

HYDRIDE DONORS AS AN ADDITIVE FOR REDUCING LOW SPEED PRE-IGNITION EVENTS

TECHNICAL FIELD

[001] This disclosure relates to fuel and lubricant compositions and methods of using the compositions to reduce low speed pre-ignition activity in combustion engines. The compositions include organic hydride donors as fuel or lubricant additives.

BACKGROUND

[001] Pre-ignition in combustion engines is an undesirable event in which undesired ignition of an air-fuel mixture occurs prior to a desired ignition (e.g., via spark plug) of the air-fuel mixture. Pre-ignition can be a problem during high load engine operation since heat from operation of the engine may heat a part of a combustion chamber to a sufficient temperature to ignite the air-fuel mixture upon contact.

[002] In recent years, engine manufacturers have developed smaller engines that provide higher power densities and excellent performance while reducing frictional and pumping losses. This performance improvement is accomplished by increasing boost pressures with use of turbochargers or mechanical superchargers, and by down-speeding the engine using higher transmission gear ratios allowed by higher torque generation at lower engine speeds. A downside is that these engines often operate in low speed and high load driving conditions, making the engines more susceptible to a pre-ignition phenomena known as stochastic pre-ignition or low speed pre-ignition (LSPI). In worst case scenarios, extremely high cylinder peak pressure builds up and leads to catastrophic engine failure. This susceptibility prevents engine manufacturers from fully optimizing engine torque at lower engine speed in such smaller, high-output engines.

SUMMARY

[003] In one aspect, there is provided a fuel composition comprising (1) greater than 50 wt. % of a hydrocarbon fuel boiling in the gasoline or diesel range and (2) a minor amount of one or more of organic hydride-based reductant.

[004] In another aspect, there is provided a method for preventing or reducing low speed pre-ignition events in an internal combustion engine, the method comprising supplying to the engine a fuel composition comprising (1) greater than 50 wt. % of a hydrocarbon fuel boiling in the gasoline or diesel range and (2) a minor amount of one or more of organic hydride-based reductant.

[005] In a further aspect, there is provided a lubricating oil composition comprising (1) greater than 50 wt. % of a base oil and (2) a minor amount of one or more of organic hydride-based reductant.

[006] In yet a further aspect, there is provided a method for preventing or reducing low speed pre-ignition events in a spark-ignited internal combustion engine, the method comprising supplying to the engine a lubricating oil composition comprising (1) greater than 50 wt. % of a base oil and (2) a minor amount of one or more of organic hydride-based reductant.

DETAILED DESCRIPTION

Definitions

[007] In this specification, the following words and expressions, if and when used, have the meanings ascribed below.

[008] The term "boosting" refers to running an engine at higher intake pressures than in naturally aspirated engines. A boosted condition can be reached by use of a turbocharger (driven by exhaust) or by a supercharger (driven by engine). Boosting allows engine manufacturers to use smaller engines that provide higher power densities to provide excellent performance while reducing frictional and pumping losses.

[009] The term "oil soluble" means that for a given additive, the amount needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity. Usually, this means that at least 0.001% by weight of the additive can be incorporated in a lubricating oil composition. The term "fuel soluble" is an analogous expression for additives dissolved, dispersed or suspended in fuel.

[010] "Gasoline" or "gasoline boiling range components" refers to a composition containing at least predominantly C₄-C₁₂ hydrocarbons. In one embodiment, gasoline or gasoline boiling range components is further defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons and further having a boiling range of from about 37.8°C (100° F) to about 204°C (400°F). In an alternative embodiment, gasoline or gasoline boiling range components is defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons, having a boiling range of from about 37.8°C (100° F) to about 204°C (400°F), and further defined to meet ASTM D4814.

[011] The term "diesel" refers to middle distillate fuels containing at least predominantly C₁₀-C₂₅ hydrocarbons. In one embodiment, diesel is further defined to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, and further having a boiling range of from about 165.6°C (330°F) to about 371.1°C (700°F). In an alternative embodiment, diesel is as defined above to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, having a boiling range of from about 165.6°C (330°F) to about 371.1°C (700°F), and further defined to meet ASTM D975.

[012] The term "alkyl" refers to saturated hydrocarbon groups, which can be linear, branched, cyclic, or a combination of cyclic, linear and/or branched.

[013] A "minor amount" means less than 50 wt. % of a composition, expressed in respect of the stated additive and in respect of the total weight of the composition, reckoned as active ingredient of the additive.

[014] A “reductant” is a reducing agent that donates an electron to another chemical species in a redox reaction. A “hydride-based reductant” donates a hydride (anion of hydrogen) to another chemical species during a redox reaction.

[015] In the context of hydrocarbon-based formulations (particularly lubricants), the term “ash” refers to metallic compounds remaining after hydrocarbons have been calcinated. This ash is mainly derived from chemicals used in certain additives, as well as solids. The term “ashless” refers to formulations or additives that do not generate ash or limit generation of ash. Ashless additives are generally free of metals (including boron), silicon, halogen, or contain these elements in concentrations below typical instrument detection limits.

[016] “Halogen” is a collective term for individual substituents that include, for example, fluorine, chlorine, bromine, iodine, and the like.

[017] An “analog” is a compound having a structure similar to another compound but differing from it in respect to a certain component such as one or more atoms, functional groups, substructures, which are replaced with other atoms, groups, or substructures.

[018] A “homolog” is a compound belonging to a series of compounds that differ from each other by a repeating unit. Alkanes are examples of homologs. For example, ethane and propane are homologs because they differ only in the length of a repeating unit ($-\text{CH}_2-$). A homolog may be considered a specific type of analog.

[019] A “derivative” is a compound that is derived from a similar compound via a chemical reaction (e.g., acid-base reaction, hydrogenation, etc.). In the context of substituent groups, a derivative may be a combination of one or more moiety. For example, a phenol moiety may be considered a derivative of aryl moiety and hydroxyl moiety. A person of ordinary skill in the related art would know the metes and bounds of what is considered a derivative.

[020] An “engine” or a “combustion engine” is a heat engine where the combustion of fuel occurs in a combustion chamber. An “internal combustion engine” is a heat engine where the combustion of fuel occurs in a confined space (“combustion

chamber"). A "spark ignition engine" is a heat engine where the combustion is ignited by a spark, usually from a spark plug. This is contrast to a "compression-ignition engine," typically a diesel engine, where the heat generated from compression together with injection of fuel is sufficient to initiate combustion without an external spark.

Introduction

[021] One possible cause of low speed pre-ignition (LSPI) is auto-ignition of engine oil droplets that enter an engine combustion chamber from a piston crevice under high pressure, during periods when the engine is operating at low speeds and compression stroke time is longest. Factors such as turbocharger use, engine design, engine coatings, piston shape, fuel choice, or engine oil additives may contribute to an increase in LSPI events. Although some engine knocking and pre-ignition problems can be resolved through use of new engine technology or optimization of engine operating conditions, reducing LSPI through new fuel and/or lubricant oil compositions may be the most cost-effective approach.

[022] The present disclosure describes hydrocarbon-based compositions (e.g., fuel, lubricating oil) and methods of use thereof, wherein the hydrocarbon-based compositions prevent LSPI events or reduce LSPI activity during operation of a combustion engine. A suitable hydrocarbon-based composition will feature an organic hydride-based reductant additive in accordance with this disclosure.

Organic Hydride-Based Reductant

[023] Provided herein are organic hydride-based reductants that prevent LSPI events or reduce LSPI activity in combustion engines. These organic hydride-based reductants are organic molecules prone to donate hydrides during a hydride transfer step. These reductants are ashless additives and usually contain carbon, hydrogen, nitrogen and/or oxygen atoms. Depending on the application, the organic hydride-based reductant is oil soluble or fuel soluble.

[024] Hydride transfer is a key step in many well-known organic reactions including important biochemical and industrial redox reactions. In these types of

reactions, reductants provide a hydride (H^-) that is transferred to substrates such as carbonyl compounds, carbon dioxide, imines, compounds containing activated C=C bonds and the like. Precise mechanism of hydride transfer is often complex and may vary with temperature, substrate, hydride donor, availability of protons, presence of Lewis acid and the like. In some cases, hydride transfer may proceed by direct transfer of hydride ion from hydride donor to the substrate or may occur in consecutive steps (e.g., transfer of electron to the substrate followed by a hydrogen atom or by a proton and second electron).

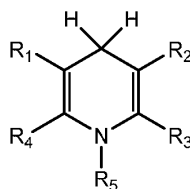
[025] Without being limited by theory, it is believed that a suitable hydride donor in accordance with the present invention can lower LSPI activity in a combustion engine by acting against oxidatively unstable chemical species that can initiate LSPI events. This may involve reduction of the oxidative unstable chemical species to a more stable, less reactive reduced species, thus inhibiting LSPI events.

[026] According to one or more embodiments of the present invention, the organic hydride-based reductant includes at least one of the following organic hydride donors: dihydropyridine (DHPD), reduced nicotinamide adenine dinucleotide (NADH), methylene tetrahydromethanopterin, acridine, triarylmethane, triamine, aryl benzoimidazoline, dioxolane, diethercyclohexadiene, cycloheptatriene, flavin adenine dinucleotide ($FADH_2$), hexahydro triazaphenalene, an analog thereof, a homolog thereof, and a derivative thereof.

[027] The following chemical structures of organic hydride-based reductants are provided for illustration. Each reductant or reductant-type is represented by a generalized structure that includes generic R groups (e.g., R_1 , R_2 , R_3 , etc.) in various substitution positions. Each R group may be a component selected from a group of suitable substituents. Varying the combination of the R group substituents can result in a set of related structures, wherein each resulting structure is an analog of the other structures within the set. Desirability of a particular substituent may depend on a number of factors including, but not limited to, organic hydride-based donor's target ability to donate hydrides, stability, solubility in oil or fuel, and the like.

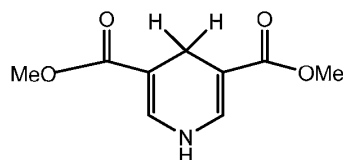
Dihydropyridine (DHPD)

[028] DHPD or DHPD-type reductant is illustrated by a generalized structure (Formula 1). Referring to Formula 1, R_1 , and R_2 , are each components independently selected from the following group: H, ester moiety, amide moiety, cyanide moiety, any derivative thereof, and the like. R_3 and R_4 are each components independently selected from the following group: H, alkyl moiety, any derivative thereof, and the like. R_5 is a component selected from the following group: H, alkyl moiety, allyl moiety, aryl moiety, benzyl moiety, alkanol moiety, any derivative thereof, and the like.

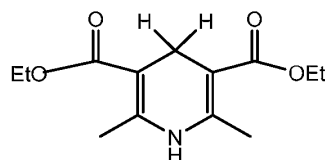


Formula 1

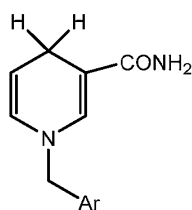
[029] Suitable analogs of DHPD include



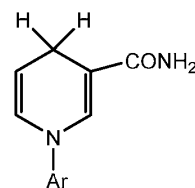
Formula 1A



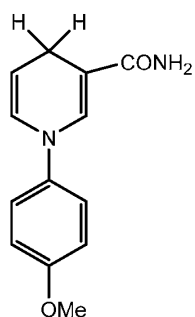
Formula 1B



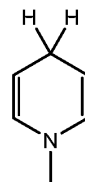
Formula 1C



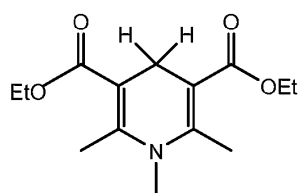
Formula 1D



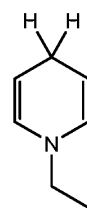
Formula 1E



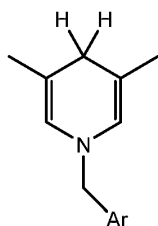
Formula 1F



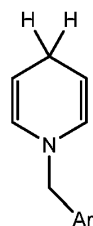
Formula 1G



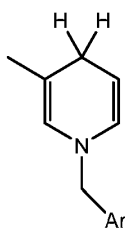
Formula 1H



Formula 1I



Formula 1J

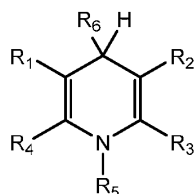


Formula 1K

Reduced Nicotinamide Adenine Dinucleotide (NADH)

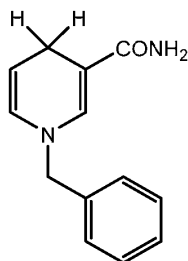
[030] NADH or NADH-type reductant is illustrated by a generalized structure (Formula 2). Referring to Formula 2, R₁ and R₂ are each components independently

selected from the following group: H, ester moiety, amide moiety, cyanide moiety, any derivative thereof, and the like. R_3 and R_4 are each components independently selected from the following group: H, alkyl moiety, any derivative thereof, and the like. R_5 is a component selected from the following group: H, alkyl moiety, allyl moiety, aryl moiety, benzyl moiety, alkanol moiety, any derivative thereof, and the like. R_6 is selected from the following group: H, alkyl moiety, any derivative thereof, and the like. In some embodiments, R_1 and R_4 or R_2 and R_3 may form a cyclic or heterocyclic structure (e.g., Formula 2C and 2E).

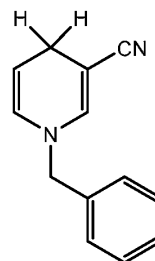


Formula 2

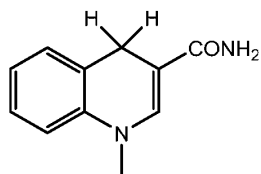
[031] Suitable analogs of NADH include



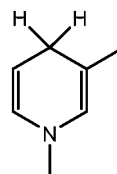
Formula 2A



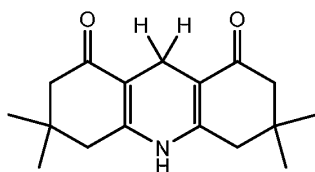
Formula 2B



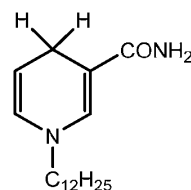
Formula 2C



Formula 2D



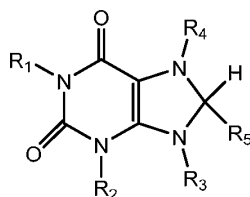
Formula 2E



Formula 2F

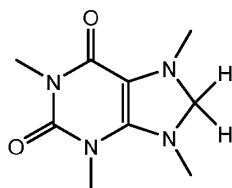
Methylene Tetrahydromethanopterin

[032] Methylene tetrahydromethanopterin or methylene tetrahydromethanopterin-type reductant is illustrated by a generalized structure (Formula 3). Referring to Formula 3, R_1 , R_2 , R_3 , and R_4 are each components independently selected from the following group: H, alkyl moiety, allyl moiety, alkanol moiety, any derivative thereof, and the like. R_5 is selected from the following group: H, alkyl moiety, any derivative thereof, and the like.

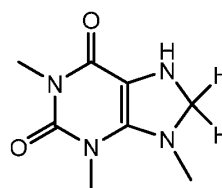


Formula 3

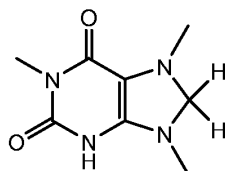
[033] Suitable analogs of methylene tetrahydromethanopterin include



Formula 3A



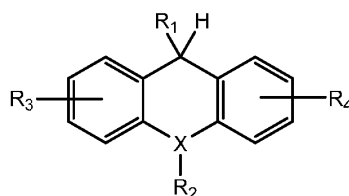
Formula 3B



Formula 3C

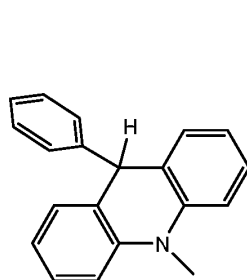
Acridine

[034] Acridine or acridine-type reductant is illustrated by a generalized structure (Formula 4). Referring to Formula 4, X is N or O (Formula 4H). When X is N, R₁ is selected from the following group: H, alkyl moiety, allyl moiety, aryl moiety, benzyl moiety, any derivative thereof, and the like. R₂ is selected from the following group: H, alkyl moiety, allyl moiety, aryl moiety, benzyl moiety, alkanol moiety, any derivative thereof, and the like. R₃ and R₄ are each components independently selected from the following group: H, alkyl moiety, aryl moiety, benzyl moiety, amine moiety, alkoxy moiety, heteroatoms, any derivative thereof, and the like. Moreover, R₃ as well as R₄ may independently occupy more than one substitution position within its respective rings. In some embodiments, R₁ and R₃ or R₁ and R₄ may form a cyclic structure (e.g., Formulas 4E and 4F).

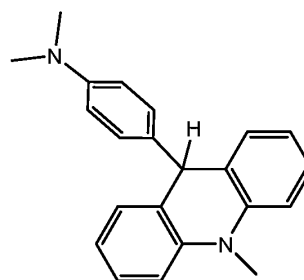


Formula 4

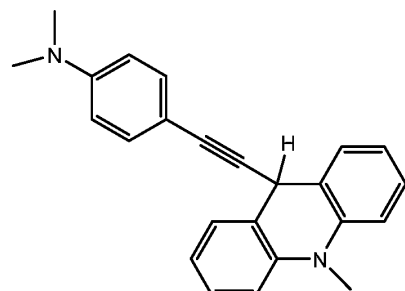
[035] Suitable analogs of acridine include



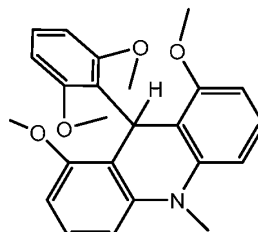
Formula 4A



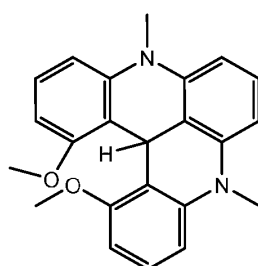
Formula 4B



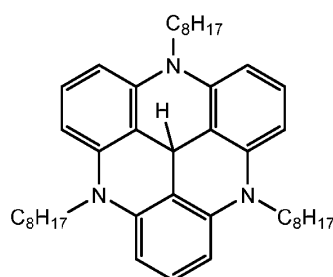
Formula 4C



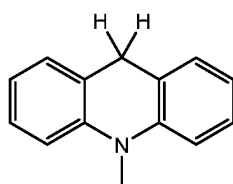
Formula 4D



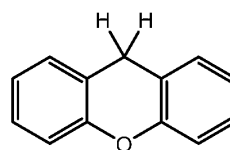
Formula 4E



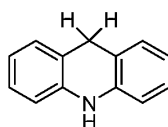
Formula 4F



Formula 4G



Formula 4H

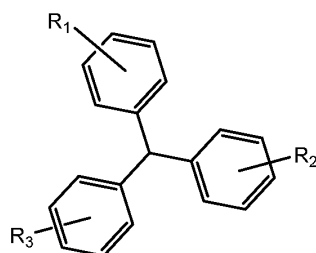


Formula 4I

Triarylmethane

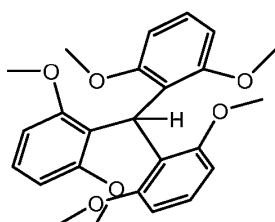
[036] Triarylmethane or triarylmethane-type reductant is illustrated by a generalized structure (Formula 5). Referring to Formula 5, R_1 , R_2 , and R_3 are independently selected from the following group: H, alkyl moiety, aryl moiety, benzyl

moiety, allyl moiety, amide moiety, ester moiety, ether moiety, hydroxyl moiety, amine moiety, any derivative thereof, and the like. In some embodiments, R_1 , R_2 , and R_3 may independently occupy more than one substitution position in their respective rings (e.g., Formula 5A and 5B).

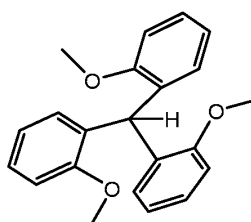


Formula 5

[037] Suitable analogs of triarylmethane include



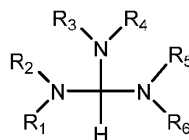
Formula 5A



Formula 5B

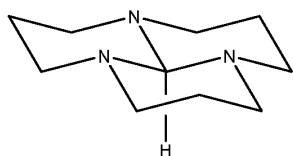
Triamine

[038] Triamine or triamine-type reductant is illustrated by a generalized structure (Formula 6), wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are connected to form three cyclic rings (e.g., Formula 6A to 6C).

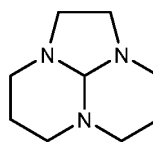


Formula 6

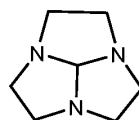
[039] Suitable analogs of triamine includes



Formula 6A



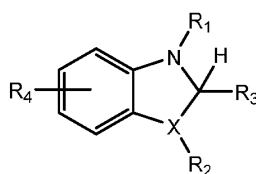
Formula 6B



Formula 6C

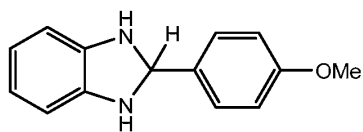
Aryl Benzoimidaline

[040] Aryl benzoimidaline or aryl benzoimidaline-type reductant is illustrated by a generalized structure (Formula 7). Referring to Formula 7, X is N, O, or S. If X is N, R₁ and R₂ are each components independently selected from the following group: H, alkyl moiety, any derivative thereof, and the like. R₃ is selected from the following group: H, alkyl moiety, alkene moiety, alkyne moiety, aryl moiety, benzyl moiety, any derivative thereof and the like. R₄ is selected from the following group: H, alkyl moiety, aryl moiety, benzyl moiety, allyl moiety, any derivative thereof, and the like. In some embodiments, R₄ may independently occupy more than one substitution position.

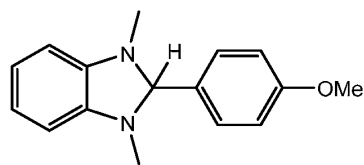


Formula 7

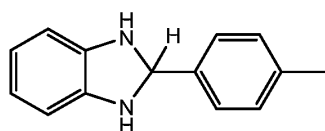
[041] Suitable analogs of aryl benzoimidaline includes



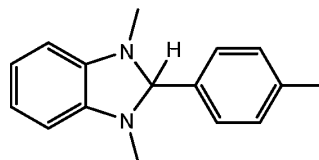
Formula 7A



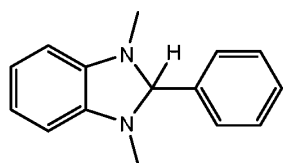
Formula 7B



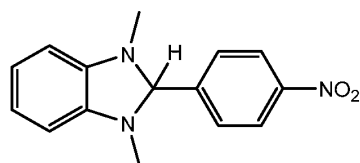
Formula 7C



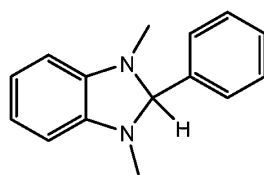
Formula 7D



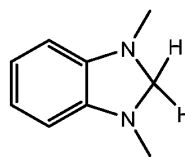
Formula 7E



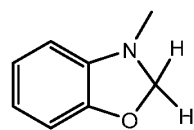
Formula 7F



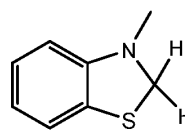
Formula 7G



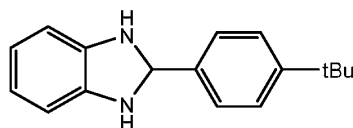
Formula 7H



Formula 7I



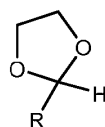
Formula 7J



Formula 7K

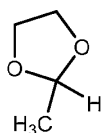
Dioxolane

[042] Dioxolane or dioxolane-type reductant is illustrated by a generalized structure (Formula 8). Referring to Formula 8, R is a component selected from the following group: H, alkyl moiety, allyl moiety, benzyl moiety, alkanol moiety, any derivative thereof, and the like.

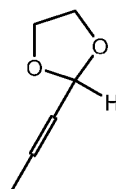


Formula 8

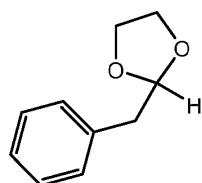
[043] Suitable analogs of dioxolane include



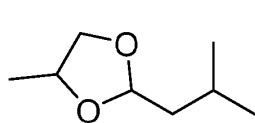
Formula 8A



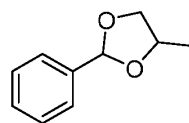
Formula 8B



Formula 8C



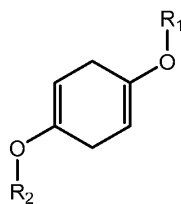
Formula 8D



Formula 8E

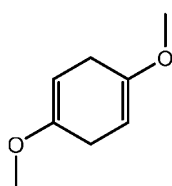
Diethercyclohexadiene

[044] Diethercyclohexadiene or diethercyclohexadiene-type reductant is illustrated by a generalized structure (Formula 9). Referring to Formula 9, R is a component selected from the following group: H, alkyl moiety, allyl moiety, benzyl moiety, alkanol moiety, any derivative thereof, and the like.

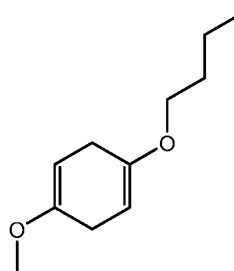


Formula 9

[045] Suitable analogs of diethercyclohexadiene includes



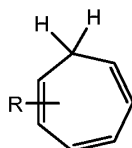
Formula 9A



Formula 9B

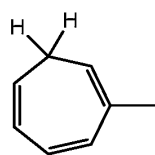
Cycloheptatriene

[046] Cycloheptatriene or cycloheptatriene-type reductant is illustrated by a generalized structure (Formula 10). Referring to Formula 10, R is a component selected from the following group: H, alkyl moiety, allyl moiety, benzyl moiety, alkanol moiety, any derivative thereof, and the like. In some embodiments, R may occupy more than one substitution position (e.g., Formula 10B).

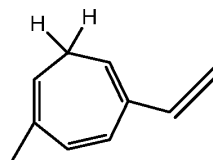


Formula 10

[047] Suitable analogs of cycloheptatriene includes



Formula 10A



Formula 10B

[048] The hydride donors described herein may be synthesized or purchased from chemical vendors. The following examples are provided for illustrative purposes and are not intended to be limiting. DHPD and DHPD-type reductants can be synthesized via a scheme utilizing an off-on switchable acyl donor in the form of different 1,4 dihydropyridine amides (*Org. Biomol. Chem.* **2015**, 13, 185-198). Dimethyl 3,5-dicarboxylatepyridine can be purchased from Sigma-Aldrich (St. Louis, MO) or prepared via known procedures (*J. Am. Chem. Soc.* **2000**, 122, 9014-9018). Formula 6A can be synthesized by a known scheme (*Syn. Comm.* **1994**, 24, 3109-3114). Para-methoxybenzene benzoimidazoline or para-tertbutylbenzene benzoimidazoline can be obtained adapting a known synthesis procedure (*Syn. Comm.* **1983**, 13, 1033-1039). Formula 2F can be obtained by adapting a known synthesis procedure (*Org. Lett.* **2013**, 15, 180-183).

Fuel Compositions

[049] The organic hydride-based donors of the present disclosure may be useful as additives in hydrocarbon fuels to prevent or reduce undesirable ignition events in combustion engines. When used in fuels, the proper concentration of the additive necessary in order to achieve the desired LSPI reduction or efficacy is dependent upon a variety of factors including the type of fuel used, the presence of other detergents or dispersants or other additives, etc. Generally, the range of concentration of the additives of the present disclosure in hydrocarbon fuel may range from 25 to 5000 parts per million (ppmw) by weight (including, but not limited to, 50

to 4000 ppm, 100 to 3500, 150 to 3000, 200 to 2500, 250 to 2000, 300 to 1500, 350 to 1000 and so forth). If other hydride donors are present in the fuel composition, a lesser amount of the additive may be used.

[050] In some embodiments, the compounds of the present disclosure may be formulated as a concentrate using an inert stable oleophilic (i.e., soluble in hydrocarbon fuel) organic solvent boiling in a range of 65°C to 205°C. An aliphatic or an aromatic hydrocarbon solvent may be used, such as benzene, toluene, xylene, or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing 2 to 8 carbon atoms, such as ethanol, isopropanol, methyl isobutyl carbinol, *n*-butanol and the like, in combination with the hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive may range from 10 to 70 wt. % (e.g., 20 to 40 wt. %).

[051] In gasoline or gasoline fuels, other well-known additives can be employed including oxygenates (e.g., ethanol, methyl *tert*-butyl ether), other anti-knock agents, and detergents/dispersants (e.g., hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, succinimides, Mannich reaction products, aromatic esters of polyalkylphenoxyalkanols, or polyalkylphenoxyaminoalkanes). Additionally, friction modifiers, antioxidants, metal deactivators and demulsifiers may be present.

[052] In diesel fuels, other well-known additives can be employed, such as pour point depressants, flow improvers, cetane improvers, lubricity additives and the like.

[053] A fuel-soluble, non-volatile carrier fluid or oil may also be used with compounds of this disclosure. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the non-volatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, synthetic polyoxyalkylene-derived oils, such as those described in U.S. Patent Nos. 3,756,793; 4,191,537; and 5,004,478; and in European Patent Appl. Pub. Nos. 356,726 and 382,159.

[054] The carrier fluids may be employed in amounts ranging from 35 to 5000 ppm by weight of the hydrocarbon fuel (e.g., 50 to 3000 ppm of the fuel). When employed in a fuel concentrate, carrier fluids may be present in amounts ranging from 20 to 60 wt. % (e.g., 30 to 50 wt. %).

Lubricating Oil Compositions

[055] The organic hydride-donors of the present disclosure may be useful as additives in lubricating oils to prevent or reduce undesirable ignition events in combustion engines. When employed in this manner, the additives are usually present in the lubricating oil composition in concentrations ranging from 0.001 to 10 wt. % (including, but not limited to, 0.01 to 5 wt. %, 0.2 to 4 wt. %, 0.5 to 3 wt. %, 1 to 2 wt. %, and so forth), based on the total weight of the lubricating oil composition. If other hydride donors are present in the lubricating oil composition, a lesser amount of the additive may be used.

[056] Oils used as the base oil will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g. a lubricating oil composition having an Society of Automotive Engineers (SAE) Viscosity Grade of 0W, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, or 15W-40.

[057] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[058] Definitions for the base stocks and base oils in this disclosure are the same as those found in American Petroleum Institute (API) Publication 1509 Annex E ("API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils," December 2016). Group I base stocks contain less than 90% saturates

and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[059] Natural oils include animal oils, vegetable oils (e.g., castor oil and lard oil), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrotreated, or solvent extracted.

[060] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈ to C₁₄ olefins, e.g., C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof, may be utilized.

[061] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

[062] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or

waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[063] Base oils for use in the lubricating oil compositions of present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils, and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils, and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[064] Typically, the base oil will have a kinematic viscosity at 100°C (ASTM D445) in a range of 2.5 to 20 mm²/s (e.g., 3 to 12 mm²/s, 4 to 10 mm²/s, or 4.5 to 8 mm²/s).

[065] The present lubricating oil compositions may also contain conventional lubricant additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with antioxidants, ashless dispersants, anti-wear agents, detergents such as metal detergents, rust inhibitors, dehazing agents, demulsifying agents, friction modifiers, metal deactivating agents, pour point depressants, viscosity modifiers, antifoaming agents, co-solvents, package compatibilizers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

[066] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is an ashless dispersant, a functionally effective amount of this ashless dispersant would be an amount sufficient to impart the desired dispersancy characteristics to the lubricant. Generally, the concentration of each of these additives,

when used, may range, unless otherwise specified, from about 0.001 to about 20 wt. %, such as about 0.01 to about 10 wt. %.

EXAMPLES

[067] The following illustrative examples are intended to be non-limiting.

[068] While LSPI can impact many types combustion engines, it can be particularly problematic in direct-injected, boosted (turbocharged or supercharged), spark-ignited (gasoline) internal combustion engines that, in operation, generate a brake mean effective pressure level of greater than 1000 kPa (10 bar) at engine speeds of from 1500 to 2500 rotations per minute (rpm), such as at engine speeds of from 1500 to 2000 rpm. Brake mean effective pressure (BMEP) is defined as the work accomplished during on engine cycle, divided by the engine swept volume, the engine torque normalized by engine displacement. The word "brake" denotes the actual torque or power available at the engine flywheel, as measured on a dynamometer. Thus, BMEP is a measure of the useful energy output of the engine.

[069] It has now been found that the fuel compositions or lubricating oil compositions of this disclosure can prevent or minimize pre-ignition problems in internal combustion engines.

EXAMPLES 1-8

[070] The test compounds were blended in gasoline or lube oil and their capacity for reducing LSPI events were determined using the test method described below.

[071] A General Motors (GM) 2.0L LHU 4-cylinder gasoline turbocharged direct-injected engine was used for LSPI testing. Each cylinder was equipped with a combustion pressure sensor.

[072] A six-segment test procedure was used to determine the number of LSPI events that occurred under conditions of an engine speed of 2000 rpm and a load of 275 Nm. The LSPI test condition is run for 28 minutes with each segment separated by

an idle period. Each segment is slightly truncated to eliminate the transient portion. Each truncated segment typically has approximately 110,000 combustion cycles (27,500 combustion cycles per cylinder). In total, the six truncated segments have approximately 660,000 combustion cycles (165,000 combustion cycles per cylinder).

[073] LSPI-impacted combustion cycles were determined by monitoring peak cylinder pressure (PP) and crank angle at 5% total heat release (AI5). LSPI-impacted combustion cycles are defined as having both (1) a PP greater than five standard deviations than the average PP for a given cylinder and truncated segment and (2) an AI5 greater than five standard deviations less than the average for a given cylinder and truncated segment.

[074] The LSPI frequency is reported as the number of LSPI-impacted combustion cycles per million combustion cycles and is calculated as follows:

$$\text{LSPI Frequency} = \left[\frac{(\text{Total Number of LSPI Impacted Combustion Cycles in Six Truncated Segments})}{(\text{Total Number of Combustion Cycles in Six Truncated Segments})} \right] \times 1,000,000$$

[075] An additive associated with a test fuel and/or test lubricant that reduces the LSPI frequency, when compared to the corresponding baseline fuel and/or baseline lubricant, is considered an additive that mitigates LSPI frequency. For testing herein, the baseline fuel was a conventional 49-state premium unleaded gasoline fuel without any deposit control additives and the baseline lubricant was representative of a conventional engine oil meeting ILSAC GF-5 and API SN specifications. The test results are set forth in Table 1.

[076] The examples summarize test results for various fuel or lubricating oil additives. For example, Example 1 shows result for DHPD as a fuel additive at 1000 ppmw in a test fuel fluid. The number of LSPI events observed when testing fuel or lubricant with additive is listed in column titled "LSPI Activity" while the number of LSPI events observed when testing fuel or lubricant without additive is listed in column

titled "Reference." For a given example, inclusion or omission of the additives is the only difference between the fuel or lubricant compositions tested in the LSPI Activity and Reference columns.

TABLE 1

	Additive Component (Formula #)	Additive Conc.	Base Fluid	LSPI Activity (events/million combustion cycles)	Reference (events/million combustion cycles)	Drop in LSPI Activity
Ex. 1	DHPD (1A)	1000 ppmw	Fuel	41	254	84%
Ex. 2	DHPD (1A)	500 ppmw	Fuel	30	358	92%
Ex. 3	Triamine (6A)	500 ppmw	Fuel	179	239	25%
Ex. 4	Triamine (6A)	1000 ppmw	Oil	322	461	30%
Ex. 5	NADH analog (2F)	500 ppmw	Fuel	207	389	47%
Ex. 6	NADH analog (2F)	1000 ppmw	Oil	78	220	64%
Ex. 7	aryl benzoimidazoline (7A)	1358 ppmw	Fuel	28	319	91%