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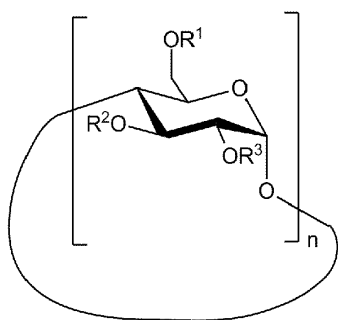
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(54) **New uses**

(57) Use, as a detergent additive in a fuel formulation, or in an additive composition for use in a fuel formulation, of a modified cyclodextrin of formula (I):



(I)

wherein n is an integer from 6 to 20, and R¹, R² and R³ are each independently selected from hydrogen, optionally substituted alkyl, optionally substituted aryl and carbonyl, provided that R¹, R² and R³ are not all hydrogen. The fuel formulation may be a gasoline or diesel formulation, in particular gasoline. The modified cyclodextrin (I) may be an alkylated cyclodextrin. It may be used in combination with an additional fuel additive, which may be present as a guest molecule within a cyclodextrin inclusion complex. The cyclodextrin (I) may also be used to reduce the concentration of a detergent additive present in the fuel formulation or additive composition.

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Description

Field of the Invention

[0001] This invention relates to the use of certain compounds in fuel formulations, and in fuel additive compositions, for new purposes.

Background to the Invention

[0002] It is known to include detergent additives in fuel formulations, in order to reduce deposits formed in systems in which the formulations are used. For example, detergent additives are often included in gasoline and diesel fuel formulations to reduce combustion-related deposits in engines running on the fuels, in particular in the injector nozzles. Fouling of engine injection systems with such combustion-related deposits can compromise engine performance, in particular efficiency, power and emissions quality.

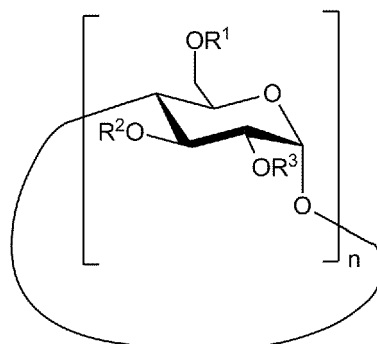
[0003] Detergent additives, also known as dispersants, are often surfactants. They act to remove, and/or to prevent the accumulation of, deposits such as combustion-related deposits which result from use of the fuel to which they are added.

[0004] It can be desirable to improve the performance of such detergent additives, and/or to provide alternative detergent additives with comparable or ideally superior performance, so as in turn to improve the performance of fuel formulations to which they are added and to provide "cleaner" fuel formulations.

[0005] It is also often desirable to reduce the concentrations of detergent additives in fuel formulations. This may be driven by consumer preferences and/or by technical or economic considerations. In cases it may be driven by a desire to reduce side effects associated with a particular additive, or with an interaction between two or more additives which are present in a formulation. Reductions in additive concentrations can be achieved through improvements in additive performance, and/or through the provision of better-performing alternatives.

Statements of the Invention

[0006] According to a first aspect of the present invention there is provided the use, as a detergent additive in a fuel formulation, of a modified cyclodextrin of formula (I) :



(I)

wherein n is an integer from 6 to 20, and R^1 , R^2 and R^3 are each independently selected from hydrogen, optionally substituted alkyl, optionally substituted aryl and carbonyl, provided that R^1 , R^2 and R^3 are not all hydrogen.

[0007] It has been found that modified cyclodextrins of formula (I) can be active as detergents, ie they can reduce deposits generated by fuel formulations in which they are used.

[0008] Modified cyclodextrins of formula (I) may also be suitable as vehicles for fuel additives, including detergent additives. The cyclodextrin molecule naturally forms a cavity which is able to accommodate an additive molecule of an appropriate size and polarity. The capture and release of the additive "guest" molecule by the cyclodextrin "host" molecule is reversible, as it does not involve the formation of covalent or ionic bonds, relying instead on hydrogen bonding, van der Waals interactions and/or electrostatic interactions. Encapsulation of the additive in this way appears not to impair its effect on a fuel formulation to which it is added. The encapsulation can however protect the additive, to a degree, from external influences such as heat, light, oxygen and other species with which the additive might otherwise interact.

It can thus help to improve the stability of the additive and/or to reduce the risk of unfavourable interactions with other species present in the formulation. It can also reduce the volatility of the encapsulated additive, again contributing to its stability during storage and use.

[0009] The inner cavity of the cyclodextrin has solubility characteristics similar to those of ethanol, making it attractive to a wide range of both hydrophilic and hydrophobic "guest" molecules. The solubility of the cyclodextrin in its own environment, however, is dependent on the number and type of substituents it carries at the R¹, R² and R³ positions. Because of this, the encapsulation of an additive inside a cyclodextrin host molecule can effectively modify the solubility of the additive, since the solubility of the complex as a whole will be determined by that of the cyclodextrin molecule rather than the guest.

[0010] Thus, a modified cyclodextrin (I) may, according to the invention, be used both as a detergent additive in its own right, and also in combination with and/or as a vehicle for a second fuel additive - for example a second detergent additive - within a fuel formulation. When used in this way, the modified cyclodextrin may impart additional benefits, such as are described below, yet can do so without, or without undue, detriment to the performance of the second fuel additive or to the cleanliness of the resultant fuel formulation.

[0011] For use in the present invention, the cyclodextrin of formula (I) is substituted in order to increase its solubility in organic (in particular hydrocarbon-based) formulations. The modified cyclodextrin (I) is thus suitably soluble in a fuel formulation in which it is adapted and/or intended to be used. Such a formulation will typically be of low polarity, although the inclusion of higher polarity components such as fatty acid methyl esters or alcohols may increase the polarity of the formulation relative to its base hydrocarbons. The natures of the groups R¹, R² and R³ should be such as to impart the desired solubility characteristics to the cyclodextrin molecule, allowing it to be tailored for use in a chosen fuel formulation.

[0012] It is believed, although we do not wish to be bound by this theory, that the greater the solubility of the modified cyclodextrin (I), in the fuel formulation, the greater its detergent effect. This may be because hydrocarbon deposits such as olefins, and larger molecules derived therefrom, can be surrounded by the cyclodextrin molecules to form micelle-like structures which present outwardly-facing hydrocarbon-soluble groups and thus help to maintain the deposits in solution in the formulation. The insides of the cyclodextrin molecules present more polar faces with a higher proportion of unsubstituted -OH groups, which are likely to be more attractive to deposit-forming molecules such as olefins and aromatic compounds: in this way, the cyclodextrin may act in a surfactant-like manner to solubilise the deposit-forming materials within the fuel formulation.

[0013] In an embodiment of the invention, in particular where the modified cyclodextrin (I) is for use in a gasoline or diesel fuel formulation, the modified cyclodextrin of formula (I) is an alkylated cyclodextrin. By "alkylated cyclodextrin" is meant a cyclodextrin of formula (I) in which at least one of the groups R¹, R² and R³ is an optionally substituted (but in particular unsubstituted) alkyl group. In an embodiment, two or at least two of the groups R¹, R² and R³ are independently selected from optionally substituted (in particular unsubstituted) alkyl groups. In an embodiment, all three of the groups R¹, R² and R³ are independently selected from optionally substituted (in particular unsubstituted) alkyl groups.

[0014] Where an alkylated cyclodextrin is substituted with two or more alkyl groups, the two or more alkyl groups may be the same.

[0015] In an alkylated cyclodextrin, suitably any of the groups R¹, R² and R³ that are not alkyl groups are hydrogen. Thus, the groups R¹, R² and R³ may be independently selected from hydrogen and optionally substituted (in particular unsubstituted) alkyl. In an embodiment, R¹ is selected from optionally substituted (in particular unsubstituted) alkyl and R² and R³ are both hydrogen. In an embodiment, R¹ and R³ are independently selected from optionally substituted (in particular unsubstituted) alkyl and R² is hydrogen.

[0016] In general, in an alkylated cyclodextrin, the overall degree of substitution at the three positions R¹, R² and R³ may for instance be 33% or greater, or 50% or greater, or 66% or greater. The degree of substitution at an individual position R¹, R² or R³ may be from 0 to 100%, for example 10% or greater, or 25% or greater, or 50% or greater, or 75% or greater. In embodiments, the alkyl substituents may be randomly distributed between the positions R¹, R² and R³.

[0017] In an alkylated cyclodextrin of formula (I), the integer n may in particular be from 6 to 8, more particularly 7.

[0018] In the context of the present invention, an "alkyl" group may be a straight or branched-chain alkyl group. It may contain up to 22 carbon atoms, or up to 20 or 18 or 16 or 14 or 12 carbon atoms, or in cases up to 6 or 5 or 4 or 3 carbon atoms. It may contain 1 carbon atom or more, or 2 or 3 carbon atoms or more, for example from 1 to 12 or from 1 to 10 or from 1 to 8 carbon atoms, or from 1 to 6 or from 1 to 4 or from 1 to 3 carbon atoms, or in cases from 2 to 8 or from 3 to 8 or from 4 to 8 carbon atoms. An alkyl group may for instance be selected from methyl, ethyl, propyl and butyl groups. It may be selected from methyl and butyl groups. A butyl group substituent may be an n-butyl group, or it may be a mixture of n-butyl and isobutyl groups.

[0019] In particular when the modified cyclodextrin (I) is an alkylated cyclodextrin, the alkyl group(s) may be selected from C1 to C12 alkyl groups, or from C2 to C12 or C3 to C12 alkyl groups. They may be selected from C1 to C10 alkyl groups, or from C2 to C10 or C3 to C10 or C4 to C10 alkyl groups. They may be selected from C1 to C8 alkyl groups, or from C2 to C8 alkyl groups, or from C3 to C8 or C4 to C8 alkyl groups. They may be selected from C1 to C6 alkyl groups, or from C2 to C6 alkyl groups, or from C3 to C6 or C4 to C6 alkyl groups. They may be selected from C1 to C5

alkyl groups, or from C2 to C5 alkyl groups, or from C3 to C5 alkyl groups. They may be selected from C1 to C4 alkyl groups, or from C2 to C4 alkyl groups, or from C3 to C4 alkyl groups.

[0020] In a specific embodiment, R¹, R² and R³ are the same and are selected from C1 to C4 alkyl groups, for example methyl.

[0021] In another specific embodiment, at least two of R¹, R² and R³ (for example two of, such as R¹ and R³) are selected from C1 to C12 or C1 to C10 or C1 to C8 alkyl groups, or from C2 to C10 or C2 to C8 or C2 to C6 alkyl groups, or from C2 to C10 or C2 to C8 or C2 to C6 alkyl groups. In particular, at least two of R¹, R² and R³ (for example two of, such as R¹ and R³) may be butyl, and the remaining group, if appropriate, may then be hydrogen. Thus, for example, the modified cyclodextrin (I) may be a heptakis(2,6-di-O-n-butyl)-cyclodextrin.

[0022] In a modified cyclodextrin of formula (I), an alkyl group may be substituted with one or more, typically one, hydroxyl groups, which may be primary, secondary or tertiary hydroxyl groups, in particular secondary. A hydroxyl-substituted alkyl group (a "hydroxyalkyl" group) may in particular be hydroxypropyl (for example 2-hydroxypropyl) or hydroxyethyl, more particularly hydroxypropyl. In an embodiment, at least one of the groups R¹, R² and R³ is a hydroxyalkyl group. In an embodiment, R¹ is a hydroxyalkyl group, in particular 2-hydroxypropyl, and in this case R² and R³ are suitably hydrogen.

[0023] An alkyl group may be substituted with one or more, typically one, amine groups -NR⁴R⁵, where R⁴ and R⁵ are each independently selected from hydrogen and optionally substituted (suitably unsubstituted) alkyl groups, in particular from hydrogen and C1 to C4 or C1 to C3 or C1 to C2 alkyl groups. An amine group -NR⁴R⁵ may in particular be -NH₂.

[0024] An "aryl" group is a group which contains an aromatic hydrocarbon ring, for example phenyl, benzyl, tolyl, xylyl, naphthyl or anthracyl. It may for example be a C5 to C18 aryl group, or a C6 to C18 aryl group, or a C6 to C14 or C6 to C10 or C6 to C8 aryl group. It may in particular be phenyl or benzyl, more particularly benzyl.

[0025] A "carbonyl" group is a group of the formula R⁶-C(O)-, where R⁶ is an optionally substituted (suitably unsubstituted) alkyl or aryl group, for example an alkyl, phenyl or benzyl group, where an alkyl group may in particular be a C1 to C4 or C1 to C3 or C1 to C2 alkyl group. A carbonyl group may in particular be acetyl or benzoyl, more particularly acetyl.

[0026] An "optionally substituted" group may be substituted with one or more, for example one or two, in particular one, substituents, which substituents may for example be selected from alkyl, more particularly C1 to C4 alkyl or C1 to C3 alkyl or C1 to C2 alkyl, for example methyl; aryl, for example phenyl; carboxylic acids and carboxylate ions, for example -CH₂CO₂H, -CO₂H or the corresponding anions; alkoxy, for example ethoxy or methoxy, in particular methoxy; amine (for example -NR⁴R⁵) and amide groups, in particular primary amine and amide groups; and -OH. In particular, such substituents may be selected from alkyl, aryl, alkoxy and -OH. Yet more particularly, they may be selected from alkyl groups, for example C1 to C4 or C1 to C3 or C1 to C2 alkyl groups, such as methyl.

[0027] An "optionally substituted" group may in particular be unsubstituted.

[0028] In an embodiment of the invention, the groups R¹, R² and R³ are independently selected from hydrogen, unsubstituted alkyl (in particular unsubstituted C1 to C12 alkyl, more particularly C1 to C8 or C1 to C4 alkyl) and hydroxyalkyl (in particular C1 to C4 hydroxyalkyl, more particularly hydroxypropyl). In an embodiment, R¹ is selected from optionally substituted alkyl (in particular unsubstituted alkyl and hydroxyalkyl) and carbonyl, and R² and R³ are both hydrogen. In an embodiment, R¹ is selected from optionally substituted alkyl (in particular unsubstituted alkyl and hydroxyalkyl), and R² and R³ are both hydrogen.

[0029] In general, the carbon chain length of the groups R¹, R² and R³ may be chosen to enhance solubility of the cyclodextrin (I) in a chosen fuel formulation, longer chain groups typically leading to a greater hydrophobicity and hence a greater affinity for lower polarity, more hydrophobic organic systems. For use in more polar formulations such as high oxygenate content gasoline or diesel fuel formulations, it may be preferred for the groups R¹, R² and R³ to be selected from shorter chain alkyl groups, in particular methyl, and/or from alkyl groups which are substituted with polar functional groups such as hydroxyl. Longer chain alkyl groups, for example butyl, may be used to render the cyclodextrin more hydrophobic. The substituents R¹, R² and R³ may also be chosen to facilitate the formation of deposit-solubilising macrostructures such as micelles within a fuel formulation in which it is used.

[0030] For use in a low polarity fuel formulation, it may be preferred for at least one, suitably two or three, of the groups R¹, R² and R³ to be a longer chain (for example C4 or greater, or C4 to C12 or C4 to C10 or C4 to C8) alkyl group, which is suitably unsubstituted. In cases such a longer chain alkyl group may be a C12 to C22 or C12 to C18 alkyl group.

[0031] In an embodiment, in particular where the modified cyclodextrin (I) is for use in a non-polar gasoline or diesel fuel formulation, the groups R¹, R² and R³ may be independently selected from hydrogen and unsubstituted alkyl (in particular C1 to C8 or C2 to C8 or C4 to C8 alkyl, for example butyl). Yet more particularly, at least two of R¹, R² and R³ (for example R¹ and R³) may be independently selected from unsubstituted alkyl (for example C1 to C8 or C2 to C8 or C4 to C8 alkyl, in particular butyl): the two or more alkyl groups may be the same.

[0032] In an embodiment, in particular where the modified cyclodextrin (I) is for use in a moderately polar fuel formulation, for example a formulation containing up to about 10% v/v of an oxygenate such as an alcohol or a fatty acid methyl ester (FAME), one or two of the groups R¹, R² and R³ (for example R¹ and R³) may be independently selected from

unsubstituted alkyl (in particular C1 to C8 or C1 to C4 alkyl, for example methyl or butyl) and the remaining group(s) may be hydrogen. Thus, for example, the modified cyclodextrin (I) may be a tri-methyl cyclodextrin or a di-O-n-butyl cyclodextrin, for example a heptakis(2,6-di-O-n-butyl)-cyclodextrin.

[0033] In an embodiment, in particular where the modified cyclodextrin (I) is for use in a more polar fuel formulation, for example a formulation containing greater than about 5 or 10% v/v of an oxygenate such as an alcohol or a FAME (or in cases 20 or 30 or 40 or 50% v/v or more of such an oxygenate), at least one of the groups R¹, R² and R³ may be an alkyl group (in particular a C1 to C4 alkyl group) substituted with a polar group such as hydroxyl: in this case, suitably at least R¹ is a hydroxyalkyl group.

[0034] In an embodiment, the modified cyclodextrin (I) is an alkylated cyclodextrin in which the alkyl group(s) are selected from unsubstituted C1 to C12 or C1 to C8 or C2 to C8 or C2 to C4 alkyl groups. For example, two of the groups R¹, R² and R³ may be independently selected from unsubstituted C2 to C8 or C2 to C4 alkyl groups.

[0035] A particularly preferred alkylated cyclodextrin is substituted with two butyl groups (for example n-butyl groups, or a mixture of n-butyl and isobutyl groups) on each monomer residue: such a cyclodextrin is suitably a β -cyclodextrin, for example heptakis(2,6-di-O-n-butyl)- β -cyclodextrin. These cyclodextrins have been found to have good solubility in a range of gasoline and diesel fuels, and are expected to exhibit a good balance (HLB balance) of hydrophilic and hydrophobic characteristics.

[0036] In the modified cyclodextrin (I), the integer n may in particular be from 4 to 10, or from 5 to 9, or more particularly from 6 to 8. When n=6 the cyclodextrin is an α -cyclodextrin, which forms a frustoconical structure having an external diameter of 1.4 nm and an internal cavity diameter of 0.6 nm. When n=7 it is a β -cyclodextrin, which forms a frustoconical structure having an external diameter of 1.5 nm and an internal diameter of 0.8 nm. When n=8 it is a γ -cyclodextrin, in which the frustocone has an external diameter of 1.7 nm and an internal diameter of 1.0 nm. Thus, the value of n affects the size of the cyclodextrin cavity. This can be important when - as described below - the cyclodextrin encapsulates a guest molecule such as an additional fuel additive. The value of n may therefore be chosen to yield a cavity of a size suitable to accommodate one or more molecules of (suitably one molecule of) a chosen guest molecule.

[0037] In an embodiment of the invention, the modified cyclodextrin (I) is a β -cyclodextrin (ie n=7).

[0038] In the context of the present invention, a fuel formulation may be any formulation, typically in liquid form, which is suitable for use as a combustible fuel. It may in particular be hydrocarbon-based, ie comprising a major proportion (for example 80% v/v or more, or 85 or 90 or 95% v/v or more) of hydrocarbon fuel components such as alkanes, cycloalkanes, alkenes and aromatic hydrocarbons. The hydrocarbon fuel components may be mineral-derived, or derived from a biological source, or synthetic. Such a formulation may contain one or more components in addition to its hydrocarbon fuel components, for example selected from oxygenates, biofuel components and fuel additives.

[0039] A fuel formulation may be suitable and/or adapted for use in any fuel-consuming system, for example an engine (more particularly an internal combustion engine), a heating appliance or a cooking appliance. It may be selected from automotive fuel formulations (for example automotive gasoline and diesel fuel formulations), aviation fuel formulations (for example aviation gasoline and jet fuel formulations), kerosene fuel formulations, marine fuel formulations (for example marine diesel formulations), industrial gas oil formulations, and heating oil formulations. In an embodiment, it is selected from automotive fuel formulations (for example automotive gasoline and diesel fuel formulations), aviation fuel formulations (for example aviation gasoline and jet fuel formulations), kerosene fuel formulations, and marine fuel formulations (for example marine diesel formulations).

[0040] In an embodiment, the fuel formulation is an automotive fuel formulation. It may be a gasoline fuel formulation, which is suitable and/or adapted for use in a spark ignition (petrol) internal combustion engine. It may be a diesel fuel formulation, which is suitable and/or adapted for use in a compression ignition (diesel) internal combustion engine.

[0041] In an embodiment, the formulation is either a gasoline fuel formulation (which may optionally contain an oxygenate such as an alcohol, in particular ethanol) or a diesel fuel formulation (which may optionally contain an oxygenate or biodiesel component such as a FAME or a hydrogenated vegetable oil, in particular a FAME). The concentrations of oxygenate or biodiesel components, where present, may be as described below.

[0042] In an embodiment of the invention, the modified cyclodextrin (I) is used as a detergent additive in a gasoline fuel formulation, in particular an automotive gasoline fuel formulation. Apart from the modified cyclodextrin (I), such a formulation may be conventional in terms of its constituents and their relative concentrations. It may for example comprise a gasoline base fuel. A gasoline base fuel is a liquid hydrocarbon distillate fuel component, or mixture of such components, containing hydrocarbons which boil in the range from 0 to 250°C (ASTM D86 or EN ISO 3405) or from 20 or 25 to 200 or 230°C. The optimal boiling ranges and distillation curves for such base fuels will typically vary according to the conditions of their intended use, for example the climate, the season and any applicable local regulatory standards or consumer preferences.

[0043] The hydrocarbon fuel component(s) in the gasoline base fuel may be obtained from any suitable source. They may for example be derived from petroleum, coal tar, natural gas or wood, in particular petroleum. Alternatively they may be synthetic products, for instance from a Fischer-Tropsch condensation process. Conveniently they may be derived in any known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or

catalytically cracked hydrocarbons, hydrocracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these. Typically, gasoline base fuels comprise components selected from one or more of the following groups: saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons and oxygenated hydrocarbons.

[0044] A gasoline base fuel will typically have a research octane number (RON) (ASTM D2699 or EN ISO 5164) of 80 or greater, or of 85 or 90 or 93 or 94 or 95 or 98 or greater, for example from 80 to 110 or from 85 to 115 or from 90 to 105 or from 93 to 102 or from 94 to 100. It will typically have a motor octane number (MON) (ASTM D2700 or EN ISO 5163) of 70 or greater, or of 75 or 80 or 84 or 85 or greater, for example from 70 to 110 or from 75 to 105 or from 84 to 95.

[0045] A gasoline base fuel will typically have an E70 value of 10% v/v or greater, or of 14 or 15 or 20% v/v or greater. Its E70 value might typically be up to 55% v/v, or up to 50% v/v. It will typically have an E100 value of 35% v/v or greater, or of 40 or 45% v/v or greater. Its E100 value might typically be up to 75% v/v, or up to 72 or 70% v/v. The E70 value for a fuel is the volume percentage of the fuel which has been distilled at 70°C, whilst the E100 value is the volume percentage of the fuel which has been distilled at 100°C. Both E70 and E100 values can be measured using the standard test method EN ISO 3405.

[0046] A gasoline base fuel might typically have a density from 0.720 to 0.775 kg/m³ at 15°C (ASTM D4052 or EN ISO 3675).

[0047] A gasoline base fuel may be or include one or more biofuel components, which are derived from biological sources. It may be or include one or more oxygenates such as alcohols, ethers, esters, carboxylic acids and their derivatives, aldehydes, ketones, and mixtures thereof, in particular from alcohols, ethers (for example dialkyl ethers such as alkyl t-butyl ethers), and mixtures thereof. Such oxygenates are suitably derived from biological sources.

[0048] The concentration of the base fuel, if present in a gasoline fuel formulation prepared or used according to the invention, may be 50% v/v or greater. It may for example be 60 or 70 or 80% v/v or greater, or 85 or 90 or 95 or 98% v/v or greater. The base fuel concentration may be up to 99.99% v/v, or up to 99.95% v/v, or up to 99.9 or 99.5% v/v. It may be up to 99% v/v, for example up to 98 or 95 or 90% v/v, or in cases up to 85 or 80% v/v.

[0049] A gasoline fuel formulation prepared or used according to the invention may comprise an alcohol. Suitable alcohols include C1 to C5 saturated or unsaturated alcohols, in particular C1 to C4 aliphatic alcohols such as methanol, ethanol, isopropanol, n-butanol and isobutanol, and certain bio-derived alcohols. The alcohol may be a C1 to C3 aliphatic alcohol, for example selected from methanol, ethanol and mixtures thereof. It may be selected from ethanol, isobutanol, n-butanol and mixtures thereof. In an embodiment, it is ethanol.

[0050] Where the gasoline fuel formulation comprises an alcohol, its concentration may be 0.5% v/v or greater based on the overall formulation. This concentration may be 1 or 2.5 or 5% v/v or greater, or 7.5 or 10% v/v or greater, or in cases 15 or 20 or 25% v/v or greater. It may be up to 30% v/v, or up to 25 or 20% v/v, or up to 15 or 12.5 or 10% v/v, or in cases up to 7.5 or 5% v/v. It may for example be from 0.5 to 20% v/v or from 0.5 to 10% v/v, or from 1 to 20 or 1 to 15% v/v, or from 5 to 15% v/v, for example 5% v/v or 10% v/v. In cases it may be up to 40 or 50 or 60 or 70 or 80 or 85 or even 90% v/v, or in cases up to 95 or 98 or 99 or 99.5% v/v. The alcohol concentration may be up to 100% v/v (in other words, the fuel formulation may consist of an alcohol or mixture of alcohols, optionally with one or more fuel additives).

[0051] A gasoline fuel formulation prepared or used according to the invention may comprise one or more additional fuel components. In an embodiment, it may comprise one or more additional biofuel components. Such additional fuel components may have boiling points within the normal gasoline boiling range, and in the case of biofuel components will have been derived - whether directly or indirectly - from biological sources.

[0052] A gasoline fuel formulation prepared or used according to the invention may be suitable and/or adapted for use in a spark ignition (petrol) internal combustion engine. It may in particular be suitable and/or adapted for use as an automotive gasoline fuel.

[0053] The MON of such a gasoline fuel formulation is suitably 70 or greater, or 75 or 80 or greater. It may be 84 or 85 or greater. The MON may for example be from 70 to 110 or from 75 to 105 or from 84 to 95. The RON of such a gasoline fuel formulation is suitably 80 or greater. It may be 85 or 90 or 93 or 94 or 95 or 98 or greater. The RON may for example be from 80 to 110 or from 85 to 115 or from 90 to 105 or from 93 to 102 or from 94 to 100.

[0054] The formulation will suitably comply with applicable current standard gasoline fuel specification(s) such as for example EN 228 in the European Union or ASTM D4814-08b in the USA. By way of example, the overall formulation may have a density from 0.720 to 0.775 kg/m³ at 15°C (ASTM D4052 or EN ISO 3675); a final boiling point (ASTM D86 or EN ISO 3405) of 210°C or less; a RON (ASTM D2699 or EN ISO 5164) of 95.0 or greater; a MON (ASTM D2700 or EN ISO 5163) of 85.0 or greater; an olefinic hydrocarbon content of from 0 to 20% v/v (ASTM D1319); and/or an oxygen content of from 0 to 5% w/w (EN 1601). It may have an E70 value of from 20 to 50% v/v, and/or an E100 value of from 46 to 71% v/v. Relevant specifications may however differ from country to country, from season to season and from year to year, and may depend on the intended use of the formulation. Moreover a formulation prepared or used according to the invention may contain fuel components with properties outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

[0055] A gasoline fuel formulation prepared or used according to the invention suitably has a low total lead content, such as at most 0.005 g/l. In an embodiment it is lead free ("unleaded"), ie it has no lead compounds in it.

[0056] In a specific embodiment, a gasoline fuel formulation in which the modified cyclodextrin (I) is used is an automotive gasoline fuel (suitably EN 228-compliant) containing up to 10% v/v, for example from 0.5 to 10% v/v or from 0.5 to 5% v/v, such as about 5% v/v, of an alcohol, in particular ethanol. In this embodiment, the modified cyclodextrin (I) may in particular be heptakis(2,6-di-O-n-butyl)- β -cyclodextrin.

[0057] A gasoline fuel formulation prepared or used according to the invention may comprise, in addition to the modified cyclodextrin (I), one or more fuel or refinery additives. Many such additives are known and commercially available. They may be present in a base fuel, or may be added to the formulation at any point during its preparation. Non-limiting examples of suitable types of fuel additives that can be included in a gasoline base fuel or gasoline fuel formulation include antioxidants, corrosion inhibitors, detergents, dehazers, antiknock additives, metal deactivators, valve-seat recession protectant compounds, viscosity control additives, octane boosters, dyes, markers, friction modifiers, and combinations thereof, as well as solvents, diluents and carriers therefor. Examples of suitable such additives are described generally in US 5,855,629. The additives may be included in the fuel formulation at an (active matter) concentration of up to 1500 ppmw (parts per million by weight), or up to 1000 or 500 or 300 ppmw, for example from 50 to 1500 ppmw or from 50 to 1000 ppmw or from 50 to 500 ppmw or from 50 to 300 ppmw.

[0058] As referred to above, the fuel formulation may include a second detergent additive in addition to the modified cyclodextrin (I). In cases, however, due to the detergent effect of the modified cyclodextrin, the fuel formulation may not need to contain any such further detergent additives, or may contain a lower concentration of such additives than would otherwise have been necessary or desirable. Thus, the modified cyclodextrin (I) may be used in the fuel formulation in the absence of other detergent additives.

[0059] In an alternative embodiment of the first aspect of the invention, the modified cyclodextrin (I) is used in a diesel fuel formulation, in particular an automotive diesel fuel formulation. Apart from the modified cyclodextrin (I), such a formulation may be conventional in terms of its constituents and their relative concentrations. It may for example comprise a diesel base fuel.

[0060] A diesel base fuel may be any fuel component, or mixture thereof, which is suitable and/or adapted for combustion within a compression ignition (diesel) engine. It will typically be a liquid hydrocarbon middle distillate fuel, more typically a gas oil. It may be petroleum-derived. It may be or contain a kerosene fuel component. It may be or contain a synthetic fuel component, for instance a product of a Fischer-Tropsch condensation process. It may be or contain a fuel component derived from a biological source, for example a hydrogenated bio-derived oil (in particular a hydrogenated vegetable oil, HVO) or mixture thereof. It may be or contain an oxygenate such as a fatty acid alkyl ester, in particular a FAME such as rapeseed methyl ester (RME) or palm oil methyl ester (POME).

[0061] A diesel base fuel will typically boil in the range from 150 or 180 to 370°C (ASTM D86 or EN ISO 3405). It will suitably have a measured cetane number (ASTM D613) of from 40 to 70 or from 40 to 65 or from 51 to 65 or 70.

[0062] A diesel fuel formulation prepared or used according to the invention may comprise a diesel base fuel at a concentration of 50% v/v or greater, or 60 or 70 or 80% v/v or greater, or 85 or 90 or 95 or 98% v/v or greater. The base fuel concentration may be up to 99.99% v/v, or up to 99.95% v/v, or up to 99.9 or 99.5% v/v. It may be up to 99% v/v, for example up to 98 or 95 or 90% v/v, or in cases up to 85 or 80% v/v.

[0063] Where the diesel fuel formulation comprises an oxygenate or biodiesel component such as a FAME, its concentration may be 1% v/v or greater, or 2 or 5% v/v or greater, based on the overall formulation, or in cases 7 or 10 or 20 or 30% v/v or greater. The FAME concentration may be up to 100% v/v (in other words, the diesel fuel formulation may consist of a FAME or mixture of FAMEs, optionally with one or more diesel fuel additives), or up to 99 or 98 or 95% v/v, or up to 90 or 80 or 70 or 60 or 50% v/v, or in cases up to 40 or 30 or 20 or 10% v/v, for example from 1 to 40% v/v.

[0064] A diesel fuel formulation prepared or used according to the invention will suitably comply with applicable current standard diesel fuel specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA). By way of example, the overall formulation may have a density from 820 to 845 kg/m³ at 15°C (ASTM D4052 or EN ISO 3675); a T95 boiling point (ASTM D86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D613) of 40 or greater, ideally of 51 or greater; a kinematic viscosity at 40°C (VK40) (ASTM D445 or EN ISO 3104) from 2 to 4.5 centistokes (mm²/s); a flash point (ASTM D93 or EN ISO 2719) of 55°C or greater; a sulphur content (ASTM D2622 or EN ISO 20846) of 50 mg/kg or less; a cloud point (IP 219) of less than -10°C; and/or a polycyclic aromatic hydrocarbons (PAH) content (EN 12916) of less than 11% w/w. Relevant specifications may however differ from country to country, from season to season and from year to year, and may depend on the intended use of the formulation. Moreover a formulation prepared or used according to the invention may contain individual fuel components with properties outside of these ranges.

[0065] A diesel fuel formulation prepared or used according to the invention may comprise, in addition to the modified cyclodextrin (I), one or more fuel or refinery additives. Many such additives are known and commercially available. They may be present in a base fuel, or may be added to the formulation at any point during its preparation. Non-limiting examples of suitable types of fuel additives that can be included in a diesel base fuel or diesel fuel formulation include cetane improvers, antistatic additives, lubricity additives, cold flow additives, and combinations thereof, as well as solvents, diluents and carriers therefor. Such additives may be included in the fuel formulation at an (active matter) con-

centration of up to 4000 ppmw, or up to 3000 or 2000 or 1000 or 500 or 300 ppmw, for example from 50 to 4000 ppmw or from 50 to 1500 ppmw or from 50 to 1000 ppmw or from 50 to 500 ppmw or from 50 to 300 ppmw.

[0066] A diesel fuel formulation prepared or used according to the invention may be suitable and/or adapted for use in a compression ignition (diesel) internal combustion engine. It may in particular be suitable and/or adapted for use as an automotive diesel fuel. In further embodiments it may be suitable and/or adapted for use as an industrial gas oil, or as a heating oil, or as a marine diesel fuel.

[0067] In accordance with the invention, the modified cyclodextrin (I) may be used in a fuel formulation at a concentration of for example 50 ppmw or greater, or 100 or 250 or 500 ppmw or greater. Its concentration may for example be up to 10,000 ppmw, or up to 5000 or 4000 or 3000 or 2000 or 1500 ppmw, such as from 100 to 4000 ppmw or from 500 to 1500 ppmw.

[0068] In an embodiment of the invention, the modified cyclodextrin (I) is used in combination with an additional fuel additive. In the context of the present invention, a fuel additive is a substance which is capable of performing a technical function when incorporated in a fuel formulation: it will typically be capable of modifying a property of, and/or the performance of, the formulation.

[0069] Where the modified cyclodextrin (I) is used in combination with an additional fuel additive, the additional additive may be suitable and/or adapted for use as a fuel additive, in particular a gasoline or diesel fuel additive. The additional additive may for example be selected from antioxidants, corrosion inhibitors, detergents and dispersant additives, anti-knock additives, metal deactivators, valve-seat recession protectant compounds, viscosity and viscosity index modifiers, combustion improvers (typically either octane boosters or cetane improvers), dyes and other markers, friction modifiers, lubricity additives, antiwear additives, antistatic additives, antifoaming agents, dehazers, cold flow additives, and combinations thereof. It may in particular be selected from antioxidants, combustion improvers, detergents, and combinations thereof; or from combustion improvers, detergents, and combinations thereof; or from antioxidants, combustion improvers, and combinations thereof.

[0070] In an embodiment, the additional fuel additive is a polar species.

[0071] In an embodiment, the additional fuel additive is a second detergent additive. By "detergent" or "detergent additive" is meant an agent which can act to remove, and/or to prevent the accumulation of, deposits such as combustion-related deposits within a fuel-consuming system, in particular within a fuel injection system such as in or on the injector nozzles. Many such agents are surfactants, for example zwitterionic surfactants or polyisobutenyl (PIB)-based surfactants such as polyisobutenyl amines, polyisobutenyl succinimides and polyisobutenyl succinic anhydrides.

[0072] Detergent additives suitable for use in fuel formulations include those disclosed in WO 2009/50287.

[0073] Suitable detergent additives typically have at least one hydrophobic hydrocarbon radical having a number-average molecular weight (M_n) of from 85 to 20,000 and at least one polar moiety, which may include a monomeric or polymeric amine, amide or imido moiety. The polar moiety may for example be selected from:

- (1) mono- or polyamino groups having up to 6 nitrogen atoms, of which at least one nitrogen atom has basic properties;
- (2) polyoxy-C2- to -C4-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;
- (3) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or
- (4) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

[0074] The hydrophobic hydrocarbon radical in the above detergent additives, which ensures adequate solubility in the base fluid, has a number-average molecular weight (M_n) 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 (1), (3) and (4), include polyalkenes (polyolefins), such as the polypropenyl, polybutenyl and polyisobutenyl radicals each having M_n of from 300 to 5000, or from 500 to 2500, or from 700 to 2300, such as from 700 to 1000.

[0075] Detergent additives comprising mono- or polyamino groups (1) may be polyalkenemono- or polyalkenepolyamines based on polypropene or conventional (ie having predominantly internal double bonds) polybutene or polyisobutene having M_n 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, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. Corresponding additives based on polypropene are described in particular in WO 94/24231.

[0076] Further suitable detergent additives comprising monoamino groups (1) are the hydrogenation products of the reaction products of polyisobutenes having an average degree of polymerisation of from 5 to 100, with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO 97/03946.

[0077] Yet further suitable detergent additives comprising monoamino groups (1) 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 196 20 262.

[0078] Detergent additives comprising polyoxy-C2-C4-alkylene moieties (2) may be polyethers or polyetheramines which are obtainable by reaction of C2-to C60-alkanols, C6- to C30-alkanediols, mono- or di-C2-C30-alkylamines, C1-C30-alkylcyclohexanols or C1-C30-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of the polyetheramines, by subsequent reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP 310 875, EP 356 725, EP 700 985 and US 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.

[0079] Detergent additives comprising moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups (3) may be 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 4 849 572.

[0080] Detergent additives comprising moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines (4) may be 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" are described in particular in EP 831 141.

[0081] In an embodiment, a detergent included in a fuel formulation which is prepared or used according to the invention is a nitrogen-containing detergent, in particular an amine- or polyamine-containing detergent. In an embodiment, such a detergent contains a hydrophobic hydrocarbon radical having a number average molecular weight in the range from 300 to 5000. The nitrogen-containing detergent may be selected from the group consisting of polyalkene monoamines, polyetheramines, polyalkene Mannich amines, polyalkene succinimides, and mixtures thereof. Conveniently, the nitrogen-containing detergent may be a polyalkene monoamine.

[0082] In an embodiment of the present invention, the modified cyclodextrin (I) is used in combination with a second detergent additive of the type referred to as (1) above, for example a polyisobutenyl (PIB) succinimide.

[0083] Detergent additives of the type described may be present, or used, in the form of an additive composition which contains the relevant detergent in an appropriate carrier or solvent, optionally together with one or more other fuel additives.

[0084] Where the modified cyclodextrin (I) is used in combination with an additional fuel additive, the additional additive may be at least partly present as a guest molecule within a host molecule of the modified cyclodextrin (I), in the form of an inclusion complex. Thus, the "guest" additive may be combined with the modified cyclodextrin so that the resultant complex can be used to impart additional effects in a fuel formulation to which it is added.

[0085] As described above, the modified cyclodextrin (I) can be tailored to increase its solubility in the fuel formulation. In this way, it can be used to modify the effective solubility of an additive in the formulation. Once encapsulated in a cyclodextrin host molecule, an additive molecule which would otherwise be relatively insoluble in the formulation can benefit from the greater solubility of its host.

[0086] A further potential benefit of additive encapsulation can arise because the cyclodextrin host may be able to release a guest molecule under certain conditions, for example conditions which weaken the association between host and guest or which degrade the cavity-forming macromolecular structure of the cyclodextrin, for instance on heating. It can therefore be possible to select, or tailor, the modified cyclodextrin (I) so as to carry - and if necessary protect - an additive under certain conditions but to release it at a desired time or location where its effect is most needed. For example, a fuel additive such as an antioxidant or a combustion improver may be of particular use within the fuel injection and combustion regions of an engine, as may a detergent: targeting its release to those regions can therefore improve its efficacy.

[0087] In this way, a modified cyclodextrin (I) can be used to target, or otherwise control, delivery of an additive which it encapsulates as a guest molecule. The additive is released from the cyclodextrin host molecule only under certain conditions, for example conditions which cause dissociation of the host-guest complex, replacement of the additive by another, competitor guest molecule, or degradation of the cyclodextrin host molecule or its macrocyclic structure (for example by evaporation or chemical degradation). Outside of the release conditions, the cyclodextrin can retain the additive and protect it from external influences. Under the release conditions, the additive can leave the cyclodextrin cavity and be available for reaction elsewhere. Thus, as described above, delivery of the additive can be targeted to a specific set of conditions, such as a specific temperature or pressure range, or a specific applied force such as a shear

force, or the introduction of another species such as a competitor guest molecule. It is possible to tailor the modified cyclodextrin (I) so as to achieve, with a chosen additive, an inclusion complex which dissociates under a desired condition or set of conditions. This may be of value in targeting delivery of an additive to a region within a fuel-consuming system, and/or to a period during use of a fuel formulation, at which the additive is likely to be of most use, for example within a fuel injection system or a combustion chamber. Instead or in addition, the modified cyclodextrin (I) may be used to target delivery of an additive to a specific environment, for example a specific climate or a specific set of operating conditions within a fuel-consuming system. Prior to delivery, for instance during storage and transportation, the additive can be protected from potentially damaging external influences. In the case of an additive which carries health or safety risks, its release may be prevented or inhibited at a specific location or during a specific time period, again for example during storage and transportation.

[0088] It has moreover been found that in certain cases, a modified cyclodextrin (I) can enhance the activity of a guest additive, or in cases modify the nature of its activity. It can increase the availability of the additive in a desired active form, and/or prolong its lifetime so that more of it is available at a given time during its use. This too can be of benefit in the formulation of additive-containing fuels.

[0089] A yet further potential advantage to the use of molecular encapsulants, as opposed to the polymeric matrices and microcapsules often used as additive delivery vehicles in the past, is that they are much smaller and thus less likely to cause blockages in for example fuel lines and fuel filters, or the build-up of undesired deposits in fuel-consuming systems.

[0090] In an embodiment of the invention, the modified cyclodextrin (I) is used together with a second detergent additive, as a combined detergent additive. In other words, the combination of the modified cyclodextrin (I) and the second detergent additive may be used to reduce the amount of deposits formed during use of a fuel formulation in which it is present. The second detergent additive may be present as a physical mixture with the modified cyclodextrin. It may, as described above, be at least partly present as a guest molecule within a cyclodextrin inclusion complex.

[0091] The modified cyclodextrin (I) may be used in combination with a mixture of two or more different additional fuel additives. Some or all of these may be present as guest molecules within modified cyclodextrin host molecules. Some or all of them may be unencapsulated in modified cyclodextrins of formula (I).

[0092] It can be seen that the modified cyclodextrin of formula (I) may be used in the fuel formulation both as a detergent additive in its own right and as a vehicle for an additional fuel additive, including a second detergent additive. In this context, it can represent an improvement over other types of (typically inert) encapsulating vehicle, in that it can contribute a functionality of its own to affect the properties and/or performance of the overall formulation.

[0093] Where the modified cyclodextrin (I) is used in combination with an additional fuel additive, in particular a second detergent additive, the (active matter) concentration of the additional additive in the fuel formulation may be for example 5 ppmw or greater, or 10 ppmw or greater, or 25 or 50 ppmw or greater. This concentration may for example be up to 1500 ppmw, or up to 1000 or 500 ppmw, or up to 300 or 200 or 150 ppmw, such as from 50 to 1000 ppmw or from 50 to 500 ppmw or from 50 to 300 ppmw or from 50 to 150 ppmw. In some cases the concentration may be from 50 to 1500 ppmw or from 500 to 1500 ppmw or from 1000 to 1500 ppmw. Due to the detergent effect of the modified cyclodextrin (I) itself, a second detergent additive may be used at a lower than usual treat rate, for example at an active matter concentration of 1000 ppmw or lower, or of 500 ppmw or lower, or of 300 or 200 or 100 ppmw or lower.

[0094] In an embodiment, it may be preferred for the fuel formulation in which the modified cyclodextrin (I) is used not to contain any cetane improvers which are present in the form of inclusion complexes within modified cyclodextrins of formula (I), and/or not to include any antioxidants which are present in the form of inclusion complexes within modified cyclodextrins of formula (I).

[0095] In the context of the present invention, use of the modified cyclodextrin (I) as a detergent additive means use for the purpose of reducing the deposits which are formed when the fuel formulation is introduced into, and/or used in, a fuel-consuming system. Such deposits may be combustion-related deposits. They may form in a fuel injection region or component within the fuel-consuming system, for example in a fuel injector nozzle. They may include, for example, oxidation and/or thermal decomposition products of fuels or lubricants used within the system.

[0096] The modified cyclodextrin (I) may be used to achieve any degree of reduction in such deposits, through any specified period and/or type of use of the formulation. It may be used to achieve, or achieve less than, a desired target maximum level of deposits through a specified period and/or type of use.

[0097] The level of deposits, in particular combustion-related deposits, generated by a fuel formulation may be determined using any suitable method. It may for instance be measured with reference to the degree of fouling of a component in a fuel-consuming system in which the fuel formulation is or has been used. The relevant component may in particular be part of a fuel injection system, more particularly a fuel injection component such as a nozzle. Degree of component fouling may be assessed in a number of ways, for instance visually; by measuring the mass of deposits in or on a fouled component; or by measuring the fluid flow (for instance, fuel flow or air flow) properties of the fouled component relative to those of the component prior to contact with the test fuel formulation.

[0098] An appropriate test might for example determine the degree of component fouling (conveniently in the form of

a percentage fouling index) under steady state conditions in an engine or other system, for instance based on the change in air flow rate through one or more of the components as a result of using the fuel formulation in the system. Conveniently the results are averaged over a number of components within the system, for example all of the fuel injector nozzles of an engine.

[0099] Deposit formation may be assessed using a simulator test such as that described in the examples below, which mimics the conditions inside an engine and provides a laboratory-scale method for comparing the cleanliness of fuel samples.

[0100] The present invention may additionally or alternatively be used to adjust any property of a fuel formulation which is equivalent to or associated with reduced deposits. For example, reduced deposit formation may be associated with improved combustion and energy efficiency for a system running on the fuel formulation, reductions in system blockages (in particular in fuel injection regions such as injector nozzles) and/or with overall better system performance.

[0101] In accordance with the invention, the modified cyclodextrin (I) may be added to the fuel formulation at any suitable time and location. Where it is used in combination with an additional fuel additive, it may be premixed with the additional additive and the premix then added to the fuel formulation, or alternatively the modified cyclodextrin (I) may be added separately, to a fuel formulation which already contains, and/or is subsequently to be mixed with, one or more additional fuel additives.

[0102] The modified cyclodextrin (I) may be added to the fuel formulation as part of a pre-prepared additive composition. Such an additive composition may contain one or more appropriate solvents or carriers, as described below in connection with the second aspect of the invention. It may contain one or more additional fuel additives, which may be at least partly present as guest molecules within cyclodextrin inclusion complexes.

[0103] A premix comprising a modified cyclodextrin of formula (I), together with one or more additional fuel additives, for example including a second detergent additive, and optionally together with one or more carriers which are suitable for use in a fuel formulation, may constitute an essential element for the carrying out of the present invention.

[0104] A modified cyclodextrin of formula (I) may be obtained from an unmodified cyclodextrin by standard chemical techniques, as would be well known to the synthetic chemist. Unmodified cyclodextrins are widely available commercially; they are typically produced from starch by enzymatic conversion. Thus, a cyclodextrin (I) may be derived from a biological source, which can be advantageous as there is increasing demand for fuel formulations to include higher concentrations of biologically-derived components.

[0105] According to a second aspect, the present invention provides the use of a modified cyclodextrin of formula (I) above as a detergent additive in an additive composition for use in a fuel formulation. The additive composition should be suitable and/or adapted and/or intended - in particular suitable and/or adapted - for use in a fuel formulation, for instance of the type described above in connection with the first aspect of the invention.

[0106] Such an additive composition may comprise a mixture of two or more different modified cyclodextrins of formula (I). It may comprise one or more additional fuel additives, for example a second detergent additive. Some of these additional additives may be present in the composition as guest molecules within cyclodextrin inclusion complexes.

[0107] The additive composition may comprise a solvent carrier, or mixture thereof, for the modified cyclodextrin and any additional additives present. Suitable such solvents are well known and commercially available. They may in particular be liquid carriers. They may conveniently be of low polarity, and/or hydrophobic, and/or non-aqueous, to render them suitable for use in fuel and in particular diesel fuel formulations.

[0108] Commonly used additive solvents include hydrocarbon solvents such as alkanes, alkenes and aromatic hydrocarbons; mixtures of hydrocarbons such as in distillate fractions; and more polar solvents such as alcohols and ethers. The nature of the solvent or solvent mixture used in the additive composition (in particular its polarity) may be chosen to suit the natures and polarities of the modified cyclodextrin (I) and any additional additive(s) present, as well as of a fuel formulation in which the additive composition is to be used, so as to optimise the stability and efficacy of the composition during use.

[0109] In an embodiment, however, the additive composition may be in solid form.

[0110] The modified cyclodextrin (I) may be used in the additive composition at a concentration of 0.5 or 1% w/w or greater, for example 5 or 10 or 20% w/w or greater. It may be used at a concentration of up to 98% w/w, or of up to 90 or 75 or 50% w/w, such as from 1 to 50% w/w. In an embodiment, in particular when the additive composition is in solid form, it may consist essentially of (for example it may contain at least 98 or 99% w/w of, or 100% of) the modified cyclodextrin (I), or of an inclusion complex comprising one or more fuel additives encapsulated within host molecules of the modified cyclodextrin (I).

[0111] An additive composition prepared or used according to the second aspect of the invention may for example be included in a fuel formulation at a concentration of 50 ppmw or greater, or 100 or 250 or 500 ppmw or greater. Its concentration may for example be up to 10,000 ppmw, or up to 5000 or 4000 or 3000 or 2000 or 1500 ppmw, such as from 100 to 4000 ppmw or from 500 to 1500 ppmw. These concentrations generally relate to the concentration of the modified cyclodextrin (I) in the fuel formulation, irrespective of any solvent carriers or other species which are present, with the cyclodextrin, in the additive composition.

[0112] Other preferred features of the second aspect of the invention, for example the natures of the modified cyclodextrin (I) and any additional fuel additive(s); the purpose(s) for which, and the concentrations at which, the modified cyclodextrin (I) is used; and the nature of the fuel formulation in which it is used, may be as described above in connection with the first aspect of the invention.

[0113] A modified cyclodextrin (I) used in the first or second aspect of the invention should be suitable for use in a fuel formulation. It may be adapted for use in such a formulation. An additive composition prepared or used according to the second aspect of the invention should be suitable for use in a fuel formulation. It may be adapted for use in such a formulation.

[0114] An additive composition which is prepared or used according to the second aspect of the invention may itself be used when carrying out the first aspect of the invention. The additive composition may be mixed with one or more fuel components, and optionally with one or more additional fuel additives. The additive composition may thus constitute an essential element for carrying out the first aspect of the invention.

[0115] The additive composition may be mixed with the other components of the fuel formulation at any suitable time prior to use of the formulation, for example at the refinery or at a distribution or dispensing point downstream of the refinery, in particular at a distribution point within a refinery or fuel depot.

[0116] According to a third aspect, the invention provides a method for formulating a fuel formulation, the method comprising (a) providing a fuel component (for example a base fuel or base oil) or mixture thereof, (b) optionally assessing the level of deposits generated by the component or mixture in a fuel-consuming system in which it is used, (c) adding to the component or mixture a modified cyclodextrin of formula (I) above and (d) assessing the level of deposits generated by the resultant cyclodextrin-containing formulation in a fuel-consuming system in which it is used. Step (d) may be carried out in order to assess the detergent effect of the modified cyclodextrin (I) on the fuel component or mixture.

[0117] In an embodiment of this third aspect of the invention, the modified cyclodextrin (I) is added to the fuel component, or mixture thereof, in the form of an additive composition prepared according to the second aspect. One or more additional fuel additives, for example a second detergent additive, may also be added to the fuel component or mixture, either with or separately to the modified cyclodextrin (I). Preferred features of the modified cyclodextrin (I), and of the fuel component(s) and additive(s) with which it is mixed, may be as described above in connection with the first and second aspects of the invention, as may the ways in which the level of deposit generation is assessed.

[0118] Because the modified cyclodextrin (I) can act as a detergent additive, it can make possible the use of lower concentrations of other detergent additives in a fuel formulation or an additive composition, without or without undue increase in the deposits generated by the formulation or by a fuel formulation in which the additive composition is used. This can in turn reduce the cost and complexity of preparing the formulation or composition, and/or can provide greater versatility in fuel and additive formulation practices.

[0119] These effects may be enhanced when the modified cyclodextrin (I) is also used to improve the activity, availability, solubility and/or stability of another detergent additive, and/or to target its delivery.

[0120] In cases, a modified cyclodextrin (I) may be used to replace - at least partly, and in some cases completely - one or more other detergent additives in a fuel formulation or additive composition. In cases it may be used as the only detergent additive in such a formulation or composition.

[0121] Thus, according to a fourth aspect, the invention provides the use of a modified cyclodextrin of formula (I) above in an additive composition or in a fuel formulation, optionally in combination with a second detergent additive, for the purpose of reducing the concentration of the or a detergent additive present in the composition or formulation.

[0122] In this context, the detergent additive for which the concentration is to be reduced may for example be a detergent additive of the type described above in connection with the first aspect of the invention, in particular a nitrogen-containing detergent, more particularly an amine- or polyamine-containing detergent.

[0123] In the context of the fourth aspect of the invention, the term "reducing" embraces any degree of reduction, including reduction to zero. The reduction may for instance be 10% or more of the original concentration of the detergent additive, or 25 or 50 or 75 or 90% or more. The reduction may for instance be 500 ppmw or more, or 750 ppmw or more, or 1000 or 1250 ppmw or more. The reduction may be as compared to the concentration of the detergent additive which would otherwise have been incorporated into the composition or formulation in order to achieve the properties and performance required and/or desired of it in the context of its intended use. This may for instance be the concentration of the additive which was present in the composition or formulation prior to the realisation that a modified cyclodextrin (I) could be used in the way provided by the present invention, and/or which was present in an otherwise analogous additive composition or fuel formulation which was intended (eg marketed) for use in an analogous context, prior to adding a modified cyclodextrin (I) to it in accordance with the invention.

[0124] The reduction in concentration of the detergent additive may be as compared to the concentration of the additive which would be predicted to be necessary to achieve a desired property or performance for the composition or formulation in the absence of the modified cyclodextrin (I). It may be as compared to the "standard treat rate" of the detergent additive in the relevant type of fuel formulation.

[0125] In accordance with a fifth aspect of the invention, there is provided a method of operating a fuel-consuming

system, and/or apparatus (for example a vehicle, or a heating appliance) which is driven by such a system, the method comprising introducing into the system a fuel formulation prepared according to the first, third or fourth aspect of the invention, or an additive composition prepared according to the second or the fourth aspect. This method may for example comprise introducing the formulation or the additive composition into a combustion chamber of a fuel-consuming system.

The system may for example be an internal combustion engine. It may be a spark-ignition (petrol) engine. It may be a compression-ignition (diesel) engine.

[0126] A method according to the fifth aspect of the invention may be carried out with the intention of reducing the deposits generated by the fuel formulation, or by a fuel formulation containing the additive composition, through its use in the fuel-consuming system.

[0127] In the context of the first to the fifth aspects of the invention, the fuel formulation may in particular be a gasoline or diesel fuel formulation, more particularly a gasoline fuel formulation, for example a gasoline formulation containing from 0.5 to 10% v/v or from 1 to 10% v/v, such as about 5% v/v, of an alcohol such as ethanol.

[0128] In the context of the present invention, "use" of a modified cyclodextrin (I) in a fuel formulation means incorporating the cyclodextrin into the formulation, typically as a blend (ie a physical mixture) with one or more fuel components, for example gasoline or diesel base fuels, and optionally in combination with one or more additional fuel additives, for example a second detergent additive.

[0129] The modified cyclodextrin (I) will conveniently - although not necessarily - be incorporated before the formulation is introduced into a fuel-consuming system. Instead or in addition, the use of a modified cyclodextrin (I) may involve running a fuel-consuming system, typically an internal combustion engine, on a fuel formulation containing the cyclodextrin, typically by introducing the formulation into a combustion chamber of an engine. It may involve running a vehicle, or other apparatus which is driven by a fuel-consuming system, on a fuel formulation containing the cyclodextrin.

[0130] "Use" of a modified cyclodextrin (I) in the ways described above may also embrace supplying the cyclodextrin together with instructions for its use in a fuel formulation for one or more of the purposes described above in connection with the first to the fifth aspects of the invention. The cyclodextrin may itself be supplied as part of a composition which is suitable and/or adapted and/or intended for use as a fuel additive, in particular an additive composition prepared according to the second aspect of the invention. In this case, the modified cyclodextrin (I) may be included in such a composition for any one or more of the purposes described above in connection with the first to the fifth aspects of the invention.

[0131] Thus a modified cyclodextrin (I) may be used, in a fuel formulation, in the form of an additive composition which has been prepared according to the second aspect of the invention, ie in which the modified cyclodextrin is used as a detergent additive. "Use" of a modified cyclodextrin (I) may therefore comprise "use" of such an additive composition.

[0132] "Use" of a modified cyclodextrin (I) in an additive composition means incorporating the cyclodextrin into the composition, typically as a blend (ie a physical mixture) with one or more solvent carriers and optionally in combination with one or more additional fuel additives, for example a second detergent additive. The cyclodextrin will conveniently - although not necessarily - be incorporated before the composition is introduced into a fuel formulation or into a fuel-consuming system. Instead or in addition, the use of a modified cyclodextrin (I) may involve running a fuel-consuming system, typically an internal combustion engine, on a fuel formulation containing the cyclodextrin in the additive composition, typically by introducing the formulation into a combustion region of the system. It may involve running a vehicle, or other apparatus which is driven by a fuel-consuming system, on a fuel formulation containing the cyclodextrin in the additive composition.

[0133] "Use" of a modified cyclodextrin (I) in the ways described above may also embrace supplying the cyclodextrin together with instructions for its use in an additive composition for one or more of the purposes described above in connection with the first to the fifth aspects of the invention.

[0134] In general, references to "adding" a component to, or "incorporating" a component in, an additive composition or a fuel formulation may be taken to embrace addition or incorporation at any point during the production of the composition or formulation or at any time prior to its use.

[0135] In embodiments, the present invention may be used to produce at least 1000 litres of a modified cyclodextrin-containing additive composition or fuel formulation, or at least 5000 or 10,000 or 20,000 or 50,000 litres.

[0136] A fuel formulation which is prepared or used according to the invention may be marketed with an indication that it benefits from an improvement due to the inclusion of the modified cyclodextrin (I), for example reduced deposit formation and/or a lower concentration of a detergent additive in the formulation. The marketing of such a formulation may comprise an activity selected from (a) providing the formulation in a container that comprises the relevant indication; (b) supplying the formulation with product literature that comprises the indication; (c) providing the indication in a publication or sign (for example at the point of sale) that describes the formulation; and (d) providing the indication in a commercial which is aired for instance on the radio, television or internet. The improvement may be attributed, in such an indication, at least partly to the presence of the modified cyclodextrin (I). The invention may involve assessing the relevant property of the formulation during or after its preparation. It may involve assessing the relevant property both before and after incorporation of the modified cyclodextrin, for example so as to confirm that the modified cyclodextrin

contributes to the relevant improvement in the formulation.

[0137] An additive composition which is prepared or used according to the invention may be marketed with an indication that it benefits from an improvement due to the inclusion of the modified cyclodextrin (I), for example reduced deposit formation by a fuel formulation in which the composition is used, and/or a lower concentration of a detergent additive in the composition. The marketing of such a composition may comprise an activity selected from (a) providing the composition in a container that comprises the relevant indication; (b) supplying the composition with product literature that comprises the indication; (c) providing the indication in a publication or sign (for example at the point of sale) that describes the composition; and (d) providing the indication in a commercial which is aired for instance on the radio, television or internet. The improvement may be attributed, in such an indication, at least partly to the presence of the modified cyclodextrin (I). The invention may involve assessing the relevant property of the composition during or after its preparation. It may involve assessing the relevant property both before and after incorporation of the modified cyclodextrin, for example so as to confirm that the modified cyclodextrin contributes to the relevant improvement in the composition.

[0138] Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and do not exclude other moieties, additives, components, integers or steps. Moreover the singular encompasses the plural unless the context otherwise requires: in particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[0139] Preferred features of each aspect of the invention may be as described in connection with any of the other aspects. Other features of the invention will become apparent from the following examples. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. For example, for the avoidance of doubt, the optional and preferred features (including concentrations) of the modified cyclodextrin (I), any additional additive(s) and the fuel formulation can apply to all aspects of the invention in which the modified cyclodextrin, the additional additive(s) or the fuel formulation are mentioned.

[0140] Moreover unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

[0141] Where upper and lower limits are quoted for a property, for example for the concentration of an additive or fuel component, then a range of values defined by a combination of any of the upper limits with any of the lower limits may also be implied.

[0142] In this specification, references to physical properties such as cyclodextrin, additive, fuel and fuel component properties are - unless stated otherwise - to properties measured under ambient conditions, ie at atmospheric pressure and at a temperature from 16 to 22 or 25°C, or from 18 to 22 or 25°C, for example about 20°C.

[0143] The present invention will now be further described with reference to the following non-limiting examples.

Example 1 - Detergency Effects (i)

[0144] Fuel formulations were prepared, in accordance with the invention, by mixing a gasoline base fuel BF1 with modified cyclodextrins of formula (I) above, or with combinations of modified cyclodextrins and a second detergent additive. For each formulation, an "inclined hot plate" (IHP) rig was used to assess the level of deposits it would be likely to generate in a fuel-consuming system.

[0145] The test method used was an intake valve deposit simulator test which corresponds closely to that described in SAE Paper 890215, Daneshgari et al, "The Influence of Temperature upon Gasoline Deposit Build-up on the Intake Valves", Detroit, USA, 27 February to 3 March 1989. The test rig utilises four inclined plates in parallel. The plates are strips of sand-blasted aluminium 50 cm long and 2.5 cm wide, having a central groove along their lengths 3 mm wide and 1 mm deep, mounted in the rig at an angle of 3 degrees to the horizontal. The temperature at the top end of each plate is maintained at 400°C and at the middle of each plate at 250°C.

[0146] Test fuels were delivered into the grooves at the top ends of the plates in 100 ml samples, at a rate of 0.6 ml/minute, from glass syringes fitted with 20 gauge steel hypodermic Luer lock needles. Once delivery was complete, after about 2 hours and 40 minutes, the plates were allowed to cool to ambient temperature (20°C), washed with n-heptane until the run-off liquid was clear, and then left to dry before assessment of any deposits present.

[0147] The assessment was performed by a trained specialist who rated the level of deposits formed on each of the test plates, on a scale from 1000 (dirtiest) to 0 (cleanest). A lower rating thus indicates that the test fuel is likely to generate a lower level of deposits in a fuel-consuming system.

[0148] The base fuel BF1 was an "E5" blend containing 5% v/v of ethanol and 95% v/v of a commercially available lead-free gasoline base fuel sourced from the Shell Group of companies, which conformed to the European gasoline fuel specification EN 228. Its properties are summarised in Table 1 below.

Table 1

Property	Units	Test method	BF1
Density @ 15°C	kg/m ³	ASTM D4052	741.3
VK40	mm ² /s	IP 71	n/a
Distillation:		ASTM D86	
0%	°C		31.8
10%			45.8
20%			50.8
30%			55.9
40%			66.7
50%			84.3
60%			101.2
70%			113.3
80%			124.0
90%			139.3
95%			150.6
100%			178.9
Measured octane number MON		ASTM D2700	85.8
Research octane number RON		ASTM D2699	97.0

[0149] Three modified cyclodextrins of formula (I) were used as candidate detergent additives:

- a randomly methyl-substituted β -cyclodextrin (RAMEB), in which on average two of the three groups R¹ to R³ were substituted with methyl.
- heptakis(2,3,6-tri-O-methyl- β -cyclodextrin (TRIMEB).
- heptakis(2,6-di-O-n-butyl)- β -cyclodextrin (RABUB).

[0150] The RAMEB and TRIMEB were sourced from Sigma Aldrich, UK and the RABUB from Cyclolab R&D Laboratory (Hungary). Each was added in solid form to the base fuel BF1, at a treat rate of 1000 ppmw. Their relative solubilities in BF1 were RABUB > TRIMEB > RAMEB, due to the natures of their substituents R¹ to R³.

[0151] Also used in the experiments was a second detergent additive D1. This was an additive package, suitable for use in automotive gasoline fuel formulations, containing as the detergent active a PIB (polyisobutenyl) amine detergent. It was added to the base fuel at a treat rate (for the overall additive package) of 2695 ppmw, corresponding to an active matter concentration of approximately 1350 ppmw.

[0152] Preparation of the test fuel samples was effected by mixing the relevant additive(s) into the base fuel, at the relevant concentration, and agitating the mixture until all solids were completely dissolved.

[0153] A second gasoline fuel, GF1, was also tested, without any detergent additive or modified cyclodextrin. GF1 was an EN 228-compliant "dirty" gasoline fuel, known to generate significant engine deposits during normal use.

[0154] The results of the IHP tests are shown in Table 2 below. The base fuel BF1 was tested twice.

Table 2

Test fuel	IHP rating (n-heptane wash)
BF1 (test 1)	600
BF1 (test 2)	600
BF1 + D1	0
BF1 + RAMEB	800-900

(continued)

Test fuel	IHP rating (n-heptane wash)
BF1 + RAMEB + D1	200
BF1 + TRIMEB	800
BF1 + TRIMEB + D1	200
BF1 + RABUB	100
BF1 + RABUB + D1	200
GF1	1000

[0155] It can be seen from Table 2 that the base fuel alone generates deposits on the inclined hot plate. These can be "cleaned up" by the addition of 2695 ppmw of the second detergent additive D1. The RAMEB- and TRIMEB-containing formulations also generate deposits, which are at least partly removed by the inclusion of D1.

[0156] The most striking results, however, are found with the RABUB-containing formulations. Here, the addition of 1000 ppmw RABUB to the base fuel appears to significantly reduce the formation of deposits, an effect which is retained in the presence of the second detergent additive D1. The RABUB thus acts, in the base fuel BF1, as a detergent, "cleaning up" deposit-forming materials in the fuel. It could therefore be used in the base fuel, either alone or in combination with a second detergent additive, to reduce the deposit-forming tendency of the fuel.

[0157] It is believed, although we do not wish to be bound by this theory, that the RABUB gives a better detergent effect than the RAMEB and TRIMEB because of its enhanced solubility in the base fuel BF1. It is believed to be able to form micelle-like structures around deposit-forming precursor molecules, with the outer surfaces of the micelles presenting non-polar, hydrocarbon-philic alkyl groups to aid their solubilisation both in the fuel and in the n-heptane solvent used to wash down the plates.

[0158] These data show that a modified cyclodextrin of formula (I) can act as a detergent additive in a gasoline fuel formulation. It can therefore be used to replace some or all of a detergent additive (such as D1) which would otherwise be deemed necessary or desirable in such a formulation. For example, it appears from these data that RABUB may be used to replace, at least partly, and potentially up to 100%, the detergent additive D1 without loss of detergency effects.

Example 2 - Detergency Effects (ii)

[0159] Example 1 was repeated, but using a slightly modified version of the IHP test in which, following delivery of the test fuels and cooling, the plates were washed with the base fuel BF1 instead of with n-heptane. This is believed to simulate more closely the conditions under which an engine component (in particular, a fuel injector valve) is likely to function during normal use of a gasoline fuel formulation prepared according to the invention.

[0160] The results are shown in Table 3 below. Again, the base fuel was tested twice.

Table 3

Test fuel	IHP rating (BF1 wash)
BF1 (test 1)	600
BF1 (test 2)	500
BF1 + D1	0
BF1 + RAMEB	800
BF1 + RAMEB + D1	400
BF1 + TRIMEB	200
BF1 + TRIMEB + D1	200
BF1 + RABUB	0
BF1 + RABUB + D1	100
GF1	1000

[0161] It can be seen from Table 3 that the deposits generated by the base fuel alone can be removed using the detergent additive D1. The RAMEB-containing formulation also generates deposits, which are at least partly cleaned up by the inclusion of D1. The addition of 1000 ppmw TRIMEB to the base fuel, however, results in a reduction in deposits relative to the base fuel alone, including in combination with D1. This indicates that the modified cyclodextrin could be used (a) as a detergent additive in its own right, and/or (b) as a vehicle for another additive without causing undue reduction in the cleanliness of the overall fuel formulation.

[0162] Again the most striking results are found with the RABUB-containing formulations. Here, the addition of 1000 ppmw RABUB to the base fuel appears to prevent the formation of deposits, both in the presence and the absence of the second detergent additive D1. The RABUB thus acts as a detergent in the base fuel.

[0163] These data show that a modified cyclodextrin of formula (I) can act as a detergent additive in a gasoline fuel formulation. They also confirm the importance of cyclodextrin solubility: when the base fuel BF1 is used to wash the plates instead of n-heptane (which more closely corresponds to the conditions inside a working engine), both TRIMEB and RABUB can be seen to have sufficient solubility in the wash fluid to contribute detergent effects and reduce deposit formation.

[0164] These findings are again consistent with the theory that the cyclodextrin molecules can assemble around molecules of deposit-forming materials, in a micelle-like formation, helping in effect to solubilise the deposits and allowing them to be washed away with the fuel instead of precipitating onto the hot plate. Thus, for example, TRIMEB would likely form a micelle with non-polar methyl groups presenting on the outside, so would be soluble in the relatively non-polar gasoline base fuel. Micelles formed by RAMEB would present a mixture of polar -OH groups and non-polar methyl groups at their outer surfaces, and thus be slightly less soluble in the base fuel than those formed by TRIMEB. RABUB, however, would present largely butyl groups on the outer surfaces of its micelles, making it much more soluble in the base fuel.

[0165] Similar results and trends are expected in other gasoline fuel formulations, as well as in diesel and other fuel formulations. In each case, the modified cyclodextrin (I) could be tailored - by appropriate choice of the substituents R^1 to R^3 - so as to optimise its solubility in the relevant fuel formulation, thus enhancing its ability to act as a detergent additive and to "clean up" deposit-forming materials from the formulation. For example, for use in a more polar gasoline fuel such as one containing a higher ethanol content, a more polar cyclodextrin (I), having fewer or more polar substituents R^1 to R^3 (for example, shorter chain alkyl groups and/or substituted alkyl groups), may be more effective as a detergent additive.

Example 3 - Choice of Modified Cyclodextrin

[0166] Three modified cyclodextrins of formula (I), and for comparison an unmodified cyclodextrin, were tested to assess their solubilities and stabilities in gasoline and diesel fuels.

[0167] The cyclodextrins were the TRIMEB and RABUB used in Examples 1 and 2; hydroxypropyl- β -cyclodextrin (HPBCD); and unmodified β -cyclodextrin ($R^1 = R^2 = R^3 = \text{hydrogen}$). The TRIMEB and the unmodified cyclodextrin were sourced from Sigma Aldrich (UK), and the RABUB and HPBCD from Cyclolab R&D Laboratory (Hungary).

[0168] The fuels tested were (a) gasoline base fuels containing 0, 5, 10, 25 and 85% v/v of ethanol (respectively, E0, E5, E10, E25 and E85); (b) 100% ethanol; (c) a diesel base fuel; and (d) a winter-grade Fischer-Tropsch derived diesel fuel. Not all cyclodextrins were tested in all fuels.

[0169] In each case, the cyclodextrin was added to the fuel at a concentration of 1000 ppmw and at room temperature.

[0170] The unmodified β -cyclodextrin was found to be insoluble in the E0 gasoline base fuel, the diesel base fuel and the Fischer-Tropsch derived fuel. This demonstrates the unsuitability of the unmodified molecule as an additive or additive vehicle in typical fuel formulations.

[0171] The TRIMEB formed a clear and bright solution in the E0 gasoline base fuel, and also in the diesel base fuel although here it required a long dissolution time. It could be partially dissolved in the Fischer-Tropsch derived fuel, with a very long dissolution time. Thus, the TRIMEB demonstrates higher solubilities in more polar environments.

[0172] The HPBCD formed hazy suspensions in the gasoline base fuel, at ethanol concentrations from 0 to 25% v/v, when included at 100 ppmw. However, it formed clear and bright solutions when included at 1000 ppmw in the E85 gasoline fuel and 100% ethanol. It was not tested in the diesel fuels.

[0173] The RABUB appeared to be very soluble in the E5 gasoline fuel and the diesel fuel, forming clear and bright solutions in both cases. It was found to be stable when stored at -20°C for two weeks in the E5 gasoline. It was also the fastest-dissolving of the cyclodextrins tested. Other alkylated β -cyclodextrins, in particular those substituted with C2 or higher alkyl groups, for example C3 to C8 alkyl groups, can therefore also be expected to be soluble in automotive gasoline and diesel fuels, and to be suitable for use in such fuels as detergent additives and/or as additive-carrying vehicles.

Example 4 - Solubility of Further Cyclodextrins

[0174] Three further modified cyclodextrins of formula (I) were tested for solubility in gasoline and diesel fuels.

[0175] The cyclodextrins were alkylated β -cyclodextrins, substituted respectively with ethyl (the compound referred to as RAEB), propyl (RAPB) and octyl (RAOB) groups. In each case the positions R¹, R² and R³ were randomly substituted with the relevant alkyl group, there being on average at least 2 substitutions out of 3 per residue in each molecule. The propyl and octyl substituents were a mixture of linear and branched chain alkyl groups. All three compounds were sourced from Cyclolab R&D Laboratory (Hungary).

[0176] The fuels tested were (a) gasoline base fuels containing 0, 10 and 85% v/v of ethanol (respectively, E0, E10 and E85); (b) 100% ethanol; and (c) a B7 diesel base fuel (ie a diesel base fuel containing 7% v/v of a FAME, in this case POME). The cyclodextrins were added to the fuels at a concentration of 1000 ppmw and at room temperature. The approximate speeds of their dissolution, and the physical appearance of the resultant solutions, were assessed by eye. The observations are summarised in Table 4 below. "Second-scale dissolution time" indicates that the cyclodextrin dissolved in a matter of seconds (ie less than a minute); "minute-scale dissolution time" means that it dissolved within several minutes but less than an hour; "hour-scale" means that it took more than one hour to dissolve.

Table 4

Fuel	RAEB	RAPB	RAOB
E0 gasoline	Clear and bright; minute-scale dissolution time	Clear and bright; dissolved on contact	Clear and bright; dissolved on contact
E10 gasoline	Clear and bright; dissolved on contact	Clear and bright; dissolved on contact	Clear and bright; dissolved on contact
E85 gasoline	Clear and bright; dissolved on contact	Clear and bright; second-scale dissolution time	Clear and bright; dissolved on contact
Ethanol	Clear and bright; second-scale dissolution time	Clear and bright; minute-scale dissolution time	Clear and bright; minute-scale dissolution time
B7 diesel	Clear and bright; hour-scale dissolution time	Clear and bright; second-scale dissolution time	Clear and bright; dissolved on contact

[0177] It can be seen from Table 4 that all of the alkylated cyclodextrins tested had good solubilities in gasoline, ethanol and ethanol-containing gasoline. The degree of solubility and speed of dissolution appear to be linked to the respective polarities of the cyclodextrin and the fuel. The polarity of the cyclodextrins increases from low (RAOB) to high (RAEB). The polarity of the fuels increases from low (E0 gasoline) to high (ethanol). In the highest polarity fuel, ethanol, the lowest polarity cyclodextrin RAOB proved the hardest to dissolve, as evidenced by its longer dissolution time. In the lowest polarity fuel (E0), the highest polarity cyclodextrin RAEB was the hardest to dissolve. In the relatively low polarity B7 diesel fuel, again the lowest polarity cyclodextrin RAOB was the easiest to dissolve. Thus, the substituents on a modified cyclodextrin (I) may be tailored to increase its affinity for a specific type of fuel in which it is intended to be used, and in turn, as discussed above in connection with Examples 1 and 2, to enhance its efficacy as a detergent additive.

Example 5 - Additive Stability

[0178] Formulations containing 1000 ppmw of TRIMEB dissolved in E10, E25, E50 and E100 gasoline fuels were stored at approximately 20°C, -2°C and -20°C for a period of six months. All of the solutions remained clear and bright throughout the six month storage period, even at the lowest temperature. Similar results were observed in an E0 gasoline fuel containing a PIB amine detergent additive, and also in a diesel base fuel once allowed to return to room temperature.

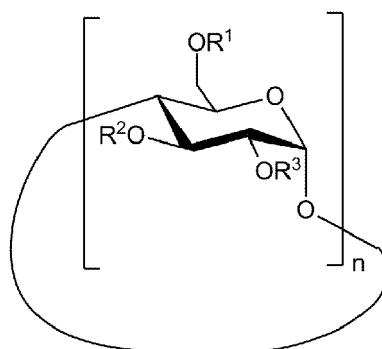
[0179] These results indicate that modified cyclodextrins of formula (I) can be suitable for use in hydrocarbon-based fuel formulations without solubility or stability issues.

[0180] In additional tests, it was found that the inclusion of up to 10,000 ppmw of TRIMEB had no significant effect on the distillation properties of either an E0 gasoline base fuel or a B7 diesel base fuel.

[0181] The results from this and Examples 3 and 4 confirm the utility of modified cyclodextrins of formula (I), in particular alkylated cyclodextrins, as additives in fuel formulations and especially in gasoline and diesel fuel formulations. They also demonstrate the "tuneability" of the compounds, as the substituents R¹ to R³ can be tailored in order to optimise their solubility and stability in any given formulation.

Claims

1. Use, as a detergent additive in a fuel formulation, or in an additive composition for use in a fuel formulation, of a modified cyclodextrin of formula (I):



(I)

wherein n is an integer from 6 to 20, and R^1 , and R^3 are each independently selected from hydrogen, optionally substituted alkyl, optionally substituted aryl and carbonyl, provided that R^1 , R^2 and R^3 are not all hydrogen.

2. Use according to claim 1, wherein in the modified cyclodextrin of formula (I), the groups R^1 , R^2 and R^3 are independently selected from hydrogen and unsubstituted C1 to C12 alkyl groups.
3. Use according to claim 2, wherein two of the groups R^1 , R^2 and R^3 are independently selected from unsubstituted C2 to C8 or C2 to C4 alkyl groups.
4. Use according to any one of the preceding claims, wherein in the modified cyclodextrin of formula (I), the integer n is from 6 to 8, in particular 7.
5. Use according to any one of the preceding claims, wherein the modified cyclodextrin of formula (I) is heptakis(2,6-di-O-n-butyl)- β -cyclodextrin.
6. Use according to any one of the preceding claims, wherein the modified cyclodextrin of formula (I) is used in the fuel formulation or additive composition in combination with an additional fuel additive, for example a second detergent additive.
7. Use according to claim 6, wherein the additional fuel additive is at least partly present as a guest molecule within a host molecule of the modified cyclodextrin (I), in the form of an inclusion complex.
8. Use according to any one of the preceding claims, wherein the fuel formulation, or the fuel formulation in which the additive composition is for use, is a gasoline fuel formulation.
9. Use according to claim 8, wherein the fuel formulation comprises from 0.5 to 10% v/v of an alcohol.
10. Use according to any one of the preceding claims, wherein the modified cyclodextrin (I) is used in a fuel formulation at a concentration of from 500 to 1500 ppmw.
11. Use according to any one of claims 1 to 9, wherein the modified cyclodextrin (I) is used in an additive composition at a concentration of from 1 to 50% w/w.
12. A method for formulating a fuel formulation, the method comprising (a) providing a fuel component or mixture thereof, (b) optionally assessing the level of deposits generated by the component or mixture in a fuel-consuming system in which it is used, (c) adding to the component or mixture a modified cyclodextrin of formula (I) as defined in any one of the preceding claims and (d) assessing the level of deposits generated by the resultant cyclodextrin-containing

formulation in a fuel-consuming system in which it is used.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 19 7730

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 1 801 187 A2 (CLARIANT PRODUKTE DEUTSCHLAND [DE]) 27 June 2007 (2007-06-27) * paragraphs [0001], [0002], [0015], [0043] *	1-12	INV. C10L10/06 C10L10/18
A	WO 2012/168151 A1 (CASTROL LTD [GB]; CHAHINE SAMIR [GB]; WEST KEVIN RICHARD [GB]) 13 December 2012 (2012-12-13) * page 1, line 1 - line 7 * * experiment 7; page 31, line 18 - page 40, line 25 *	1-12	
A,D	EP 0 831 141 A1 (BP CHEMICALS ADDITIVES [GB]) 25 March 1998 (1998-03-25) * claims 1,8 *	1-12	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10L
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 April 2015	Examiner Klaes, Daphne
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