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(54) **BIODIESEL FUEL ADDITIVE**

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(57) **ABSTRACT**

The present invention relates generally to a composition and method for decreasing the emissions from combustion of fuel that contains biodiesel, where the composition contains at least one ignition accelerator and at least one plant extract or synthetic component similar to a portion of a plant extract. The ignition accelerator is preferably a peroxide, for example, di-tert-butyl peroxide. The composition may optionally contain meadowfoam oil or jojoba oil. The composition may also enhance the lubricity of the fuel that contains biodiesel.

## BIODIESEL FUEL ADDITIVE

### RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. application Ser. No. 11/322,048, filed on Dec. 29, 2005, and is a continuation-in-part of U.S. application Ser. No. 10/171,507, filed Jun. 12, 2002, which is a continuation-in-part of U.S. application Ser. No. 10/084,603, filed Feb. 26, 2002, which claims the benefit of U.S. Provisional application Ser. No. 60/278,011, filed Mar. 22, 2001; and is a continuation-in-part of U.S. application Ser. No. 10/084,838, filed Feb. 26, 2002, which claims priority to International Patent Application No. PCT/US01/40509, filed on Apr. 12, 2001 under the Patent Cooperation Treaty (PCT), which was published by the International Bureau in English on Oct. 25, 2001, which designates the U.S. and claims the benefit of U.S. Provisional Application No. 60/197,788, filed Apr. 14, 2000.

### FIELD OF THE INVENTION

[0002] The present invention relates generally to a composition and a method for decreasing emissions from combustion of diesel fuel that contains at least some biodiesel as a component.

### BACKGROUND OF THE INVENTION

[0003] The interest in improving fuel efficiency has become paramount as our natural resources dwindle and the cost of fuel continues to rise. Fuel efficiency can be improved by adding a fuel additive. Several existing fuel additives are known to increase fuel efficiency, for example, U.S. Pat. Nos. 4,274,835, 5,826,369, and 6,193,766 describe fuel additives that improve combustion. Despite the successes of these inventions, there still remains a need for fuel additives that improve combustion.

[0004] Hydrocarbon fuels typically contain a complex mixture of hydrocarbons—molecules containing various configurations of hydrogen and carbon atoms. They may also contain various additives, including detergents, anti-icing agents, emulsifiers, corrosion inhibitors, dyes, deposit modifiers, and non-hydrocarbons such as oxygenates.

[0005] When such hydrocarbon fuels are combusted, a variety of pollutants are generated. These combustion products include ozone, particulates, carbon monoxide, nitrogen oxides (NO, NO<sub>2</sub>, and N<sub>2</sub>O, collectively known as NO<sub>x</sub>), sulfur dioxide, and lead. Both the U.S. Environmental Protection Agency (EPA) and the California Air Resources Board (CARB) have adopted ambient air quality standards directed to these pollutants. Both agencies have also adopted specifications for lower-emission gasolines. The Phase 2 California Reformulated Gasoline (CaRFG2) regulations became operative in Mar. 1, 1996. Governor Davis signed Executive Order D-5-99 on Mar. 25, 1999, which directs the phase-out of methyl tertiary butyl ether (MTBE) in California's gasoline by Dec. 31, 2002. The Phase 3 California Reformulated Gasoline (CaRFG3) regulations were approved on Aug. 3, 2000, and became operative on Sep. 2, 2000.

[0006] Diesel engines run under lean fuel conditions. As a result, emissions of hydrocarbons and carbon monoxide are normally low. However, diesel exhaust contains relatively

high levels of nitrogen oxides and particulates. Emission standards have been adopted in the US and Europe to lower emissions of nitrogen oxides and particulates. The states of Texas and California have enacted their own strict limits on diesel emissions.

[0007] Biodiesel is a vegetable oil- or animal fat-based fuel in which the native free fatty acids are converted to mono-alkyl esters, most commonly methyl esters. The biodiesel may generally be blended with petroleum based diesel to create the final fuel. The most common blend is 20% biodiesel, 80% petroleum-based diesel, generally referred to as B20, where the number after B refers to the percent biodiesel in the blend. Pure biodiesel is B100. The biodiesel can be blended with petroleum-based diesel at any level, for example, but not limited to 5%, 10%, 15%, etc.

[0008] Emissions from combustion of pure biodiesel and biodiesel blends are generally lower than from combustion of petroleum-based diesel. See, for example, EPA's report titled "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions", available at [www.epa.gov/otag/models/biodsl.htm](http://www.epa.gov/otag/models/biodsl.htm). The decreases in regulated emissions from combustion of biodiesel compared to conventional diesel ranged from a 12% decline in particulate matter for B20 to a 67% decline in total unburned hydrocarbons for B100. NO<sub>x</sub> emissions for combustion of B100 were 10% higher than for combustion of conventional diesel. The NO<sub>x</sub> emissions for combustion of B20 were 2% higher than for combustion of conventional diesel. More recent data suggest that the increase in NO<sub>x</sub> emissions for B20 can be even higher, 2.4-3% higher than for combustion of conventional diesel.

[0009] Government regulations on emissions from diesel-fueled vehicles are likely to become stricter in the future. Further, NO<sub>x</sub> emissions from vehicles that are fueled with biodiesel and biodiesel blends are slightly higher than for vehicles that are fueled with conventional diesel fuels. There is a need for additives that can be blended with diesel fuels that contain biodiesel to decrease emissions, particularly emissions of NO<sub>x</sub>.

### SUMMARY OF THE INVENTION

[0010] One aspect of the present invention involves a fuel additive for reducing the pollutant emission produced during the combustion of fuel comprising biodiesel. In one embodiment, there is a fuel additive for biodiesel fuel, the fuel additive comprising: a first component comprising an ignition accelerator; and, a second component selected from the group consisting of a plant extract, a synthetic form of a plant extract, and a combination thereof. In some embodiments, the ignition accelerator comprises a peroxide. In some embodiments, the peroxide is selected from the group consisting of hydrogen peroxide, benzoyl peroxide, di-tert-butyl peroxide, cumene hydroperoxide, di-oleal peroxide, soybean hydroperoxide, di-ethyl peroxide and any combination thereof. In some embodiments, the peroxide comprises di-tert-butyl peroxide. In some embodiments, the fuel additive further comprises a third component, the third component comprising a compound selected from the group consisting of long chain fatty acids, long chain fatty esters, and any combination thereof. In some embodiments, the fuel additive comprises a synthetic long chain fatty acid, a synthetic long chain fatty ester, or both a synthetic long

chain fatty acid and a synthetic long chain fatty ester. In some embodiments, the third component further comprises an oil selected from the group consisting of meadowfoam oil, jojoba oil, and a combination thereof. In some embodiments, the fuel additive further comprises a solvent. In some embodiments, the solvent comprises an aromatic solvent. In some embodiments, the fuel additive further comprises an alkyl nitrate. In some embodiments comprising an alkyl nitrate, the alkyl nitrate comprises 2-ethylhexylnitrate. In some embodiments, the plant extract comprises a green extract of a plant. In some embodiments comprising a green extract, the green extract is chlorophyll. In some embodiments, the plant extract comprises an extract of a plant of the Leguminosae family. In some embodiments, the second component is selected from the group consisting of beta-carotene, alpha-carotene, a carotenoid, a chlorophyll, a color body, isomixtene, and any combination thereof. In some embodiments, the plant extract comprises one or more chlorophylls. In some embodiments, the fuel additive has a ratio of chlorophyll a to chlorophyll b of approximately 0.1 to approximately 80. In some embodiments, the second component comprises chlorophyll and carotenoid. In some embodiments, the fuel additive has a ratio of chlorophyll to carotenoid of approximately 0.1 to approximately 100. In some embodiments, the fuel additive further comprises a stabilizing component. In some embodiments having a stabilizing compound, the stabilizing component comprises at least one compound selected from the group consisting of: 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline; ethoxyquinoline; 2-tert-butylphenol; 2,6-di-tert-butylphenol; 2-tert-butyl-4-n-butylphenol; 2,4,6-tri-tert-butylphenol; 2,6-di-tert-butyl-4-n-butylphenol; 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butylphenol; 2,2'-methylene-bis(6-t-butyl-4-methylphenol); n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate; 1,1,3-tris(3-t-butyl-6-methyl-4-hydroxyphenyl) butane; pentaerythritoltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]; di-n-octadecyl(3,5-di-t-butyl-4-hydroxybenzyl)phosphonate; 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) mesitylene; tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate; N,N'-diphenylphenylenediamine; p octyldiphenylamine; p,p dioctyldiphenylamine; N-phenyl-1-naphthylamine; N-phenyl-2-naphthylamine; N-(p dodecyl)phenyl-2-naphthylamine; di-1-naphthylamine; and di-2-naphthylamine; phenothiazines; N-alkylphenothiazines; imino(bisbenzyl); 6-(t-butyl)phenol; 2,6-di-(t-butyl)phenol; 4-methyl-2,6-di-(t-butyl) phenol; 4,4'-methylenebis(—2,6-di-(t-butyl)phenol); a diphenylamine; a dinaphthylamine; and a phenylnaphthylamine.

[0011] In another aspect of the present invention, there is a fuel composition comprising: about 0.32 to about 799 g of ignition accelerator; about 0.001 g to about 60 g of plant extract or synthetic form of a plant extract, or mixtures thereof per gallon of the fuel comprising biodiesel. In some embodiments, the fuel composition further comprises 2-ethylhexylnitrate. In some embodiments comprising 2-ethylhexylnitrate, the level of 2-ethylhexylnitrate is about 1 ppm to about 5000 ppm.

[0012] In another aspect of the present invention, there is a method of decreasing pollutant emissions in the combustion of biodiesel fuel comprising combusting a fuel comprising: combining the biodiesel fuel with a fuel additive, the fuel additive comprising: a first component comprising an ignition accelerator; and a second component selected from

the group consisting of a plant extract, a synthetic form of a plant extract, and mixtures thereof.

[0013] In another aspect of the present invention, there is a method of increasing lubricity of a fuel comprising biodiesel comprising: adding an additive to said fuel comprising biodiesel, said additive comprising: a first component comprising an ignition accelerator; a second component selected from the group consisting of a plant extract, a synthetic form of a plant extract, and mixtures thereof; and, at least one oil selected from the group consisting of meadowfoam oil, jojoba oil, and mixtures thereof.

[0014] The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention. It should be appreciated that the conception and specific embodiment disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized that such equivalent constructions do not depart from the invention as set forth in the appended claims. The novel features which are believed to be characteristic of the invention, both as to its organization and method of operation, together with further objects and advantages will be better understood from the following description when considered in connection with the accompanying figures. It is to be expressly understood, however, that each of the figures is provided for the purpose of illustration and description only and is not intended as a definition of the limits of the present invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

### Introduction

[0015] The following description and examples illustrate preferred embodiments of the present invention in detail. Those of skill in the art will recognize that there are numerous variations and modifications of this invention that are encompassed by its scope. Accordingly, the description of preferred embodiments should not be deemed to limit the scope of the present invention.

[0016] Although described in the context of an additive and a method for decreasing emissions from combustion of diesel fuels that may comprise biodiesel, the additive and the method according to embodiments of the present invention may also be applied to other hydrocarbon fuels, for example, diesel fuels that are derived from petroleum or alternative fuels that may not comprise biodiesel. The additive and method may also have application to gasoline fuels, residual fuels, and other hydrocarbon fuels. The application to fuels that comprise biodiesel is a preferred embodiment.

### Diesel Fuels

[0017] Diesel fuels that are derived from petroleum include that portion of crude oil that distills within the temperature range of approximately 150° C. to 370° C. (698° F.), which is higher than the boiling range of gasoline. Diesel fuels can also be obtained from synthetic fuels such as shale oil, Fischer-Tropsch fuels derived from synthesis

gas, products of coal liquefaction, etc. Any source of diesel fuel may potentially be suitable as a base fuel for blending with biodiesel.

[0018] Diesel fuel is ignited in an internal combustion engine cylinder by the heat of air under high compression—in contrast to motor gasoline, which is ignited by an electrical spark. Because of the mode of ignition, a high cetane number is generally preferred in a good diesel fuel. Diesel fuel is close in boiling range and composition to the lighter heating oils. There are generally two grades of diesel fuel established by the ASTM: Diesel 1 and Diesel 2. Diesel 1 is a kerosene-type fuel, lighter, more volatile and cleaner burning than Diesel 2. Diesel 1 is used in engine applications where there are frequent changes in speed and load. Diesel 2 is used in industrial and heavy mobile service.

[0019] Suitable diesel fuels may include both high and low sulfur fuels. Low sulfur fuels generally include those containing 500 ppm (on a weight basis) or less sulfur, and may contain as little as 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 ppm or less sulfur, or even 0 ppm sulfur, for example, in the case of synthetic diesel fuels. High sulfur diesel fuels typically include those containing more than 500 ppm sulfur, for example, as much as 1, 2, 3, 4, or 5 wt. % sulfur or more. Diesel fuels that contain low levels of sulfur may provide a lower degree of lubricity than diesel fuels that contain higher levels of sulfur.

[0020] Fuels that boil in an approximate range of 150° C. to 330° C. may work best in diesel engines because they are completely consumed during combustion, with no waste of fuel or excess emissions. Paraffins, which offer the best cetane rating, are generally preferred for diesel blending. The higher the paraffin content of a fuel, the more easily it burns, providing quicker warm-ups and complete combustion. Heavier crude components that boil at higher ranges, although less desirable, may also be used. Naphthenes are the next lightest components and aromatics are the heaviest fractions found in diesel. Using these heavier components helps minimize diesel fuel waxiness. At low temperatures, paraffins tend to solidify, plugging fuel filters.

#### Biodiesel

[0021] As described, for example, on the website of the National Biodiesel Board ([www.biodiesel.org](http://www.biodiesel.org)), biodiesel is a product that may comprise mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel may be produced by acid or base-catalyzed transesterification of the oil with an alcohol. Although methanol is commonly used as the alcohol, other alcohols may also be suitable.

[0022] Some older diesel engines may be able to burn vegetable oils or animal fats that are not esterified. The term biodiesel as used in this application includes both biodiesel (the esterified oils or fats) and nonesterified oils and fats. The term biodiesel as used herein generally encompasses both esterified and nonesterified oils and fats and is broader than the conventional term.

[0023] When the term biodiesel is to be limited to the conventional meaning that includes only esterified oils and fats, the term “conventional biodiesel” or “esterified biodiesel” may be used.

[0024] Both conventional biodiesel and nonesterified biodiesel may be blended with petroleum diesel for use in

motor vehicles. The blends are commonly described as “BXX”, where XX is the percent biodiesel in the blend. B20, for example, is 20% biodiesel, 80% conventional diesel. B100 is 100% biodiesel. The term biodiesel is technically the pure fuel produced by the transesterification process, where the biodiesel is conventional biodiesel. The blends are more properly described as BXX. Although B20 is commonly described as “biodiesel”, the term B20 may be preferred to distinguish over pure biodiesel, B100.

[0025] Conventional esterified biodiesel fuel may be used in diesel vehicles with or without blending. B100, for example, is an acceptable fuel for most conventional diesel vehicles. The viscosity of nonesterified biodiesel fuel may generally be too high to be utilized without blending. Blending the nonesterified biodiesel fuel can reduce the viscosity. Blending of nonesterified biodiesel fuel is generally preferred. The biodiesel can be blended with petroleum-based diesel at any level., for example, but not limited to 5%, 10%, 15%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 99%, etc.

[0026] Table 1 below shows emission data for both conventional biodiesel (B100) and conventional B20 compared to conventional diesel. The data were reported on the National Biodiesel Board Website, [www.biodiesel.org](http://www.biodiesel.org), based on EPA’s report titled “A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions”. Data on nonesterified biodiesel were not reported.

TABLE 1

Average Biodiesel Emissions Compared to Conventional Diesel			
Emission Type	B100	B20	B20 With Additive
Hydrocarbons	−67%	−20%	−33%
Carbon Monoxide	−48%	−12%	−19%
Particulate Matter	−47%	−12%	−18%
NO <sub>x</sub>	+10%	+2%	−5%

[0027] Emissions of hydrocarbons, carbon monoxide, and particulate matter from combustion of biodiesel (B100) and B20 were significantly lower than the corresponding emissions from combustion of conventional diesel fuel. Although NO<sub>x</sub> emissions for biodiesel and biodiesel blends may be slightly higher than for conventional diesel, the NO<sub>x</sub> emissions may vary, depending on the engine family and the testing procedure.

[0028] As shown in the Examples below, emissions from combustion of fuels comprising biodiesel and the additive according to embodiments of the present invention may be lower than emissions from combustion of fuels comprising the same fuel that does not comprise the additive according to embodiments of the present invention.

[0029] The last column in Table 1, “B20 With Additive” shows emission data from Example 1 for B20 that comprises an additive according to embodiments of the present invention. The emissions for all of the emission types in Table 1 for B20 that comprises the additive according to embodiments of the present invention were lower than the emissions for B20 alone.

[0030] The reductions in the emissions for B20 that comprises the additive according to embodiments of the present

invention compared to B20 alone range from a 6% decrease in particulate matter emissions to a 13% decrease in the hydrocarbon emissions. The additive according to embodiments of the present invention was effective in lowering all four of the emission types compared to B20 alone. The reductions in emissions compared to conventional diesel were between 5 and 37%.

[0031] The NO<sub>x</sub> emissions for B20 were 2% higher than the NO<sub>x</sub> emissions for conventional diesel. The NO<sub>x</sub> emissions for B20 that comprises the additive according to embodiments of the present invention were 5% lower than the NO<sub>x</sub> emissions from conventional diesel fuel and 7% lower than the NO<sub>x</sub> emissions for B20.

[0032] The additive according to embodiments of the present invention is effective in lowering emissions for diesel fuels that comprise biodiesel, compared to both conventional diesel and B20.

#### Additive

[0033] The additive according to embodiments of the present invention may comprise a first component comprising at least one ignition accelerator and at least one second component comprising at least one material selected from the group consisting of a plant extract, a synthetic form of a plant extract, and mixtures thereof. A synthetic form of a plant extract, as that expression is used herein, refers to one or more synthetically produced compositions that naturally occur in plant extracts. The synthetic compositions may include, for example, carotenoids, xanthophylls, chlorophylls, or color bodies.

[0034] The additive may further comprise additional components such as, but not limited to, long chain fatty acids or esters and/or a solvent. As used herein, the term "long chain" refers to a molecule with a carbon chain of about 16 carbons atoms or greater. The long chain fatty acids or esters may comprise, for example, meadowfoam oil, jojoba oil, or mixtures thereof. Other oils that may comprise long chain fatty acids or esters may also be suitable. Synthetic long chain fatty acids or esters may also be suitable. Other components such as cetane improvers, stabilizing compounds, or other components may be added as additional components.

[0035] The long chain fatty acids or esters and the solvent are optional components of the additive according to embodiments of the present invention. Additives that may comprise long chain fatty acids or esters in addition to the first component and the second component are preferred embodiments.

#### Ignition Accelerators

[0036] The additive according to embodiments of the present invention may comprise at least one ignition accelerator as a first component. The ignition accelerator may be an organic nitrate or a peroxide. Peroxides are generally preferred as ignition accelerators in the additive according to embodiments of the present invention.

#### Organic Nitrate Ignition Accelerators

[0037] If the ignition accelerator is an organic nitrate, preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to 10 carbon atoms. The alkyl

group may be either linear or branched. Specific examples of nitrate compounds suitable for use in preferred embodiments include, but are not limited to, the following: methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, 2-ethylhexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, n-dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, isopropylcyclohexyl nitrate, and the esters of alkoxy substituted aliphatic alcohols, such as 1-methoxypropyl-2-nitrate, 1-ethoxypropyl-2 nitrate, 1-isopropoxy-butyl nitrate, 1 -ethoxybutyl nitrate and the like. Preferred alkyl nitrates are ethyl nitrate, propyl nitrate, amyl nitrates, and hexyl nitrates. Other preferred alkyl nitrates are mixtures of primary amyl nitrates or primary hexyl nitrates. By primary is meant that the nitrate functional group is attached to a carbon atom which is attached to two hydrogen atoms. Examples of primary hexyl nitrates include n-hexyl nitrate, 2-ethylhexyl nitrate (2-EHN), 4-methyl-n-pentyl nitrate, and the like. Preparation of the nitrate esters may be accomplished by any of the commonly used methods: such as, for example, esterification of the appropriate alcohol, or reaction of a suitable alkyl halide with silver nitrate.

[0038] The organic nitrate ignition accelerator 2-ethylhexyl nitrate is an exemplary organic nitrate ignition accelerator. Although other levels are useful and within the scope of the present invention, organic nitrate ignition accelerators are preferably used at final concentrations of 1 -5000 ppm in fuel compositions.

#### Conventional Ignition Accelerators

[0039] In a preferred embodiment, conventional ignition accelerators may be used as the first component ignition accelerator in the additive according to embodiments of the present invention. Conventional ignition accelerators may include, for example, but not limited to, hydrogen peroxide, benzoyl peroxide, di-tert-butyl peroxide (DTBP), cumene hydroperoxide, di-oleal peroxide, soybean hydroperoxide, and di-ethyl peroxide. Other organic peroxides and hydroperoxides may also be suitable. DTBP is an exemplary ignition accelerator.

[0040] In an embodiment, the additive according to embodiments of the present invention may comprise an organic nitrate ignition accelerator in addition to a conventional ignition accelerator. In an embodiment, the additive according to embodiments of the present invention may comprise both di-tert-butyl peroxide (DTBP) and 2-ethylhexyl nitrate (2-EHN). The 2-EHN may alternatively be added to the diesel fuel separately from the additive.

#### Second Component Plant Extracts

[0041] The second component of the additive according to embodiments of the present invention may comprise at least material selected from the group consisting of a plant extract, a synthetic composition that is similar to a portion of a plant extract, and mixtures thereof. The plant extract or synthetic composition that is similar to a plant extract may comprise at least one carotenoid and/or at least one chlorophyll component. The second component may comprise synthetic carotenoids or chlorophylls as well as natural carotenoids and chlorophylls.

[0042] Carotenoids are fat soluble pigments that are derived from a 40-carbon polyene chain. The chain may be terminated by rings and may also contain oxygen-containing groups. The hydrocarbon carotenoids are known as carotenes, while the oxygenated derivatives of the carotenoids are known as Xanthophylls.

[0043] Beta-carotene is a natural carotenoid that is present in a number of fruits and vegetables such as carrots, spinach, peaches, apricots, and sweet potatoes.

[0044] "Iso-Mixtene", a product of DSM Chemicals (formerly, Roche Vitamins, Inc.) is an intermediate in the synthesis of pure trans-beta-carotene. Iso-Mixtene is an admixture of approximately 89-98% trans  $\beta$  carotene and approximately 1.4 to approximately 11% of isomeric forms of cis  $\beta$  carotene. Iso-Mixtene may be suitable as a second component in the additive according to embodiments of the present invention.

[0045] Carotenoids can be biological antioxidants, protecting cells and tissues from free radicals.

#### Plant Extract

[0046] The term "plant extract" or "plant oil extract", as used herein, is a broad term and is used in its ordinary sense, including, without limitation, those components present in the plant material that are extractable in n-hexane, other suitable nonpolar solvent, or a polar solvent. The term "extractable" is a broader term than "soluble". Some plant materials may be extractable in a solvent, even if the components may not be soluble in the solvent.

[0047] Plant extracts may, for example, contain color bodies or components of color bodies. A color body is an assembly of molecules that imparts color to a system. In a botanical sense the classical color body is a chloroplast (literally translated as color body) a cell organelle which contains chlorophyll, proteins and other pigments and structures necessary for the photosynthetic process. The entire organelle may be transported as an entity.

[0048] The plant extract may preferably comprise an extract from the green portion of a plant. Extracts of the portions of the plant that are not green may be less desirable plant extracts than are plant extracts from the green portions of the plant. Extracts from, for example, bark or other portions of the plant that are not green may generally be less suitable for use as plant extracts in the additive according to embodiments of the present invention than are extracts from the green portion of the plant.

[0049] Chlorophyll may be used as a substitute for, or in addition to, all or a portion of the plant extract. The plant extract may comprise chlorophyll. Chlorophyll is the green pigment in plants that accomplishes photosynthesis, the process in which carbon dioxide and water combine to form glucose and oxygen. The plant extract typically also contains many other compounds, including, but not limited to, organometallics, antioxidants, oils, lipids thermal stabilizers or the starting materials for these types of products, and approximately 300 other compounds primarily comprising low to high molecular weight antioxidants.

[0050] In a preferred embodiment, the second component may comprise a plant extract from, e.g., vetch, hops, barley, or alfalfa. While the plant extract from vetch is preferred in many embodiments, in other embodiments it may be desir-

able to substitute, in whole or in part, another plant extract, including, but not limited to, alfalfa, hops extract, fescue extract, barley extract, green clover extract, wheat extract, extract of the green portions of grains, green food materials extract, green hedges or green leaves or green grass extract, any flowers containing green portions, the leafy or green portion of a plant of any member of the legume family, chlorophyll or chlorophyll containing extracts, or combinations or mixtures thereof. Suitable legumes include legume selected from the group consisting of lima bean, kidney bean, pinto bean, red bean, soy bean, great northern bean, lentil, navy bean, black turtle bean, pea, garbanzo bean, and black eye pea. Suitable grains include fescue, clover, wheat, oats, barley, rye, sorghum, flax, triticale, rice, corn, spelt, millet, amaranth, buckwheat, quinoa, kamut, and teff.

[0051] Especially preferred plant extracts are those derived from plants that are members of the Fabaceae (Leguminosae) plant family, commonly referred to as the pulse family, and also as the pea or legume family. The Leguminosae family includes over 700 genera and 17,000 species, including shrubs, trees, and herbs. The family is divided into three subfamilies: *Mimosoideae*, which are mainly tropical trees and shrubs; *Caesalpinioideae*, which include tropical and sub-tropical shrubs; and *Papilionoideae* which includes peas and beans. A common feature of most members of the Leguminosae family is the presence of root nodules containing nitrogen-fixing *Rhizobium* bacteria. Many members of the Leguminosae family also accumulate high levels of vegetable oils in their seeds. The Leguminosae family includes the lead-plum, hog peanut, wild bean, Canadian milk vetch, indigo, soybean, pale vetchling, marsh vetchling, veiny pea, round-headed bush clover, perennial lupine, hop clover, alfalfa, white sweet clover, yellow sweet clover, white prairie-clover, purple prairie-clover, common locust, small wild bean, red clover, white clover, narrow-leaved vetch, hairy vetch, garden pea, chick pea, string green, kidney bean, mung bean, lima bean, broad bean, lentil, peanut or groundnut, and the cowpea, to name but a few.

[0052] The plant extract may be obtained using extraction methods well known to those of skill in the art. Solvent extraction methods are generally preferred. Any suitable extraction solvent which is capable of separating the oil and oil-soluble fractions from the plant material may be used. Polar or nonpolar solvents may be used. Nonpolar extraction solvents may be used most often conventionally. Polar solvents may be used in an alternative embodiment. The solvent may include a single solvent, or a mixture of two or more solvents. The plant extract may be extractable in a solvent even though the plant extract may not be soluble in the solvent.

[0053] Suitable nonpolar solvents include, but are not limited to, cyclic, straight chain, and branched-chain alkanes containing from about 5 or fewer to 12 or more carbon atoms. Specific examples of acyclic alkane extractants include pentane, hexane, heptane, octane, nonane, decane, mixed hexanes, mixed heptanes, mixed octanes, isooctane, and the like. Examples of the cycloalkane extractants include cyclopentane, cyclohexane, cycloheptane, cyclooctane, methylcyclohexane, and the like. Alkenes such as hexenes, heptenes, octenes, nonenes, and decenes are also suitable for use, as are aromatic hydrocarbons such as benzene, toluene, and xylene. Halogenated hydrocarbons

such as chlorobenzene, dichlorobenzene, trichlorobenzene, methylene chloride, chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene, trichloroethane, and trichlorotrifluoroethane may also be used. Generally preferred nonpolar solvents are C6 to C12 alkanes, particularly n-hexane.

[0054] Suitable polar solvents may include, but are not limited to, acetone, methyl ethyl ketone, other ketones, methanol, ethanol, other alcohols, tetrahydrofuran, methylene chloride, chloroform, or any other suitable polar solvent.

[0055] Hexane extraction is the most commonly used technique for extracting oil from seeds. It is a highly efficient extraction method that extracts virtually all oil-soluble fractions in the plant material. In a typical hexane extraction, the plant material is comminuted. Grasses and leafy plants may be chopped into small pieces. Seeds are typically ground or flaked. The plant material is typically exposed to hexane at an elevated temperature. Hexane is a highly flammable, colorless, volatile solvent that extracts the extractable portions of the plant material, and dissolves out the oil, typically leaving only a few weight percent of the oil in the residual plant material. The plant extract/solvent mixture may be heated, for example, with a steam bath or other suitable heating means to flash off the hexane. Alternatively, hexane may be removed by evaporation at reduced pressure, with or without heating. The resulting extract may be suitable for use in the formulations of preferred embodiments.

[0056] Plant oil extracts for use in edible items or cosmetics typically undergo additional processing steps to remove impurities that may affect the appearance, shelf life, taste, and the like, to yield a refined oil. These impurities may include phospholipids, mucilaginous gums, free fatty acids, color pigments and fine plant particles. Different methods are used to remove these by-products including water precipitation or precipitation with aqueous solutions of organic acids. Color compounds are typically removed by bleaching, wherein the oil is typically passed through an adsorbent such as diatomaceous clay. Deodorization may also be conducted, typically through steam distillation. Such additional processing steps are generally unnecessary. However, oils subjected to such treatments may be suitable for use as plant extracts in the additives according to the preferred embodiments.

[0057] Other preferred extraction processes include, but are not limited to, supercritical fluid extraction, typically with carbon dioxide. Other gases, such as helium, argon, xenon, and nitrogen may also be suitable for use as solvents in supercritical fluid extraction methods.

[0058] Any other suitable method may be used to obtain the desired plant extract fractions, including, but not limited to, mechanical pressing. Mechanical pressing, also known as expeller pressing, removes oil through the use of continuously driven screws that crush the seed or other oil-bearing material into a pulp from which the oil is expressed. Friction created in the process can generate temperatures between about 50° C. and 90° C., or external heat may be applied. Cold pressing generally refers to mechanical pressing conducted at a temperature of 40° C. or less, with no external heat applied.

[0059] The yield of plant extract or plant oil extract that may be obtained from a plant material may depend upon any

number of factors, but primarily upon the oil content of the plant material. For example, a typical oil content of vetch (hexane extraction, dry basis) is approximately 4 to 5 wt. %, while that for barley is approximately 6 to 7.5 wt. %, and that for alfalfa is approximately 2 to 4.2 wt. %.

[0060] The most preferred form of solvent-extracted material comprises a material having a paste or mud-like consistency after extraction, namely, a solid or semi-solid, rather than a liquid, after extraction. Such pastes typically contain a higher concentration ratio of chlorophyll a to chlorophyll b in the extract. The color of such a material is generally a deep black-green with some degree of fluorescence throughout the material. Such a material can be recovered from many or all the plant sources enumerated for the Leguminosae family. While such a form is generally preferred for most embodiments, in certain other embodiments a liquid or some other form may be preferred.

[0061] There are several forms of chlorophyll. All plants, algae, and cyanobacterial that carry out photosynthesis contain chlorophyll a. Chlorophyll b occurs only in green algae and plants. Chlorophyll c is found only in photosynthetic members of Chromista and in dinoflagellates. Chlorophyll c differs from other chlorophylls in being unsaturated at positions 17 and 18. Further, chlorophyll c has a free acid at position 17. Most chlorophylls have an ester group at position 17.

[0062] Chlorophyll a and b differ from each other in having different sidechains. The sidechain at position 7 in chlorophyll a is  $-\text{CH}_3$ , while the sidechain in chlorophyll b is  $-\text{CHO}$ . The absorption spectra of chlorophyll a and b complement each other in absorbing sunlight at different wavelengths. Very little light is absorbed by either chlorophyll between 500-600 nm, in the green region. This is the reason why plants are green.

[0063] Higher plants generally have chlorophyll a/b ratios of about 1.3-1.4, while green algae LHC II have chlorophyll a/b ratios between 0.7 and 2.7. *Prochlorococcus marinus* is a photosynthetic prokaryote that contains divinyl derivatives of chlorophyll a and b (DV-Chls a and b). The MED4 strain has a DV-Chl a/b ratio ranging from 11.4 to 15.0, while the SS120 strain has a DV-Chl a/b ratio ranging from 1.1 to 2.2 (F. Partensky, J. La Roche, K. Wyman, and P. G. Falkowski, *Photosynthesis Research* 51, 109 (1997)). The chlorophyll a/b ratio can therefore vary over a considerable range, particularly for the divinyl chlorophyll derivatives contained in *Prochlorococcus marinus*.

[0064] The chlorophyll a/b ratio and the ratio of chlorophyll to carotenoid species can vary in a single plant species when the plant is subjected to stress. Chlorophyll concentrations in plant leaves can decrease in response to stress such as dehydration, flooding, freezing, ozone, herbicides, competition, disease, insects and ectomycorrhizal deficiency (G. A. Carter and A. K. Knapp, *Am. J. of Botany* 88, 677 (2001)).

[0065] For example, the chlorophyll and chlorophyll a and b concentrations can vary depending on the light intensity that the plant experiences. Generally, chlorophyll concentrations may be lower in plants that are exposed to sun. The total chlorophyll concentration (chlorophyll a and b) in mahogany plants that were exposed to sun was about 1.78  $\mu\text{mol.g}^{-1}$ , while the total chlorophyll concentration in

mahogany plants that were exposed to shade was 3.15  $\mu\text{mol.g}^{-1}$  (J. F. de Carvalho Goncalves, R. A. Marengo, and G. Vieira, *R. Bras. Fisiol. Veg.* 13, 149 (2001)) The total chlorophyll concentration in the mahogany plants that were in the shade was approximately 75% greater than the total chlorophyll concentration of the mahogany plants that were exposed to sun. The corresponding concentrations for Tonka bean plants that were exposed to sun and shade, respectively, were 2.45 and 3.93  $\mu\text{mol.g}^{-1}$ , a 60% difference.

[0066] The chlorophyll a/b ratios for the mahogany plants that were in the sun and the shade were 1.87 and 1.62, respectively. The corresponding ratios for Tonka bean plants that were raised in sun and shade were 2.6 and 2.85.

[0067] The chlorophyll/carotenoid ratio also varies with plants that are raised in the sun and the shade. Mahogany plants that were raised in the sun had a chlorophyll/carotenoid ratio of 2.06, while mahogany plants that were raised in shade had a chlorophyll/carotenoid ratio of 3.89. The chlorophyll/carotenoid ratios for Tonka bean plants that were raised in the sun and the shade were 2.97 and 3.25, respectively (de Carvalho Goncalves, et. al.). According to Goncalves, et. al., either chlorophyll or carotenoid synthesis may increase to enhance acclimation to higher irradiation. The change in the chlorophyll/carotenoid ratio in mahogany was larger than the change in Tonka bean plants. The Goncalves et. al. reference suggested that the Tonka bean plant has a different strategy than mahogany for sun acclimation. The Tonka bean plants have thick and leathery leaves, in contrast to the thinner and tender leaves of mahogany.

[0068] It is believed that the efficiency of plant extracts in reducing emissions from diesel fuel that comprises biodiesel will depend on the total chlorophyll concentration and/or the chlorophyll a/b ratio. It is believed that plant extracts from plants that are grown under stressed conditions provide better emission reduction.

[0069] Plant extracts that have chlorophyll a/b ratios in a range of approximately 0.7 to approximately 15 may be suitable as plant extracts in the additive according to embodiments of the present invention, where the chlorophyll a/b ratios include ratios for divinyl derivatives of chlorophyll a and b as well as for chlorophyll a and b.

[0070] The chlorophyll a/b ratio may more preferably be in a range of approximately 0.1 to approximately 80, even more preferably in a range of 0.7 to approximately 5, and most preferably in a ratio of approximately 1.3 to approximately 3.

[0071] The chlorophyll/carotenoid ratio may be in a range of approximately 0.1 to approximately 100, more preferably in a range of approximately 0.5 to approximately 50, and even more preferably, in a range of approximately 2 to approximately 20.

[0072] Synthetic portions of plant extracts, for example synthetic carotenoids, chlorophylls, or xanthophylls may be used instead of, or in addition to, the natural plant extracts.

$\beta$ -carotene

[0073]  $\beta$ -carotene may be added to the additive as an optional separate component or may be present or naturally occurring in one of the other base components, such as, for example, one of the components of the plant extract.  $\beta$ -Caro-

tene is a high molecular weight antioxidant. In plants, it functions as a scavenger of oxygen radicals and protects chlorophyll from oxidation. While not wishing to be limited to any particular mechanism, it is believed that the  $\beta$ -carotene in the formulations of preferred embodiments may scavenge oxygen radicals in the combustion process or may act as an oxygen solubilizer or oxygen getter for the available oxygen that is present in the air/fuel stream for combustion.

[0074] The  $\beta$ -carotene may be natural or synthetic. In a preferred embodiment, the  $\beta$ -carotene is provided in a form equivalent to vitamin A having a purity of 1.6 million units of vitamin A activity. Vitamin A of lesser purity may also be suitable for use, provided that the amount used is adjusted to yield an equivalent activity. For example, if the purity is 800,000 units of vitamin A activity, the amount used is doubled to yield the desired activity.

[0075]  $\beta$ -Carotene may be present as a cetane improver in preferred embodiments. The  $\beta$ -carotene may be added to the fuel formulation as an isolated component or may be present or naturally occurring in another component, such as, for example, a plant oil extract. The  $\beta$ -carotene may be the sole cetane improver additive to the fuel, or may be present as part of a fuel additive package.  $\beta$ -Carotene is a high molecular weight antioxidant. In plants, it functions as a scavenger of oxygen radicals and protects chlorophyll from oxidation.  $\beta$ -Carotene may also be present in the fuel additive according to embodiments of the present invention as a second component.

[0076] The  $\beta$ -carotene may be natural or synthetic. In a preferred embodiment, the  $\beta$ -carotene is provided in a form equivalent to vitamin A having a purity of 1.6 million units of vitamin A activity. Vitamin A of lesser purity may also be suitable for use, provided that the amount used is adjusted to yield an equivalent activity. For example, if the purity is 800,000 units of vitamin A activity, the amount used is doubled to yield the desired activity.

[0077] Precursors or derivatives of  $\beta$ -carotene, for example, vitamin A, may be suitable for use in preferred embodiments. While not wishing to be limited to any particular mechanism, it is believed that the  $\beta$ -carotene, or a precursor or derivative of a carotene or carotenoid, in the formulations of preferred embodiments may scavenge oxygen radicals in the combustion process or may act as an oxygen solubilizer or oxygen getter for the available oxygen that is present in the air/fuel stream for combustion.

[0078] While  $\beta$ -carotene is preferred in many embodiments, in other embodiments it may be desirable to substitute another carotene or carotenoid, or precursor or derivative of another carotene or carotenoid, for example,  $\alpha$ -carotene or carotenoids as described below, for  $\beta$ -carotene. Alternatively, another component may supplement the  $\beta$ -carotene, including, but not limited to,  $\alpha$ -carotene, or additional carotenoids from algae xeaxabthin, cryptoxanthin, lycopene, lutein, broccoli concentrate, spinach concentrate, tomato concentrate, kale concentrate, cabbage concentrate, brussels sprouts concentrate and phospholipids, green tea extract, milk thistle extract, curcumin extract, quercetin, bromelain, cranberry and cranberry powder extract, pineapple extract, pineapple leaves extract, rosemary extract, grapeseed extract, ginkgo biloba extract, polyphenols, flavonoids, ginger root extract, hawthorn berry extract, bilberry

extract, butylated hydroxytoluene (BHT), oil extract of marigolds, any and all oil extracts of carrots, fruits, vegetables, flowers, grasses, natural grains, leaves from trees, leaves from hedges, hay, any living plant or tree, and combinations or mixtures thereof.

**[0079]** Vegetable carotenoids of guaranteed potency are particularly preferred, including those containing lycopene, lutein,  $\alpha$ -carotene, other carotenoids from carrots or algae, betatene, and natural carrot extract. In certain particularly preferred embodiments, a substitute for  $\beta$ -carotene is present in an amount sufficient to yield an equivalent vitamin A activity as for a preferred quantity of  $\beta$ -carotene. However, in other embodiments vitamin A activity may not be a preferred method for determining the quantity of substitute, or the substitute may not have an equivalent vitamin A activity.

**[0080]** In addition to adding  $\beta$ -carotene in a liquid form to a fuel formulation,  $\beta$ -carotene (or another carotene or carotenoid, or a precursor or derivative of a carotene or carotenoid) may also be added in solid form, for example, in dehydrated form, or in the form of an encapsulated liquid or solid. The preservation and storage of solutions or suspensions of  $\beta$ -carotene or other plant-based materials carries enormous benefits, such as reduced weight and storage space, and increased stability and resistance to oxidation.  $\beta$ -Carotene in dehydrated form may be prepared by methods including freeze-drying, vacuum or air-drying, lyophilization, spray-drying, fluidized bed drying, and other preservation and dehydration methods as are known in the art.  $\beta$ -Carotene in dehydrated form may be added to fuel in the dehydrated form, or may be added as a reconstituted liquid in an appropriate solvent. In a preferred embodiment, a solid containing  $\beta$ -carotene is added to the fuel to be additized. Suitable solid forms include, but are not limited to, tablets, granules, powders, encapsulated solids and/or encapsulated liquids, and the like. Additional components may also be present in the solid form. Any suitable encapsulating material may be used, preferably a polymeric or other material that is soluble in the fuel to be additized. The encapsulating material dissolves in the fuel, releasing the encapsulated material. The tablet preferably dissolves in the fuel or a diluent over an acceptable period of time. Dissolving aids may be included in the tablet, e.g., small granules or particles of active ingredient may be present in a matrix with high solubility in the fuel. A combination of solid and liquid dosing methods may be utilized, and the solid may be added to the fuel or a diluent at any preferred time.

**[0081]** The following components may be used in combination with  $\beta$ -carotene in cetane improvers of preferred embodiments: butylated hydroxytoluene, lycopene, lutein, all types of carotenoids, oil extract from carrots, beets, hops, grapes, marigolds, fruits, vegetables, palm oil, palm kernel oil, palm tree oil, bell pepper, cottonseed oil, rice bran oil, any plant that is naturally orange, red, purple, or yellow in color that is growing in nature, or any other material that may be a natural oxygen scavenger but yet remains organic in nature. In certain embodiments, it may be preferred to substitute one or more of these components in whole or in part for the  $\beta$ -carotene.

**[0082]** The oil extracted from the following products may also be used in combination with  $\beta$ -carotene:  $\alpha$ -carotene, and additional carotenoids from algae xeaxabthin, cryptox-

anthin, lycopene, lutein, broccoli concentrate, spinach concentrate, tomato concentrate, kale concentrate, cabbage concentrate, Brussels sprouts concentrate and phospholipids. In addition, the oil extracts from green tea extract, milk thistle extract, curcumin extract, quercetin, bromelain, cranberry and cranberry powder extract, pineapple extract, pineapple leaves extract, rosemary extract, grapeseed extract, ginkgo biloba extract, polyphenols, flavonoids, ginger root extract, hawthorn berry extract, bilberry extract, butylated hydroxytoluene, oil extract of marigolds, oil of hops, oil extract of jojoba, any and all oil extract of carrots, fruits, vegetables, flowers, grasses, natural grains, leaves from trees, leaves from hedges, hay, feed stocks for man and animal, and weeds, the oil extract of any living plant, or the oil extract of any fresh water or salt water fish, such as shark, including but not limited to squalene, squalane, all fresh and salt water fish oils, and fish oil extracts, or the oil extract of animals, such as whale.

**[0083]** In certain embodiments, the cetane improving carotene or carotenoid, or a precursor or derivative of a carotene or carotenoid is present in combination with one or more conventional cetane improvers, for example, an alkyl nitrate. When an additional cetane improving additive is present, 2-ethylhexyl nitrate is especially preferred. However, it should be understood that while pure 2-ethylhexyl nitrate is desired, other alkyl nitrates or other grades of 2-ethylhexyl nitrate are also suitable. Further, one of skill will appreciate that other alkyl nitrates or conventional cetane improvers or ignition accelerators, as described above, perform similarly to 2-ethylhexyl nitrate and can be substituted accordingly. Desirably, many different formulations of cetane improver may be made, each having a different alkyl nitrate or more than one alkyl nitrate and/or proportions thereof relative to the  $\beta$ -carotene.

#### Stabilizing Compounds or Antioxidants

**[0084]** The plant extract, carotene, carotenoids, iso-Mixtene, the chlorophyll, the diesel, the biodiesel, or other components of the diesel fuel that comprises biodiesel may be susceptible to oxidation. Oxidation may degrade the performance of the fuel.

**[0085]** At least one stabilizing compound or antioxidant may be added to the diesel fuel that comprises biodiesel to stabilize the components against oxidation. U.S. Pat. No. 6,630,324, for example, which is hereby incorporated by reference herein in its entirety, discloses dissolving or otherwise preparing  $\beta$ -carotene in a solvent under an inert atmosphere such as nitrogen, helium, or argon. The  $\beta$ -carotene dissolved or otherwise prepared under an inert atmosphere is referred to as "non-oxygenated  $\beta$ -carotene". The inert atmosphere may protect the  $\beta$ -carotene and/or the other components from oxidation. See also co-pending PCT publication No. WO01/79398, filed Apr. 12, 2001, U.S. patent application Ser. No. 10/084,602, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,603, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,237, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,835, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,601, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,836, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,579, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,243, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,833, filed on

Feb. 26, 2002, U.S. patent application Ser. No. 10/084,236, filed on Feb. 26, 2002, U.S. patent application Ser. No. 10/084,831, filed on Feb. 26, 2002, PCT Application No. U.S.02/06137, filed on Feb. 26, 2002, and Canadian Application No. 2,273,327, filed on Feb. 26, 2002, all of which are incorporated herein by reference in their entirety.

[0086] In a preferred embodiment, a cetane improver comprising carotene can be formulated by the following method. Under an inert atmosphere, (e.g., nitrogen, helium, or argon) three grams of  $\beta$ -carotene (1.6 million International units of vitamin A activity per gram) are dissolved in 200 ml of a liquid hydrocarbon carrier comprising toluene. It is preferred to dissolve the  $\beta$ -carotene with heating and stirring. P-Carotene dissolved or otherwise prepared under an inert atmosphere is referred to as "non-oxygenated  $\beta$ -carotene." Substitutes or supplements to  $\beta$ -carotene, including other carotenes or carotenoids or precursors or derivatives of carotenes or carotenoids, are referred to as "non-oxygenated carotenes or carotenoids or precursors or derivatives of carotenes or carotenoids." Next, approximately 946 milliliters of a 100% solution of 2-ethylhexyl nitrate is added to the mixture and toluene is added so as to obtain a total volume of 3.785 liters.

[0087] In a broad sense, the inert atmosphere may be considered to be a stabilizing compound or antioxidant that stabilizes the components against oxidation. Other, more conventional stabilizing compounds are described below.

[0088] Other stabilizing compounds or antioxidants are disclosed, for example, in Publication No. U.S. 2005/0160662 A1, U.S. patent application Ser. No. 10/517,901, filed on Jun. 10, 2003, which is incorporated herein by reference in its entirety. In a preferred embodiment, the stabilizing compound of the '901 application contains a quinoline moiety, preferably 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline, commonly referred to as ethoxyquin. The compound is marketed under the trademark SANTOQUIN® by Solutia Inc. of St. Louis, Mo. SANTOQUIN® is widely used as an antioxidant for animal feed and forage

[0089] Other suitable stabilizing compounds for  $\beta$ -carotene, carotenes, carotenoids, diesel, biodiesel, or the other components of the diesel fuel that comprises biodiesel according to embodiments of the present invention include, but are not limited to, butylated hydroxyanisole, butylated hydroxytoluene, gallates such as octyl gallate, dodecyl gallate, and propyl gallate; fatty acid esters including, but not limited to, methyl esters such as methyl linoleate, methyl oleate, methyl stearate, and other esters such as ascorbic palmitate, disulfuram, tocopherols, such as gamma-tocopherol, delta-tocopherol, and alpha tocopherol, and tocopherol derivatives and precursors, deodorized extract of rosemary, propionate esters and thiopropionate esters such as lauryl thiodipropionate or dilauryl thiodipropionate, betalactoglobulin; ascorbic acid, amino acids such as phenylalanine, cysteine, tryptophan, methionine, glutamic acid, glutamine, arginine, leucine, tyrosine, lysine, serine, histidine, threonine, asparagine, glycine, aspartic acid, isoleucine, valine, and alanine; 2,2,6,6-tetramethylpiperidinoxy, also referred to as tanoan; 2,2,6,6 tetramethyl-4-hydroxypiperidine-1-oxyl, also referred to as tanol; dimethyl-p-phenylaminophenoxyasilane; di-p-anisylazoxides, 2,2,4-trimethyl-6-ethoxy-1,2,3,4-tetrahydroquinoline; dihydrosantoquin; santoquin; p-hydroxydiphenylamine, and

carbonates, phthalates, and adipates thereof, and diludin, a 1,4-dihydropyridine derivative.

[0090] While not wishing to be bound to any particular mechanism or theory, it is believed that the stabilizing compound may act as a preservative or stabilizer by inhibiting oxidation of carotene, carotenoids, diesel, biodiesel, the plant extract, the ignition inhibitor, or other components of the fuel comprising biodiesel and the additive according to embodiments of the present invention. When a stabilizing compound such as ethoxyquin is present in combination with beta-carotene, it may not be necessary to prepare the fuel additive that may comprise carotene under an inert atmosphere, as described, for example, in application Ser. No. 10/789,836, filed on Feb. 27, 2004. As also described in the '836 application, the combination of a stabilizing compound such as ethoxyquin in combination with cetane improving compounds such as beta-carotene may result in a synergistic increase in cetane number.

[0091] Other substances with antioxidant properties may also be suitable for use in the formulations of preferred embodiments, either as substitutes for p-carotene or additional components, including phenolic antioxidants, amine antioxidants, sulfurized phenolic compounds, organic phosphites, and the like, as enumerated elsewhere in this application. Preferably, the antioxidant is oil soluble. If the antioxidant is insoluble or only sparingly soluble in aqueous solution, it may be desirable to use a surfactant to improve its solubility.

[0092] Suitable thermal stabilizers as known in the art include liquid mixtures of alkyl phenols, including 2-tert-butylphenol, 2,6-di-tert-butylphenol, 2-tert-butyl-4-n-butylphenol, 2,4,6-tri-tert-butylphenol, and 2,6-di-tert-butyl-4-n-butylphenol which are suited for use as stabilizers for middle distillate fuels (U.S. Pat. No. 5,076,814 and U.S. Pat. No. 5,024,775 to Hanlon, et al.). Other commercially available hindered phenolic antioxidants that also exhibit a thermal stability effect include 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butylphenol; 2,2'-methylene-bis(6-t-butyl-4-methylphenol); n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate; 1,1,3-tris(3-t-butyl-6-methyl-4-hydroxyphenyl) butane; pentaerythritoltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]; di-n-octadecyl(3,5-di-t-butyl-4-hydroxybenzyl)phosphonate; 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) mesitylene; and tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate (U.S. Pat. No. 4,007,157, U.S. Pat. No. 3,920,661). The term thermal stabilizer may be a broader term than "stabilizer" or "antioxidant". Resistance to oxidation may be a form of thermal stability.

[0093] Other thermal stabilizers include: pentaerythritol co-esters derived from pentaerythritol, (3-alkyl-4-hydroxyphenyl)-alkanoic acids and alkylthioalkanoic acids or lower alkyl esters of such acids which are useful as stabilizers of organic material normally susceptible to oxidative and/or thermal deterioration. (U.S. Pat. No. 4,806,675 and U.S. Pat. No. 4,734,519 to Dunski, et al.); the reaction product of malonic acid, dodecyl aldehyde and tallowamine (U.S. Pat. No. 4,670,021 to Nelson, et al.); hindered phenyl phosphites (U.S. Pat. No. 4,207,229 to Spivack); hindered piperidine carboxylic acids and metal salts thereof (U.S. Pat. No. 4,191,829 and U.S. Pat. No. 4,191,682 to Ramey, et al.); acylated derivatives of 2,6-dihydroxy-9-azabicyclo[3.3.1] nonane (U.S. Pat. No. 4,000,113 to Stephen); bicyclic hin-

dered amines (U.S. Pat. No. 3,991,012 to Ramey, et al.); sulfur containing derivatives of dialkyl-4-hydroxyphenyltriazine (U.S. Pat. No. 3,941,745 to Dexter, et al.); bicyclic hindered amino acids and metal salts thereof (U.S. Pat. No. 4,051,102 to Ramey, et al.); trialkylsubstituted hydroxybenzyl malonates (U.S. Pat. No. 4,081,475 to Spivack); hindered piperidine carboxylic acids and metal salts thereof (U.S. Pat. No. 4,089,842 to Ramey, et al.); pyrrolidine dicarboxylic acids and esters (U.S. Pat. No. 4,093,586 to Stephen); metal salts of N,N-disubstituted  $\beta$ -alanines (U.S. Pat. No. 4,077,941 to Stephen, et al.); hydrocarbyl thioalkylene phosphites (U.S. Pat. No. 3,524,909); hydroxybenzyl thioalkylene phosphites (U.S. Pat. No. 3,655,833); and the like.

[0094] Certain compounds are capable of performing as both antioxidants and as thermal stabilizers. Therefore, in certain embodiments it may be preferred to prepare formulations containing a hydrophobic plant oil extract in combination with a single compound that provides both a thermal stability and antioxidant effect, rather than two different compounds, one providing thermal stability and the other antioxidant activity. Examples of compounds known in the art as providing some degree of both oxidation resistance and thermal stability include diphenylamines, dinaphthylamines, and phenylnaphthylamines, either substituted or unsubstituted, e.g., N,N'-diphenylphenylenediamine, p-octyldiphenylamine, p,p'-dioctyldiphenylamine, N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine, N-(p-dodecyl)phenyl-2-naphthylamine, di-1-naphthylamine, and di-2-naphthylamine; phenothiazines such as N-alkylphenothiazines; imino(bisbenzyl); and hindered phenols such as 6-(t-butyl)phenol, 2,6-di-(t-butyl)phenol, 4-methyl-2,6-di-(t-butyl)phenol, 4,4'-methylenebis(2,6-di-(t-butyl)phenol), and the like.

[0095] Certain lubricating fluid base stocks are known in the art to exhibit high thermal stability. Such base stocks may be capable of imparting thermal stability to the formulations of preferred embodiments, and as such may be substituted, in part or in whole, for jojoba oil. Suitable base stocks include polyalphaolefins, dibasic acid esters, polyol esters, alkylated aromatics, polyalkylene glycols, and phosphate esters.

#### Antioxidants

[0096] Various compounds known for use as oxidation inhibitors can be utilized in fuel formulations of various embodiments. These include phenolic antioxidants, amine antioxidants, sulfurized phenolic compounds, and organic phosphites, among others. For best results, the antioxidant includes predominately or entirely either (1) a hindered phenol antioxidant such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), and mixed methylene bridged polyalkyl phenols, or (2) an aromatic amine antioxidant such as the cycloalkyl-di-lower alkyl amines, and phenylenediamines, or a combination of one or more such phenolic antioxidants with one or more such amine antioxidants. Particularly preferred are combinations of tertiary butyl phenols, such as 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol and o-tert-butylphenol. Also useful are N,N'-di-lower-alkyl phenylenediamines, such as N,N'-di-sec-butyl-p-phenylenediamine, and its analogs, as well as combinations of such phenylenediamines and such tertiary butyl phenols.

[0097] The compound 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline, commonly referred to as ethoxyquin is a preferred embodiment of a thermal stabilizer, stabilizing compound, or antioxidant. The compound is marketed under the trademark SANTOQUIN® by Solutia Inc. of St. Louis, Mo.

[0098] The terms thermal stabilizer, stabilizing compound, and antioxidant are closely related. As used herein, the term "stabilizing compound" is meant to encompass thermal stabilizers, stabilizing compounds, and antioxidants.

#### Optional Components of the Additive According to Embodiments of the Present Invention

[0099] The additive according to embodiments of the present invention may comprise additional components in addition to the at least one ignition accelerator first component and the at least one second component selected from the group consisting of a plant extract, a synthetic composition that is similar to a plant extract, and mixtures thereof.

[0100] For example, the additive may further comprise components comprising long chain fatty acids or esters or mixtures thereof, for example, but not limited to, meadowfoam oil, jojoba oil, or mixtures thereof. Synthetic long chain fatty acids or esters may also be utilized as the optional components comprising long chain fatty acids or esters.

[0101] The additive may also further comprise a solvent as an additional component. Both the component comprising long chain fatty acids or esters and the component comprising a solvent are optional components. Both optional components are preferred components of the additive according to embodiments of the present invention.

[0102] The stabilizing compound is another optional component of the additive. The optional stabilizing compound may also be added to the fuel separately from the fuel additive according to embodiments of the present invention.

#### Meadowfoam Oil

[0103] Meadowfoam is an annual plant that is native to the Northwest area of the United States. The botanical name of the plant is *Limnanthes alba*. The plant is called "Meadowfoam", because the fields of white flowers of the blooming plant resemble a meadow of.

[0104] Meadowfoam seeds may contain approximately 20-30% oil. The oil may be removed by crushing the seed and utilizing a solvent extraction process. The meadowfoam oil may comprise over 98 percent long-chain fatty acids. The long chain fatty acids have very high levels of mono-unsaturation and very low levels of polyunsaturation. Meadowfoam oil is one of the most stable vegetable oils known. Meadowfoam is most similar to high erucic acid rapeseed oil (Dan Burden, Ag Marketing Resource Center, Iowa State University, November 2003). Rapeseed oil is slightly more saturated than meadowfoam oil (E. A. Oelke, E. S. Oplinger, C. V. Hanson, K. A., Kelling, Alternative Field Crops Manual, University of Wisconsin-Extension, Cooperative Extension, University of Minnesota, Center for Alternative Plant & Animal Products and the Minnesota Extension Service).

[0105] The stability of meadowfoam oil does not appear to be due to common antioxidants. One possible explanation for the oxidative stability of meadowfoam oil may be its

unusual fatty acid composition. The main fatty acid from meadowfoam oil is 5-eicosenoic acid, which was found to be nearly 5 times more stable to oxidation than the most common fatty acid, oleic acid, and 16 times more stable than other monounsaturated fatty acids. See "Oxidative Stability Index of Vegetable Oils in Binary Mixtures with Meadowfoam Oil," Terry, et al., United States Department of Agriculture, Agricultural Research Service, 1997.

[0106] The typical fatty acid composition of meadowfoam oil is approximately 58-64% C20:1 ( $\Delta 5$ ), 3-6% C22:1 ( $\Delta 5$ ), 10-14% C22:1 ( $\Delta 3$ ), and 15-21% C22:2 ( $\Delta 5\Delta 13$ ).

[0107] According to the Oil Stability Index (OSI) is becoming the most widely used method to assess the stability of lipid materials. The OSI analysis involves exposing the oil to a stream of air at a specified temperature. The final result is reported as the number of hours required to overcome the oil's resistance at the specified temperature.

[0108] The OSI value for meadowfoam oil was higher than the OSI values for other oils. It was suggested on the meadowfoam.com website that the high stability of the meadowfoam seed oil was due to the presence of naturally occurring tocopherols (antioxidants) and the absence of polyunsaturated fatty acids that might be susceptible to oxidation. The tocopherols may be considered as stabilizing compounds, stabilizing the meadowfoam oil toward oxidation.

[0109] Meadowfoam oil may also be used to increase the stability of other oils by blending the meadowfoam oil with the other oils.

#### Jojoba Oil

[0110] In an embodiment, the additive according to embodiments of the present invention may comprise jojoba oil in addition to or instead of meadowfoam oil as an optional long chain component. Jojoba oil is a liquid that has antioxidant characteristics and is capable of withstanding very high temperatures without losing its antioxidant abilities. Jojoba oil is a liquid wax ester mixture extracted from ground or crushed seeds from shrubs native to Arizona, California and northern Mexico. The source of jojoba oil is the *Simmondsia chinensis* shrub, commonly called the jojoba plant. It is a woody evergreen shrub with thick, leathery, bluish-green leaves and dark brown, nutlike fruit. Jojoba oil may be extracted from the fruit by conventional pressing or solvent extraction methods. The oil is clear and golden in color. Jojoba oil is composed almost completely of wax esters of monounsaturated, straight-chain acids and alcohols with high molecular weights (C16-C26). Jojoba oil is typically defined as a liquid wax ester with the generic formula RCOOR", wherein RCO represents oleic acid (C18), eicosanoic acid (C20) and/or erucic acid (C22), and wherein —OR" represents eicosenyl alcohol (C20), docosenyl alcohol (C22) and/or tetrasenyl alcohol (C24) moieties. Pure esters or mixed esters having the formula RCOOR", wherein R is a C20-C22 alk(en)yl group and wherein R" is a C20-C22 alk(en)yl group, may be suitable substitutes, in part or in whole, for jojoba oil. Acids and alcohols including monounsaturated straight-chain alkenyl groups are most preferred.

[0111] While not wishing to be limited to any particular mechanism, it is believed that the jojoba oil may act to prevent or retard pre-oxidation of the plant oil extract and/or

$\beta$ -carotene components of the formulation prior to combustion by imparting thermal stability to the formulation. Jojoba oil generally reduces cetane in fuels. In formulations wherein a higher cetane number is preferred, it may generally be preferred to reduce the content of jojoba oil in the formulation.

[0112] Meadowfoam oil or jojoba oil can be used in lubricants. In an embodiment according to an embodiment of the present invention, additives that comprise meadowfoam oil or jojoba oil may enhance the lubricity of the diesel fuel. For example, additives comprising meadowfoam oil and/or jojoba oil may enhance the lifetime of engine components such as fuel pumps.

[0113] The lubricity of additives comprising meadowfoam oil may be important in light of the fact that low emission diesel fuel may generally have low sulfur levels. Low sulfur diesel generally suffers from poor lubricity characteristics. Biodiesel is a very low sulfur diesel fuel. In an embodiment, the optional meadowfoam oil in the additive according to embodiments of the present invention may provide added lubricity to the diesel fuel that comprises biodiesel.

[0114] Although meadowfoam oil or jojoba oil are preferred optional components of the additive according to embodiments of the present invention, other oils comprising long chain fatty acids or esters may also be suitable. The optional component comprising long chain fatty acids or esters may be selected from the group consisting of meadowfoam oil, jojoba oil, natural or synthetic long chain fatty acids, natural or synthetic long chain fatty esters, and mixtures thereof. The long chain fatty acids and/or esters may be pure compounds or mixtures.

#### Solvents

[0115] Solvents suitable for use in conjunction with the formulations of preferred embodiments are miscible and compatible with one or more components of the formulation. Preferred solvents include the aromatic solvents, such as benzene, toluene, o-xylene, m-xylene, p-xylene, and the like, as well as nonpolar solvents such as cyclohexanes, hexanes, heptanes, octanes, nonanes, and the like. Suitable solvents may also include the base fuel, for example Diesel 1, Diesel 2, biodiesel and the like. Depending upon the material to be solvated, other liquids may also be suitable for use as solvents, such as oxygenates, carrier fluids, or even additives as enumerated herein. Aromatic solvents or carrier fluids may generally be preferred.

[0116] Aromatic 100 and Aromatic 150 are examples of suitable solvents, although other solvents may also be suitable. According to the ExxonMobil Chemical Sales Specification Rev 11 (03/01), Aromatic 100 contains 98.0 min. volume % aromatics, has a 154° C. min IBP and a 174° C. max DP. Aromatic 150 contains 98.0 min. aromatics, has a 179° C. IBP and a 213° C. max DP.

[0117] The examples of Aromatic 100 and Aromatic 150 as solvents are illustrative examples only and are not meant to be limiting.

[0118] The amount of solvent may preferably be sufficient to keep the components dissolved in the fuel. The optimal amount of solvent may depend on the components, the fuel blend, and the cost of the solvent. The cost of the solvent may be higher than the other fuel components. Advanta-

geously, the amount of solvent may be minimized in order to minimize the cost. The cost of the solvent may not be a factor when the solvent is diesel or biodiesel.

Quantities of Components of the Additive According to Embodiments of the Present Invention

[0119] An additive for reducing emissions from combustion of diesel fuels comprising biodiesel may comprise an ignition accelerator and at least one material selected from the group consisting of a plant extract, a synthetic composition that is similar to a portion of a plant extract, and mixtures thereof. The ignition accelerator may preferably be an organic peroxide or an organic hydroperoxide. In an embodiment, organic nitrate ignition accelerators may also be used.

[0120] In an embodiment where the ignition accelerator is di-tert-butyl peroxide (DTBP), the additive may comprise approximately 0.32 to approximately 799 g of DTBP and approximately 0.001 to approximately 60 g of plant extract or synthetic composition similar to a plant extract per gallon of diesel fuel, where the volume of diesel fuel is the total volume of diesel fuel comprising both diesel fuel and biodiesel. More preferably, the additive may comprise approximately 0.32 to approximately 80 g of DTBP and approximately 0.001 to approximately 6 g of plant extract or synthetic composition similar to a plant extract per gallon of diesel fuel. Most preferably, the additive may comprise approximately 9.5 to approximately 30 g of DTBP and approximately 0.002 to approximately 0.6 g of plant extract or synthetic composition similar to a plant extract per gallon of diesel fuel.

[0121] If other ignition accelerators are utilized, the quantities in the additive may be determined by one skilled in the art. The quantities may be similar to the quantities of DTBP.

[0122] Meadowfoam oil, jojoba oil, and/or a solvent are optional components of the additive according to embodiments of the present invention. If meadowfoam oil, jojoba oil, or a mixture of meadowfoam oil and jojoba oil are present in the additive according to embodiments of the present invention, the additive may comprise approximately 0.001 to approximately 0.544 g of meadowfoam oil and/or jojoba oil per gallon of diesel fuel, more preferably approximately 0.001 to approximately 0.05 g of meadowfoam oil and/or jojoba oil per gallon of diesel fuel, and most preferably approximately 0.002 to approximately 0.03 g of meadowfoam oil and/or jojoba oil per gallon of diesel fuel.

[0123] If a solvent is present in the additive according to embodiments of the present invention, the additive may comprise approximately 0.12 g to approximately 106 g of solvent per gallon of diesel fuel, more preferably approximately 0.12 g to approximately 10.6 g of solvent per gallon of diesel fuel, and most preferably approximately 0.23 to approximately 10.6 g of solvent per gallon of diesel fuel.

[0124] It is to be understood that synthetic plant extracts may be substituted, all or in part, for the plant extract in the additive. Synthetic long chain fatty acids or esters may be substituted, all or in part, for the meadowfoam oil and/or jojoba oil.

[0125] If the additive comprises 2-ethylhexyl nitrate (2-EHN), the additive may comprise approximately 0.025 to approximately 19 g of 2-EHN per gallon of diesel fuel, more

preferably approximately 0.075 to approximately 15.2 g of 2-EHN per gallon of diesel fuel, and most preferably 0.12 to approximately 11.4 g of 2-EHN per gallon of diesel fuel.

[0126] In an embodiment, the additive may comprise sufficient 2-EHN to provide approximately 1 ppm to approximately 5000 ppm 2-EHN in the fuel comprising biodiesel, more preferably approximately 2 ppm to approximately 4000 ppm 2-EHN, and most preferably approximately 5 ppm to approximately 3000 ppm 2-EHN in the fuel comprising biodiesel.

[0127] In an embodiment, the optional 2-EHN may also be added to the diesel fuel separately from the additive.

Method of Decreasing Pollutant Emissions in the Combustion of Diesel Fuel That Comprises Biodiesel

[0128] A method of decreasing pollutant emissions in the combustion of diesel fuel that comprises biodiesel comprises combusting the diesel fuel that comprises biodiesel and the additive according to embodiments of the present invention in a motor vehicle. The method may further comprise adding the additive to the diesel fuel, where the additive is added to the diesel fuel before combusting the diesel fuel.

[0129] The emissions from the motor vehicle that combusts the diesel fuel that comprises biodiesel and the additive according to embodiments of the present invention may be reduced compared to the emissions from a motor vehicle that combusts the same fuel that does not comprise the additive according to embodiments of the present invention, as shown in the examples below.

[0130] The additive may comprise at least one ignition accelerator and at least one second component comprising at least one material selected from the group consisting of a plant extract, a synthetic composition that is similar to a portion of a plant extract, and mixtures thereof.

A Method of Increasing the Lubricity of Diesel Fuel That Comprises Biodiesel

[0131] A method of increasing the lubricity of diesel fuel that comprises biodiesel is provided. Biodiesel fuel may have low sulfur levels. Diesel fuels having low sulfur levels may have low lubricity. The method comprises adding an additive to the diesel fuel, where the additive may comprise: at least one ignition accelerator; at least one second component comprising at least one material selected from the group consisting of a plant extract, a synthetic composition that is similar to a portion of a plant extract, and mixtures thereof; and at least one oil selected from the group consisting of meadowfoam oil, jojoba oil, and mixtures thereof.

[0132] The ignition accelerator may comprise an organic nitrate or a peroxide. The ignition accelerator is preferably a peroxide. In an exemplary embodiment, the ignition accelerator may comprise di-tert-butyl peroxide. Other organic peroxides may also be suitable.

[0133] The meadowfoam oil or jojoba oil in the additive may enhance the lubricity of the diesel fuel.

[0134] The following examples illustrate embodiments of various aspects of the invention. The examples are not meant to be limiting on the scope of the claims.

## EXAMPLE 1

[0135] A solution containing fescue extract and meadowfoam oil was formed by blending 995 mL of Aromatic 150, 5 mL of meadowfoam oil, and 5.1 g of fescue extract (hexane extracted). The solution is referred to as “Additive 2”, or “Fescue Extract Meadowfoam Oil Stock Solution”, or “Extract Additive” in the Examples below.

[0136] Table 2 provides a list of treatment mixtures that were prepared:

TABLE 2

Treatment Mixtures		
Treatment	Additive 2: Vol. of Fescue Extract-Meadowfoam Oil Stock Solution (mL per gallon of B20)	Vol. of DTBP (mL per gallon B20)
1	None	34.05
2	None	37.85
3	None	23.0
4	4.0	23.0

TABLE 2-continued

Treatment Mixtures		
Treatment	Additive 2: Vol. of Fescue Extract-Meadowfoam Oil Stock Solution (mL per gallon of B20)	Vol. of DTBP (mL per gallon B20)
5	4.0	13.89
6	4.0	19.0

[0137] Table 3 provides emission results for various pollutants using the treatments described above, prepared with the fescue/meadowfoam additive (Additive 2 or Extract Additive). A baseline of non-additized B20 bio-diesel was measured on Day 1. This was used a reference to determine emission reductions in the additized samples. The weighted averages provided in Table 3 were calculated using weighing factors of 1/4 for cold start results and 3/4 for hot start results. The table provides data for total hydrocarbon (THC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), carbon dioxide (CO<sub>2</sub>), and particulate matter (PM). The units are ppm, except for PM. The units for particulate matter are g/BHP-hr (grams per brakehorsepower-hour).

TABLE 3

SAMPLE		RUN # (START)	THC	CO	NOX	CO <sub>2</sub>	PM
DAY 1							
Test 1	Baseline B20 (No Additive)	1 (cold)	0.146	3.435	5.833	566.51	0.202
		2 (hot)	0.106	2.676	4.877	544.50	0.182
		3 (hot)	0.111	2.611	4.886	541.14	0.185
		4 (hot)	0.111	2.597	4.915	541.31	0.190
		Weighted Average	0.109	2.628	5.027	542.32	0.196
Test 2	Treatment 1: DTBP 34.05 mL/gal B20	1 (cold)	0.096	2.733	5.437	566.85	0.182
		2 (hot)	0.091	2.319	4.645	543.06	0.181
		3 (hot)	0.089	2.329	4.658	545.47	0.180
		4 (hot)	0.086	2.297	4.654	544.02	0.175
		Weighted Average	0.089	2.315	4.764	544.18	0.179
DAY 2							
Test 1	Treatment 2: DTBP 37.85 mL/gal B20	1 (cold)	0.087	2.890	5.654	569.74	0.210
		2 (hot)	0.079	2.303	4.655	546.09	0.172
		3 (hot)	0.085	2.293	4.626	540.89	0.173
		4 (hot)	0.084	2.314	4.616	542.35	0.175
		Weighted Average	0.083	2.303	4.778	543.11	0.173
Test 2	Treatment 3: 23.0 mL DTBP/gal B20	1 (cold)	0.089	2.866	5.504	567.00	0.183
		2 (hot)	0.089	2.381	4.708	546.06	0.175
		3 (hot)	0.088	2.367	4.691	542.74	0.175
		4 (hot)	0.09	2.356	4.692	544.70	0.177
		Weighted Average	0.089	2.368	4.812	544.60	0.176
DAY 3							
Test 1	Treatment 4: 23.0 mL DTBP/gal B20 + 4 mL Additive 2/ gal B20	1 (cold)	0.091	3.010	5.658	567.65	0.192
		2 (hot)	0.088	2.447	4.647	546.62	0.184
		3 (hot)	0.093	2.396	4.638	543.93	0.182
		4 (hot)	0.09	2.413	4.647	544.13	0.182
		Weighted Average	0.090	2.419	4.789	544.89	0.183
Test 2	Treatment 4: 23.0 mL DTBP/gal B20 + 4 mL Additive 2/ gal B20	1 (cold)	0.079	2.841	5.435	564.74	0.171
		2 (hot)	0.085	2.442	4.726	547.29	0.176
		3 (hot)	0.087	2.407	4.709	545.21	0.18
		4 (hot)	0.09	2.401	4.702	544.98	0.185
		Weighted Average	0.087	2.417	4.816	545.83	0.180

TABLE 3-continued

SAMPLE		RUN # (START)	THC	CO	NOX	CO <sub>2</sub>	PM
DAY 4							
Test 1	Treatment 5: 13.89 mL	1 (cold)	0.079	2.841	5.435	564.74	0.176
	DTBP/gal B20 + 4 mL	2 (hot)	0.089	2.457	4.753	544.60	0.191
	Additive 2/	3 (hot)	0.095	2.453	4.754	545.80	0.188
	gal B20	4 (hot)	0.89	2.432	4.714	543.89	0.183
		Weighted Average	0.091	2.447	4.840	544.76	0.187
Test 2	Treatment 6: 19.0 mL	1 (cold)	0.105	3.069	5.682	570.90	0.191
	DTBP/gal B20 + 4 mL	2 (hot)	0.086	2.498	4.714	543.91	0.184
	Additive 2/	3 (hot)	0.086	2.461	4.704	543.03	0.19
	gal B20	4 (hot)	0.09	2.450	4.738	543.33	0.182
		Weighted Average	0.087	2.470	4.856	543.42	0.185
DAY 5							
Test 1	Treatment 6: 19.0 mL	1 (cold)	0.103	3.187	5.680	569.18	—
	DTBP/gal B20 + 4 mL	2 (hot)	0.088	2.483	4.662	540.88	—
	Additive 2/	3 (hot)	0.087	2.461	4.696	542.87	—
	gal B20	4 (hot)	0.086	2.497	4.707	544.34	—
		Weighted Average	0.087	2.480	4.830	542.70	—
Test 2	Treatment 6: 19.0 mL	1 (cold)	0.089	3.060	5.614	570.96	—
	DTBP/gal B20 + 4 mL	2 (hot)	0.094	2.484	4.729	545.69	—
	Additive 2/	3 (hot)	0.088	2.451	4.712	542.87	—
	gal B20	4 (hot)	0.085	2.424	4.717	541.47	—
		Weighted Average	0.089	2.453	4.947	543.34	—

[0138] Table 4 shows the change in emissions for the various treatments in comparison to the baseline B20 data. The changes are the differences between the emissions for each treatment compared to the average emissions for the B20 baseline runs. The first number in the emission change

table (Table 4) is the difference ( $\Delta$ ) between the emissions for each treatment and the baseline emissions for the average emissions for the B20 base fuel. The second number is the percent difference (%  $\Delta$ ) between the emissions for each treatment and the baseline B20 emissions.

TABLE 4

Treatment No.	Treatment Amounts/ gal B20	THC ppm $\Delta$ % $\Delta$	CO ppm $\Delta$ % $\Delta$	NO <sub>x</sub> ppm $\Delta$ % $\Delta$	CO <sub>2</sub> ppm $\Delta$ % $\Delta$	PM g/BHP- hr $\Delta$ % $\Delta$
1	34.05 ml	-0.02	-0.313	-0.263	+1.86	-0.0017
	DTBP	-18%	-11.9%	-5.23%	+0.34%	-8.67%
2	37.85 ml	-0.026	-0.325	-0.249	+0.79	-0.023
	DTBP	-24%	-12.4%	-4.95%	+0.15%	-11.7%
3	23.0 ml DTBP	-0.02	-0.26	-0.215	+2.28	-0.02
		-18%	-9.89%	-4.28%	+0.42%	-10.2%
4	23.0 ml DTBP + 4 ml	-0.019	-0.209	-0.238	+2.57	-0.013
	Extract	-17%	-7.95%	-4.73%	+0.47%	-6.63%
	Additive					
4	23.0 ml DTBP + 4 ml	-0.022	-0.211	-0.211	+3.51	-0.016
	Extract	-20%	-8.03%	-4.20%	+0.65%	-8.16%
	Additive					
5	13.89 ml	-0.018	-0.181	-0.187	+2.44	-0.009
	DTBP + 4 ml	-17%	-6.89%	-3.72%	+0.45%	-4.59%
	Extract					
	Additive					
6	19.0 ml DTBP + 4 ml	-0.022	-0.158	-0.171	+1.1	-0.011
	Extract	-20%	-6.01%	-3.40%	+0.20%	-5.61%
	Additive					
6	19.0 ml DTBP + 4 ml	-0.022	-0.0148	-0.197	+0.38	—
	Extract	-20%	-5.63%	-3.92%	+0.07%	—
	Additive					
6	19.0 ml DTBP + 4 ml	-0.02	-0.175	-0.08	+1.02	—
	Extract	-18.3%	-6.66%	-1.59%	+0.188%	—
	Additive					

[0139] All of the treatments reduced the emissions of all of the regulated pollutants. Although there were small increases in the emissions of CO<sub>2</sub> over the base case of pure B20 carbon dioxide emissions in diesel exhaust gas are not presently subject to regulation.

[0140] The emission reductions with the additive according to embodiments of the present invention are shown in Treatments 4, 5, and 6. Total hydrocarbon emissions were reduced by 27-20% with the additive of the present invention, compared to baseline B20. The CO emissions were lowered by 6.01-8.03%, NO<sub>x</sub> by 3.40-4.73%, and particulate matter by 4.59-8.16%, compared to the base B20 that did not comprise the additive according to embodiments of the present invention. The additive according to embodiments of the present invention was effective in lowering emissions of total hydrocarbon, carbon monoxide, NO<sub>x</sub>, and particulate matter, compared to the base B20 fuel.

[0141] The above description discloses several methods and materials of the present invention. This invention is susceptible to modifications in the methods and materials, such as the choice of base fuel, the components selected for the base formulation, as well as alterations in the formulation of fuels and additive mixtures. Such modifications will become apparent to those skilled in the art from a consideration of this disclosure or practice of the invention disclosed herein. Consequently, it is not intended that this invention be limited to the specific embodiments disclosed herein, but that it cover all modifications and alternatives coming within the true scope and spirit of the invention as embodied in the attached claims. All references cited herein are hereby incorporated by reference in their entireties.

What is claimed is:

1. A fuel additive for biodiesel fuel, said fuel additive comprising:

a first component comprising an ignition accelerator;  
and,

a second component selected from the group consisting of  
a plant extract, a synthetic form of a plant extract, and  
a combination thereof.

2. The fuel additive of claim 1, wherein said ignition accelerator comprises a peroxide.

3. The fuel additive of claim 2, wherein said peroxide is selected from the group consisting of hydrogen peroxide, benzoyl peroxide, di-tert-butyl peroxide, cumene hydroperoxide, di-oleal peroxide, soybean hydroperoxide, di-ethyl peroxide and any combination thereof.

4. The fuel additive of claim 2, wherein said peroxide comprises di-tert-butyl peroxide.

5. The fuel additive of claim 1, further comprising a third component, said third component comprising a compound selected from the group consisting of long chain fatty acids, long chain fatty esters, and any combination thereof.

6. The fuel additive of claim 5, comprising a synthetic long chain fatty acid, a synthetic long chain fatty ester, or both a synthetic long chain fatty acid and a synthetic long chain fatty ester.

7. The fuel additive of claim 5, wherein said third component further comprises an oil selected from the group consisting of meadowfoam oil, jojoba oil, and a combination thereof.

8. The fuel additive of claim 1, further comprising a solvent.

9. The fuel additive of claim 8, wherein said solvent comprises an aromatic solvent.

10. The fuel additive of claim 1, further comprising an alkyl nitrate.

11. The fuel additive of claim 10, wherein said alkyl nitrate comprises 2-ethylhexylnitrate.

12. The fuel additive of claim 1, wherein said plant extract comprises a green extract of a plant.

13. The fuel additive of claim 12, wherein said green extract is chlorophyll.

14. The fuel additive of claim 1, wherein the plant extract comprises an extract of a plant of the Leguminosae family.

15. The fuel additive of claim 1, wherein said second component is selected from the group consisting of beta-carotene, alpha-carotene, a carotenoid, a chlorophyll, a color body, isomixtene, and any combination thereof.

16. The fuel additive of claim 1, wherein said plant extract comprises one or more chlorophylls.

17. The fuel additive of claim 16, wherein said fuel additive has a ratio of chlorophyll a to chlorophyll b of approximately 0.1 to approximately 80.

18. The fuel additive of claim 1, wherein said second component comprises chlorophyll and carotenoid.

19. The fuel additive of claim 18, wherein said fuel additive has a ratio of chlorophyll to carotenoid of approximately 0.1 to approximately 100.

20. The fuel additive of claim 1, further comprising a stabilizing component.

21. The fuel additive of claim 19, wherein said stabilizing component comprises at least one compound selected from the group consisting of: 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline; ethoxyquinoline; 2-tert-butylphenol; 2,6-di-tert-butylphenol; 2-tert-butyl-4-n-butylphenol; 2,4,6-tri-tert-butylphenol; 2,6-di-tert-butyl-4-n-butylphenol; 2,6-di-tert-butyl-4-methylphenol; 2,6-di-tert-butylphenol; 2,2'-methylene-bis(6-tert-butyl-4-methylphenol); n-octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; 1,1,3-tris(3-tert-butyl-6-methyl-4-hydroxyphenyl) butane; pentaerythrityltetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]; di-n-octadecyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate; 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)mesitylene; tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate; N,N'-diphenylphenylenediamine; p-octyldiphenylamine; p,p'-dioctyldiphenylamine; N-phenyl-1-naphthylamine; N-phenyl-2-naphthylamine; N-(p-dodecyl)phenyl-2-naphthylamine; di-1-naphthylamine; and di-2-naphthylamine; phenothiazines; N-alkylphenothiazines; imino(bisbenzyl); 6-(tert-butyl)phenol; 2,6-di-(tert-butyl)phenol; 4-methyl-2,6-di-(tert-butyl)phenol; 4,4'-methylenebis(2,6-di-(tert-butyl)phenol); a diphenylamine; a dinaphthylamine; and a phenylnaphthylamine.

22.

23. A fuel composition comprising:

about 0.32 to about 799 g of ignition accelerator;

about 0.001 g to about 60 g of plant extract or synthetic form of a plant extract, or mixtures thereof per gallon of the fuel comprising biodiesel.

24. The fuel composition of claim 22, further comprising 2-ethylhexylnitrate.

25. The fuel composition of claim 23, wherein the level of said 2-ethylhexylnitrate is about 1 ppm to about 5000 ppm.

26. A method of decreasing pollutant emissions in the combustion of biodiesel fuel comprising combusting a fuel comprising:

combining said biodiesel fuel with a fuel additive, said fuel additive comprising:

a first component comprising an ignition accelerator; and

a second component selected from the group consisting of a plant extract, a synthetic form of a plant extract, and mixtures thereof.

27. A method of increasing lubricity of a fuel comprising biodiesel comprising:

adding an additive to said fuel comprising biodiesel, said additive comprising:

a first component comprising an ignition accelerator;

a second component selected from the group consisting of a plant extract, a synthetic form of a plant extract, and mixtures thereof; and,

at least one oil selected from the group consisting of meadowfoam oil, jojoba oil, and mixtures thereof.

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