing performance. Such polar components may include for example oxygenates, and sulphur and nitrogen containing compounds. A low level of sulphur in a Fischer-Tropsch derived fuel is generally indicative of low levels of both oxygenates and nitrogen-containing compounds, since all are removed by the same treatment processes.

A preferred Fischer-Tropsch derived gasoil fuel for use herein is a liquid hydrocarbon middle distillate fuel with a distillation range similar to that of a petroleum derived diesel, that is typically within the 160°C to 400°C range, preferably with a T95 of 360°C or less. Again, Fischer-Tropsch derived fuels tend to be low in undesirable fuel components such as sulphur, nitrogen and aromatics.

A preferred Fischer-Tropsch derived gasoil for use herein meets the EN15940 specification.

A preferred Fischer-Tropsch derived gasoil fuel will typically have a density (as measured by EN ISO 12185) of from 0.76 to 0.80, preferably from 0.77 to 0.79, more preferably from 0.775 to 0.785 g/cm³ at 15°C.

A preferred Fischer-Tropsch derived gasoil fuel for use herein has a cetane number (ASTM D613) of greater than 70, suitably from 70 to 85, most suitably from 70 to 77.

A preferred Fischer-Tropsch derived gasoil fuel for use herein has a kinematic viscosity at 40°C (as measured

according to ASTM D445) in the range from 2.0 mm²/s to 5.0 mm²/s, preferably from 2.5 mm²/s to 4.0 mm²/s.

5 A preferred Fischer-Tropsch derived gasoil for use herein has a sulphur content (ASTM D2622) of 5 ppmw (parts per million by weight) or less, preferably of 2 ppmw or less.

10 A preferred Fischer-Tropsch derived gasoil fuel for use in the present invention is that produced as a distinct finished product, that is suitable for sale and used in applications that require the particular characteristics of a gasoil fuel. In particular, it exhibits a distillation range falling within the range normally relating to Fischer-Tropsch derived gasoil fuels, as set out above.

15 A fuel composition used in the present invention may include a mixture of two or more paraffinic gasoils, such as two or more Fisher-Tropsch derived gasoil fuels.

20 When present, the Fischer-Tropsch derived components used herein (i.e. the Fischer-Tropsch derived gasoil) will preferably comprise no more than 3% w/w, more preferably no more than 2% w/w, even more preferably no more than 1% w/w of cycloparaffins (naphthenes), by weight of the Fischer-Tropsch derived component.

25 When present, the Fischer-Tropsch derived components used herein (i.e. the Fischer-Tropsch derived gasoil) preferably comprise no more than 1% w/w, more preferably no more than 0.5% w/w, of olefins, by weight of the Fischer-Tropsch derived component.

30 The fuel compositions described herein for use in the present invention are particularly suitable for use as a diesel fuel, in which case the fuel composition is a diesel fuel composition, and can be used for arctic applications, as winter grade diesel fuel due to the

excellent cold flow properties.

For example, a cloud point of -10°C or lower (EN 23015) or a cold filter plugging point (CFPP) of -20°C or lower (as measured by EN 116) may be possible with fuel compositions herein.

Generally speaking, in the context of the present invention the fuel composition may be additivated with fuel additives, in addition to the detergent additive already mentioned.

Unless otherwise stated, the (active matter) concentration of each such additive in a fuel composition is preferably up to 10000 ppmw, more preferably in the range from 1 to 1000 ppmw, advantageously from 1 to 400 ppmw, such as from 1 to 200 ppmw. Such additives may be added at various stages during the production of a fuel composition; those added to a base fuel at the refinery for example might be selected from anti-static agents, pipeline drag reducers, middle distillate flow improvers (MDFI) (e.g., ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers), lubricity enhancers, anti-oxidants and wax anti-settling agents.

Other components which may be incorporated as fuel additives, for instance in combination with said detergent additive, include lubricity enhancers; dehazers, e.g. alkoxyated phenol formaldehyde polymers; anti-foaming agents (e.g. commercially available polyether-modified polysiloxanes); ignition improvers (cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in US4208190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g. a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the

succinic acid derivative having on at least one of its
alpha-carbon atoms an unsubstituted or substituted
aliphatic hydrocarbon group containing from 20 to 500
carbon atoms, e.g. the pentaerythritol diester of
5 polyisobutylene-substituted succinic acid); corrosion
inhibitors; reodorants; anti-wear additives; anti-
oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol,
or phenylenediamines such as N,N'-di-sec-butyl-p-
phenylenediamine); metal deactivators; static dissipator
10 additives; and mixtures thereof.

In a preferred embodiment of the present invention
the other additive components in the detergent additive
package are selected from anti-corrosion additives, metal
passivators, antioxidants, metal deactivators, re-
15 odorants, and the like, and mixtures thereof.

The present invention may in particular be
applicable where the fuel composition is used or intended
to be used in a direct injection diesel engine, for
example of the rotary pump, in-line pump, unit pump,
20 electronic unit injector or common rail type, or in an
indirect injection diesel engine, or in an HCCI engine.
The fuel composition may be suitable for use in heavy-
and/or light-duty diesel engines, and in engines designed
for on-road use or off-road use.

25 In order to be suitable for at least the uses listed
above, it is preferred that the final fuel composition is
a diesel fuel composition, preferably which meets the
EN590 specification (October 2017).

In the case of a GTL base fuel being included in the
30 fuel composition herein, it is preferred that the final
fuel composition fuel meets the EN15940 specification
(2019).

The present invention may also be applicable where

the fuel composition is used or intended to be used in a stationary application such as a heating oil system, heating oil burner, and/or stationary power generators.

A suitable heating oil composition for use herein
5 has characteristics according to standard DIN 51603 (2020).

The invention is illustrated by the following non-limiting examples.

Examples

Example 1

Four fuel samples were used in Example 1 as set out in Table 1 below.

Table 1

Fuel No.	Fuel Type	Performance Additive Package 1 ² (ppm)
1	GTL Fuel ¹	0
2	GTL Fuel ¹	500
3	B7 (93% EN590 diesel base fuel, 7% FAME)	0
4	B7 (93% EN590 diesel base fuel, 7% FAME)	500

- 15 1. GTL fuel according to DIN EN15940 2019-10, class A, commercially available from Shell having the physicochemical characteristics set out in Table 2 below
2. Commercially available additive package containing a PIBSI detergent additive. None of the other components
20 in Performance Additive Package 1 have a biocidal effect.
- Table 2 (GTL Fuel used in Example 1)

<u>Test Parameter</u>	<u>Test Method</u>	<u>Units</u>	
Density at 15°C	ASTM D 4052	kg/m ³	778.8
Distillation	ASTM D86		
IBP	ASTM D86	°C	177.0
5% v/v	ASTM D86	°C	199.1
10% v/v	ASTM D86	°C	206.3
15% v/v	ASTM D86	°C	213.7
20% v/v	ASTM D86	°C	221.4

30% v/v	ASTM D86	°C	237.7
40% v/v	ASTM D86	°C	253.7
50% v/v	ASTM D86	°C	268.3
60% v/v	ASTM D86	°C	282.4
70% v/v	ASTM D86	°C	296.6
80% v/v	ASTM D86	°C	311.6
85% v/v	ASTM D86	°C	320.3
90% v/v	ASTM D86	°C	329.2
95% v/v	ASTM D86	°C	341.2
FBP	ASTM D86	°C	346.2
Recovery	ASTM D86	%vol	97.4
Residue	ASTM D86	%vol	1.4
Loss	ASTM D86	%vol	1.2
E250	ASTM D86	%vol	28.6
E300	ASTM D86	%vol	73.5
Water Content	DIN EN ISO 12937	mg/kg	42
Cloud Point	DIN EN 23015	°C	-20
CFPP	DIN EN 16329	°C	-29
K _v 20	ASTM D445	mm ² /s	3.8369

Test Procedure

Test Microorganisms

5 A defined inoculum with known hydrocarbon degrading capacity was used, ex. contaminated field diesel sample. 1ml was withdrawn from the contaminated field diesel sample and used to inoculate an aqueous medium/fuel mixture in the ratio 70:30ml. This was done for each of the fuels in Table 1 above and allowed to grow for 8 days to form cultures or microbial communities. Incubation was carried out in the dark at 25°C. 100µl from the aqueous phase of each microbial community was then used to inoculate the microcosms.

15 Microcosm Set Up

A stainless steel coupon (to promote biofilm growth) was inserted into a vial. 5ml of Bushnell Haas nutrient medium (aqueous phase) was decanted in and overlaid with 5ml of fuel. Microbial communities were then inoculated with either the GTL fuel or B7 cultures. Therefore, two inocula were derived from one field sample.

Testing Protocol

Microbial growth and diversity was assessed over 1 month by dry biomass weight to determine the amount of growth. This is simple technique designed to give a direct measurement of the total microbial burden at the end of the experiment. Growth visible at the interface was captured, solvent washed to remove fuel residues, dried in an oven, cooled and weighed. The results of Example 1 are shown in Figure 1. In Figure 1 the key to the fuel samples is as follows:

GA1 = GTL fuel (additivated) (Community 1)

GU1 = GTL fuel (unadditivated) (Community 1)

DA1 = B7 fuel (additivated) (Community 1)

DU1 = B7 fuel (unadditivated) (Community 1)

GA2 = GTL fuel (additivated) (Community 2)

GU2 = GTL fuel (unadditivated) (Community 2)

DA2 = B7 fuel (additivated) (Community 2)

DU2 = B7 fuel (unadditivated) (Community 2)

As can be seen from Figure 1 there was a reduction in biomass growth in the fuels containing Performance Additive Package 1 (containing a PIBSI detergent additive) compared with the comparative fuels not containing a performance additive package. This is particularly surprising for a nitrogen-containing detergent in view of nitrogen being a nutrient for microbes.

Example 2

The fuels used in Example 2 are set out in Table 5 below. Each fuel contained an EN590 base fuel or a GTL EN15940 base fuel, either with or without FAME, and either with or without a performance additive package/detergent additive as indicated. The physicochemical properties of the EN590 base fuel used in

this example are set out in Table 3 below. The physicochemical properties of the GTL fuel used in this example are set out in Table 4 below. The FAME in the B7 fuels (containing 7% biofuel) was derived from SME/RME.

5 The FAME used in the B30 fuels (containing 30% of biofuel, respectively) was derived from SME/RME and POME. The FAME used in the B50 fuels (containing 50% of biofuel) was derived from POME.

The additives used were as follows:

10 Performance Additive Package 2: containing detergent additives. None of the other components present in Performance Additive Package 2 have a biocidal effect. Performance Additive Package 2 is used in all fuel formulations apart from EN 590 B0.

15 Performance Additive Package 3: containing detergent additives. None of the other components present in Performance Additive Package 3 have a biocidal effect. Performance Additive Package 3 is used in GTL and EN590 B0 fuel formulations. Performance Additive Package 3 is

20 a special additive formulation tailored for heating fuel formulations typically containing no FAME. The fuel formulations tested herein also contain no FAME.

Detergent Additive 1: PIBSI detergent additive (used in EN 590 B7 fuel formulations).

25 Detergent Additive 2: quaternary ammonium based detergent additive (used in EN 590 B7 fuel formulations).

Table 3 (EN590 Base Fuel used in Example 2)

<u>Test Parameter</u>	<u>Test Method</u>	<u>Units</u>	
Density at 15°C	ASTM D 4052	kg/m ³	833.4
Flash Point	DIN EN ISO 2719	°C	68.5
CN	DIN EN ISO 5165		53.3
Distillation	ASTM D86		

IBP	ASTM D86	°C	177.1
5% v/v	ASTM D86	°C	202.6
10% v/v	ASTM D86	°C	215.0
15% v/v	ASTM D86	°C	223.2
20% v/v	ASTM D86	°C	229.8
30% v/v	ASTM D86	°C	241.9
40% v/v	ASTM D86	°C	253.5
50% v/v	ASTM D86	°C	263.2
60% v/v	ASTM D86	°C	273.7
70% v/v	ASTM D86	°C	285.2
80% v/v	ASTM D86	°C	299.2
85% v/v	ASTM D86	°C	307.9
90% v/v	ASTM D86	°C	319.4
95% v/v	ASTM D86	°C	337.4
FBP	ASTM D86	°C	351.4
Residue & Loss	ASTM D86	%vol	2.0
E250	ASTM D86	%vol	37.6
E300	ASTM D86	%vol	81.1
E350	ASTM D86	%vol	97.9
S	DIN EN ISO 20884	mg/kg	<5
Cloud Point	ASTM D 2500	°C	-11
CFPP	DIN EN 116	°C	-28
kV40	ASTM D445	mm ² /kg	2.6027
HFRR (WS Avg.)	DIN ISO 12156-1	µm	345
Aromatic type (IP391)	DIN EN 12916:2006		
Mono aromatics	DIN EN 12916:2006	%wt	20.1
Di aromatics	DIN EN 12916:2006	%wt	2.4
Tri+ aromatics	DIN EN 12916:2006	%wt	0.2
FAME content	DIN EN 14078	%vol	<0.1
NZ	DIN 51558 T1	mgKOH/g	0.00
Water Content	DIN EN ISO 12937	mg/kg	41
Rancimat - mod.	DIN EN 15751	H	25.1

Table 4 (GTL Fuel Used in Example 2)

<u>Test Parameter</u>	<u>Test Method</u>	<u>Units</u>	
HFRR (WS Avg.)	DIN ISO 12156-1	µm	630
Water Content	DIN EN ISO 12937	mg/kg	26
CN	DIN 51773		70.2
Density at 15°C	DIN EN ISO 12185	kg/m ³	776.2
Distillation	DIN EN ISO 3405		
IBP	DIN EN ISO 3405	°C	175.9
5% v/v	DIN EN ISO 3405	°C	195.0
10% v/v	DIN EN ISO 3405	°C	203.0
20% v/v	DIN EN ISO 3405	°C	220.5
30% v/v	DIN EN ISO 3405	°C	238.5
40% v/v	DIN EN ISO 3405	°C	255.1
50% v/v	DIN EN ISO 3405	°C	269.7
60% v/v	DIN EN ISO 3405	°C	283.6
70% v/v	DIN EN ISO 3405	°C	297.5
80% v/v	DIN EN ISO 3405	°C	312.1
90% v/v	DIN EN ISO 3405	°C	328.4
95% v/v	DIN EN ISO 3405	°C	338.9
FBP	DIN EN ISO 3405	°C	343.5
Residue & Loss	DIN EN ISO 3405	%vol	2.2
E250	DIN EN ISO 3405	%vol	37.5
E300	DIN EN ISO 3405	%vol	72.6
K _v 40	DIN EN ISO 3104	mm ² /s	2.520
FAME Content	DIN EN 14078	%vol	<0.1
Flash Point	DIN EN ISO 2719	°C	67.5

S	DIN EN ISO 20884	mg/kg	<5
Cloud Point	DIN EN 23015	°C	-18
CFPP	DIN EN 116	°C	-25
C m/m %	ASTM D 5291 mod	%m/m	84.90
H m/m %	ASTM D 5291 mod	%m/m	15.10
O m/m %	ASTM D 5291 mod	%m/m	<0.50

The testing protocol was the same as that in Example 1 with assessment of the observed microbial growth in all tested fuel types over a period of 3 months (2 time points of 4 weeks and 12 weeks) based on total biomass dry weight. Three replicate microcosms were set up for each time point. One microbial community was used as inoculum.

The results are shown in Table 5 below. Figure 2 is a graphical representation of the data shown in Table 5, and in particular shows the average dry biomass weight (g) after 4 weeks and after 12 weeks of all fuels tested in Example 2, with and without additive.

Figure 3 is a graphical representation of the data shown in Table 5, and in particular shows the average dry biomass weight (g) for all fuel formulations tested with and without Performance Additive Package 2, Performance Additive Package 3, Detergent Additive 1 and Detergent Additive 2. Hence, in Figure 3, the block entitled 'Perf Additive package 2' represents the average dry biomass weight (g) for all formulations shown in Table 5 containing Performance Additive Package 2, the block entitled 'Perf Additive package 3' represents the average dry biomass weight (g) for all formulations shown in Table 5 containing Performance Additive Package 3, the block entitled 'none' represents the average dry biomass weight (g) for all formulations shown in Table 5

containing no performance additive package and no
detergent additive, the block entitled 'Det Additive 1'
represents the average dry biomass weight (g) for all
formulations shown in Table 5 containing Detergent
5 Additive 1, and the block entitled 'Det Additive 2'
represents the average dry biomass weight (g) for all
formulations shown in Table 5 containing Detergent
Additive 2.

Table 5

Additive	Fuel Type (A = additive)	Week	FAME	Additive Type	FAME Origin	Biomass (g)
No	GTL	week 4	B0	None	None	0.0397
No	GTL	week 4	B0	None	None	0.0466
No	GTL	week 4	B0	None	None	0.0961
Yes	GTL+A	week 4	B0	Performance Additive Package 2	None	0.0811
Yes	GTL+A	week 4	B0	Performance Additive Package 2	None	0.0588
Yes	GTL+A	Week 4	B0	Performance Additive Package 2	None	0.0353
Yes	GTL+A	week 4	B0	Performance Additive Package 3	None	0.0357
Yes	GTL+A	week 4	B0	Performance Additive Package 3	None	0.0381
Yes	GTL+A	week 4	B0	Performance Additive Package 3	None	0.042
No	GTL	week 4	B7	None	SME/RME	0.0686
No	GTL	week 4	B7	None	SME/RME	0.0475
No	GTL	week 4	B7	None	SME/RME	0.0751
Yes	GTL+A	week 4	B7	Performance Additive Package 2	SME/RME	0.0595
Yes	GTL+A	week 4	B7	Performance Additive Package 2	SME/RME	0.0475
Yes	GTL+A	week 4	B7	Performance Additive Package 2	SME/RME	0.0489
No	GTL	week 4	B30	None	SME/RME	0.1513
No	GTL	week 4	B30	None	SME/RME	0.1217
No	GTL	week 4	B30	None	SME/RME	0.1425
Yes	GTL+A	week 4	B30	Performance Additive Package 2	SME/RME	0.1053
Yes	GTL+A	week 4	B30	Performance Additive Package 2	SME/RME	0.0878
Yes	GTL+A	week 4	B30	Performance Additive Package 2	SME/RME	0.1102
No	EN590	week 4	B0	None	None	0.085
No	EN590	week 4	B0	None	None	-0.0284
No	EN590	week 4	B0	None	None	0.1764
Yes	EN590+A	week 4	B0	Performance Additive Package 3	None	0.1687

Yes	EN590+A	week 4	B0	Performance Additive Package 3	None	0.0777
Yes	EN590+A	week 4	B0	Performance Additive Package 3	None	0.14
No	EN590	week 4	B7	None	SME/RME	0.0811
No	EN590	week 4	B7	None	SME/RME	0.0572
No	EN590	week 4	B7	None	SME/RME	0.0696
Yes	EN590+A	week 4	B7	Detergent Additive 1	SME/RME	0.0632
Yes	EN590+A	week 4	B7	Detergent Additive 1	SME/RME	0.0348
Yes	EN590+A	week 4	B7	Detergent Additive 1	SME/RME	0.0539
Yes	EN590+A	week 4	B7	Detergent Additive 2	SME/RME	0.0524
Yes	EN590+A	week 4	B7	Detergent Additive 2	SME/RME	0.0428
Yes	EN590+A	week 4	B7	Detergent Additive 2	SME/RME	0.0351
Yes	EN590+A	week 4	B7	Performance Additive Package 2	SME/RME	0.0313
Yes	EN590+A	week 4	B7	Performance Additive Package 2	SME/RME	0.0318
Yes	EN590+A	week 4	B7	Performance Additive Package 2	SME/RME	0.0444
No	EN590	week 4	B30	None	POME	0.1348
No	EN590	week 4	B30	None	POME	0.096
No	EN590	week 4	B30	None	POME	0.0557
Yes	EN590+A	week 4	B30	Performance Additive Package 2	POME	0.0761
Yes	EN590+A	week 4	B30	Performance Additive Package 2	POME	0.1083
Yes	EN590+A	week 4	B30	Performance Additive Package 2	POME	0.0647
No	EN590	week 4	B50	None	POME	0.0828
No	EN590	week 4	B50	None	POME	0.2233
No	EN590	week 4	B50	None	POME	0.2121
Yes	EN590+A	week 4	B50	Performance Additive Package 2	POME	0.1178
Yes	EN590+A	week 4	B50	Performance Additive Package 2	POME	0.0916
Yes	EN590+A	week 4	B50	Performance Additive Package 2	POME	0.0796
No	GTL	week 12	B0	None	None	0.1224
No	GTL	week 12	B0	None	None	0.0954
No	GTL	week 12	B0	None	None	0.0756

Yes	GTL+A	week 12	B0	Performance Additive Package 2	None	0.1984
Yes	GTL+A	week 12	B0	Performance Additive Package 2	None	0.2239
Yes	GTL+A	week 12	B0	Performance Additive Package 2	None	0.0625
Yes	GTL+A	week 12	B0	Performance Additive Package 3	None	0.1107
Yes	GTL+A	week 12	B0	Performance Additive Package 3	None	0.0371
Yes	GTL+A	week 12	B0	Performance Additive Package 3	None	0.0559
No	GTL	week 12	B7	None	SME/RME	0.0571
No	GTL	week 12	B7	None	SME/RME	0.0631
No	GTL	week 12	B7	None	SME/RME	0.1005
Yes	GTL+A	week 12	B7	Performance Additive Package 2	SME/RME	0.0508
Yes	GTL+A	week 12	B7	Performance Additive Package 2	SME/RME	0.0489
Yes	GTL+A	week 12	B7	Performance Additive Package 2	SME/RME	0.0455
No	GTL	week 12	B30	None	SME/RME	0.1336
No	GTL	week 12	B30	None	SME/RME	0.1367
No	GTL	week 12	B30	None	SME/RME	0.1075
Yes	GTL+A	week 12	B30	Performance Additive Package 2	SME/RME	0.1529
Yes	GTL+A	week 12	B30	Performance Additive Package 2	SME/RME	0.4002
Yes	GTL+A	week 12	B30	Performance Additive Package 2	SME/RME	0.0633
No	EN590	week 12	B0	None	None	0.1201
No	EN590	week 12	B0	None	None	0.0756
No	EN590	week 12	B0	None	None	0.0631
Yes	EN590+A	week 12	B0	Performance Additive Package 3	None	0.052
Yes	EN590+A	week 12	B0	Performance Additive Package 3	None	0.1099
Yes	EN590+A	week 12	B0	Performance Additive Package 3	None	0.0865
No	EN590	week 12	B7	None	SME/RME	0.0389
No	EN590	week 12	B7	None	SME/RME	0.0407
No	EN590	week 12	B7	None	SME/RME	0.0367
Yes	EN590+A	week 12	B7	Detergent Additive 1	SME/RME	0.0447
Yes	EN590+A	week 12	B7	Detergent Additive 1	SME/RME	0.0429

Yes	EN590+A	week 12	B7	Detergent Additive 1	SME/RME	0.0345
Yes	EN590+A	week 12	B7	Detergent Additive 2	SME/RME	0.0475
Yes	EN590+A	week 12	B7	Detergent Additive 2	SME/RME	0.0483
Yes	EN590+A	week 12	B7	Detergent Additive 2	SME/RME	0.0563
Yes	EN590+A	week 12	B7	Performance Additive Package 2	SME/RME	0.3515
Yes	EN590+A	week 12	B7	Performance Additive Package 2	SME/RME	0.0513
Yes	EN590+A	week 12	B7	Performance Additive Package 2	SME/RME	0.06
No	EN590	week 12	B30	None	POME	0.5307
No	EN590	week 12	B30	None	POME	0.2122
No	EN590	week 12	B30	None	POME	0.163
Yes	EN590+A	week 12	B30	Performance Additive Package 2	POME	0.1895
Yes	EN590+A	week 12	B30	Performance Additive Package 2	POME	0.2436
Yes	EN590+A	week 12	B30	Performance Additive Package 2	POME	0.4804
No	EN590	week 12	B50	None	POME	0.394
No	EN590	week 12	B50	None	POME	0.4321
No	EN590	week 12	B50	None	POME	0.2501
Yes	EN590+A	week 12	B50	Performance Additive Package 2	POME	0.4049
Yes	EN590+A	week 12	B50	Performance Additive Package 2	POME	0.2606
Yes	EN590+A	week 12	B50	Performance Additive Package 2	POME	0.2285

C L A I M S

1. Use of a detergent additive in a fuel composition for reducing microbial growth.
2. Use according to Claim 1 wherein the detergent
5 additive is selected from polyolefin substituted succinimides or succinimides of polyamines, aliphatic amines, Mannich bases or amines, polyolefin maleic anhydrides, and quaternary ammonium salts, and mixtures thereof.
- 10 3. Use according to Claim 1 or 2 wherein the detergent additive is a polyolefin substituted succinimide, preferably a polyisobutylene succinimide.
4. Use according to Claim 1 or 2 wherein the detergent additive is a quaternary ammonium salt.
- 15 5. Use according to any of Claims 1 to 4 wherein the detergent additive is present in the fuel composition at a level of from 5 ppmw to 10000 ppmw.
6. Use according to any of Claims 1 to 5 wherein the detergent additive is a nitrogen-containing detergent.
- 20 7. Use according to any of Claims 1 to 6 wherein the detergent additive is a component of a performance additive package.
8. Use according to any of Claims 1 to 7 wherein the fuel composition is selected from a diesel fuel
25 composition, a heating oil composition, an aviation fuel composition, and a marine fuel composition.
9. Use according to any of Claims 1 to 8 wherein the fuel composition is a diesel fuel composition.
10. Use according to Claim 9 wherein the diesel fuel
30 composition comprises a petroleum derived diesel base fuel.

11. Use according to Claim 9 or 10 wherein the diesel fuel composition comprises a paraffinic base fuel selected from hydrotreated vegetable oil, Fischer-Tropsch derived base fuels, and mixtures thereof.
- 5 12. Use according to any of Claims 9 to 11 wherein the diesel fuel composition comprises a biodiesel component, preferably a fatty acid alkyl ester.
- 10 13. Method for reducing microbial growth in a fuel composition, which method comprises a step of introducing a detergent additive into said fuel composition.