Abstract: An emulsified biofuel composition comprising: (A) a continuous phase comprising about 50-95 wt% of at least one liquid oil of vegetable or animal origin or mixtures thereof; (B) a water-containing dispersed phase comprising about 1-50 wt% water; (C) about 1-25 wt% of hydroxyl-containing organic compound selected from the group consisting of mono-, di-, tri- and polyhydric alcohols, provided that when a monohydric alcohol is used there is also present at least one of tert-butyl alcohol, at least one C2-C4 alkylene glycol or a mixture of both; (D) about 0.05-10 wt% of at least one emulsifier; wherein the dispersed water-containing droplets have an average particle size of less than about 20 microns. The biofuel is prepared from these components by mixing under high shear conditions, preferably with ultrasonic energy. The emulsifier(s) preferably exhibit a hydrophilic-lipophilic balance of about 8.5 to about 18 and the biofuel includes a cetane enhancer and mixture of an alcohol and mono- or poly-alkylene glycol.
The present application claims the benefit of Application Serial No. 60/795,365, filed April 27, 2006, entitled Biofuel Additive and Method of Producing a Biofuel, the disclosure of which is hereby incorporated herein by-reference.

BACKGROUND OF THE INVENTION

The present invention relates to fuel additives, methods of making such additives and fuel compositions employing such additives, wherein the fuel is substantially based on vegetable or animal sources.

Efforts to find alternative fuels to those derived from petroleum, such as gasoline and diesel fuel, have led to the development of biodiesel fuel. Traditional biodiesel is produced by transesterification of vegetable oils or fats. In such a process, a vegetable fat or oil reacts with an esterifying agent, typically an alcohol, for example methanol or ethanol, with or without a catalyst and with the input of additional energy usually at atmospheric pressure. The time of the reaction can range from 0.5 to 8 hours depending on the temperature.

The terms "oils" and "fats" are often considered synonyms, and for the purposes of the present application can be considered chemically interchangeable, the distinction between such products being that they are merely distinguished on the basis of their physical state. For example, an "oil" is typically used to describe products that are liquid at ambient or room temperature whereas the term "fat" is used to describe products that are typically substantially solid at room temperature. However, even such a differentiation is somewhat artificial in that it is subject to the definition of room temperature. For example, the same product may be considered a "fat" in one latitude at a given time of the year.
and be considered an "oil" at another latitude or at another time of the year. To avoid confusion with other types of oils (such as essential oils or oils derived from petroleum), these products will be identified to the extent possible as "vegetable or animal oils" or "vegetable or animal fats" but unless the context clearly indicates otherwise, a reference to fats and oils should be understood to refer to vegetable or animal oil components useful in the present invention, as opposed to, e.g., petroleum oils. In other words, if an oil obtained from petroleum, such as diesel oil, gas oil and the like, is present in the compositions of the present invention at all, it is present as an additive or minor component, in other words, in an amount less than 50 wt%; for example, less than about 40, 30, 20, 10, 5 or even 3 wt%—such as from greater than about 0 wt% to less than about 5 wt%, or 10 wt%, or 15 wt% or 20 wt%, or 25 wt%.

[0005] A common vegetable-oil-derived fuel, typically used as a fuel for diesel engines is referred to as "biodiesel." Biodiesel is made utilizing the chemical reaction known as transesterification. The process forms two principal products, fatty acid methyl esters (FAME, the chemical name for biodiesel) and glycerin. In this reaction a vegetable oil or fat reacts with an esterifying agent, usually an alcohol (e.g., methanol or ethanol), with or without a catalyst and with the input of additional energy, normally at atmospheric pressure. The reaction time can vary from about 0.5 to about 8 hours depending on the temperature and whether or not a catalyst is used. A biodiesel fuel generated in this way and used in its pure form (in other words without being "diluted" with another fuel, whether a petroleum based fuel or ethanol) at 100% is referred to as "B 100". If it is diluted with another fuel, e.g., diesel fuel or gas oil, it is typically identified by the percentage of biodiesel present, e.g., B5, B20, B30, etc. The principal physical and chemical properties
of traditional biodiesel are as follows: methyl ester content > 96.5%; Density at 15 °C ranges from about 0.86 to about 0.90 g/cc; viscosity at 40 °C between about 3.5 and about 5.0 mmVs; flammability point > 110 °C; Cetane number > 51; net heating value equal to about 33175 kJ/L (compared to typical No. 2 diesel fuel, biodiesel has about 8.65% less heating value expressed as BTU/gal.; i.e., 118,296 versus 129,500).

[0006] Furthermore, traditional biodiesel fuel exhibits a distillation curve that is different from traditional gas oil. This results in a flame profile that is longer and more compact because of the greater viscosity and density of biodiesel compared to petroleum-based diesel fuel. Such a flame can create operational problems if the pressure of the volumetric fuel pump is not increased slightly, e.g., about 1-1.5 atm. For the same reason, modified fuel nozzles having a form more suited to the characteristics of biodiesel need to be used; for example, 60° nozzles open at the center perform best.

[0007] In addition, the use of biodiesel requires further adjustments of the relationship of primary air to secondary air (regulation of the combustion head). However, this introduces further complications since increasing secondary air improves cold performance of the engine, but slightly worsens equilibrium combustion and vice versa. Another disadvantage of traditional biodiesel arises from the high solvent power of methyl ester. This can cause damage to incompatible plastics, generally present as liners and seals, and may also create problems with deposits of gas oil inadvertently left in the storage tanks. Therefore, substitution for, or at least the periodic maintenance of the polymeric components, is also required (including, for example, the intake and return tubes, the compression seals of the pump, the bending elements, and the liners and seals).
Furthermore, the cleaning of tanks and heaters in order to remove all residues of fossil fuels is also strongly advised.

[0008] Traditional biodiesel mixed with lubricating oil may also create a variety of problems because of the increase in the iodine number of the mixture; iodine number being an indicator of organic unsaturation. If the iodine number of the oil is greater than about 115, the mixture is susceptible to polymerization, and gummy deposits can form in the lubrication lines, reducing the flow of the lubricant. This can result in an undesirable need to replace the motor's lubricant oil. In addition, because the composition of biodiesel is very different from gas oil, its behavior in terms of exhaust emissions sometimes markedly varies from that of gas oil, particularly NOx emissions.

[0009] When traditional biodiesel is used in an engine with fuel injectors, deposits tend to form in the injectors, at least two to three times more so than when gas oil is used. Such deposits are usually carbon deposits and tend to wear away with time, particularly in "common rail" type motors. However, deposit problems can be avoided with traditional biodiesel fuel if the injection pressure is increased, e.g., to about 100 bar.

[0010] Methanol used in the transesterification process results in a minimal addition of fossil-based CO₂ in the balance of traditional biodiesel. If the source of oil used to produce the biodiesel is derived from renewable sources (typically referred to as biomass), then all of the CO₂ produced by the combustion of the biodiesel is renewable. However, the problem of nitrogen oxides, currently considered among the most undesirable by-products of combustion, is the weak point of traditional biodiesel fuel. On average NOx emissions increase 10-13% with respect to gas oil on account of the high oxygen content of the biofuel. Even mixes containing less than 100% biodiesel cause an increase in NOx
emissions. For example, for B20, the increase is around a 2-3% over gas oil. On the other hand, CO emissions for B100 are on average about 40% less than for gas oil whereas a B20 biodiesel mixture emits around 15% less CO. Carbon monoxide in the motor area does not generate significant problems and can be considered a lesser pollutant. It is rather an indicator of poor combustion since it is the result of a lack of oxygen.

[0011] Particulate emissions from the burning of biodiesel may be related to the chemical composition of the source used to synthesize the biodiesel and also may be indicative of combustion-related problems. The danger associated with such particulates varies with their chemical composition and to the average dimension of the particles. Additionally, the particles can also absorb and/or adsorb a certain amount of aromatic substances that are considered more or less carcinogenic and/or mutagenic. SO₂ emission can be a problem if the biodiesel is not entirely devoid of sulfur. Obviously the mixture of gas oil and biodiesel leads to an increase in emissions of SO₂ that is proportionate to the content of fossil fuel. The use of traditional biofuel in boilers has not yet been the subject of in-depth study. For example, the measured quantity of particulate emissions, NOₓ, SO₂ and CO, from the stack of a 1750 kWatt boiler fed with biodiesel compared with those emitted from one that burns gas oil containing 0.25 wt% sulfur show that the pollutants emitted by biodiesel are less than those of gas oil—with the exception of NOₓ, which is higher.

[0012] Finally, on the basis of raw materials costs, biodiesel is significantly more expensive, for example, as currently calculated based on European costs, than regular diesel fuel. Final costs "at the pump" can be equivalent since there currently are government incentives to encourage the use of a non-petroleum-based fuel.
Thus, further improvements in the field of non-petroleum based fuels, especially fuels based on renewable vegetable sources would be highly desirable, particularly where such fuels exhibit acceptable performance characteristics.

SUMMARY OF THE INVENTION

In one embodiment an emulsified biofuel composition suitable for use in diesel engines comprises: (A) a continuous phase comprising about 50-95 wt% of at least one liquid oil of vegetable or animal origin or mixtures thereof; (B) a water-containing dispersed phase comprising about 1-50 wt% water; (C) about 1-25 wt% of hydroxyl-containing organic compound selected from the group consisting of mono-, di-, tri- and polyhydric alcohols, provided that when a monohydric alcohol is used there is also present at least one of tert-butyl alcohol, at least one C2-C4 alkylene glycol or a mixture of both; (D) about 0.05-10 wt% of at least one emulsifier; wherein the dispersed water-containing droplets have an average particle size of less than about 20 microns. The biofuel is prepared from these components by mixing under high shear conditions, preferably with ultrasonic energy. The at least one emulsifier preferably exhibits a hydrophilic-lipophilic balance of about 8.5 to about 18 and the biofuel includes a cetane enhancer and mixture of an alcohol and mono- or poly-alkylene glycol.

In one embodiment the dispersed aqueous phase in an emulsified fuel comprising a vegetable oil continuous phase exhibits an average droplet particle size of about 0.01 to about 15 microns and the emulsifier(s) exhibit a hydrophilic-lipophilic balance, HLB, of about 8.5 to about 18.

In another embodiment an emulsified fuel mixture is prepared from the following components: (A) vegetable or animal oil or fat, including mixtures thereof; and B) water; and (C) at least one alcohol selected from the group...
consisting of C1 to C4 alcohols; and, (D) at least one surfactant or emulsifier and optionally a supplementary low viscosity, low density combustible liquid selected from the group consisting of hydrocarbon solvents, paint thinner, turpentine, mineral spirits and mixtures thereof. In one embodiment, the latter emulsified fuel mixture can be prepared according to the following method: (I) components (C) and (D) are mixed with one another to produce an additive and the additive is combined with water (B) to form mixture (II). Mixture (II) is added with concurrent mixing, at a suitable rate to the vegetable oil, component (A), in order to produce a substantially emulsified mixture.

DETAILED DESCRIPTION
[0017] As used herein the following terms or phrases have the indicated meanings.

[0018] The term "emulsion" refers to a mixture or dispersion of two immiscible substances, liquids in the present invention, in which one substance, the dispersed phase, is dispersed in the other substance, the continuous phase. An emulsion is stabilized, in other words the dispersed phase remains dispersed during the relevant time period, such as during storage and/or immediately prior to and during use, with the assistance of one or more substances known as emulsifiers. An emulsion can be a water-in-oil emulsion or an oil-in-water emulsion depending on such variables as the amount of oil (as well as type of oil) and water present, the conditions used to prepare the emulsion, the emulsifier type and amount, the temperature and combinations of such variables. The particle size or droplet size of the dispersed phase can vary over a significant range and the emulsion can remain stable, but its properties and suitability for a specific use may vary depending on the particle size of the dispersed phase. Particle size is typically expressed in terms of mean or average size since the
uniformity of the dispersed phase can also vary depending on the variables noted above. Particle size does not require that the particles are necessarily spheres and the size of the particles can be based on a major or average dimension of each particle, although in a system comprising a dispersed liquid phase in a continuous liquid phase, fluid dynamics suggest that the dispersed particles will tend to be substantially spherical.

[0019] The term "emulsifier" refers to a compound or mixture of compounds that has the capacity to promote formation of an emulsion and/or substantially stabilize an emulsion, at least for the short-term, i.e., during the time of practical or commercial interest. An emulsifier provides stability against significant or substantial aggregation or coalescence of the dispersed phase of an emulsion. An emulsifier is typically considered to be a surface active substance in that it is capable of interacting with the dispersed and continuous phases of an emulsion at the interface between the two. For purposes herein a "surfactant" and an "emulsifier" are considered equivalent or interchangeable terms. Furthermore, within the generic term surfactant are included the various types of surfactants such as nonionic, ionic or partially ionic, anionic, amphoteric, cationic and zwitterionic surfactants.

[0020] The term "cetane number" refers to a measure of diesel fuel ignition characteristics which is analogous to octane number for gasoline and, similarly, higher values indicate better performance. A specific test has been developed and accepted by the fuel industry and it is defined, for example, by various standards setting organizations including ASTM D613, IP 41, and EN ISO 5165. The test method determines the rating of diesel fuel oil in terms of an arbitrary scale of cetane numbers using a standard single cylinder, four-stroke cycle, variable compression ratio,
indirect injected diesel engine. The cetane number scale covers the range from zero to 100 but typical test results for diesel fuel and fuels intended for use in diesel applications are typically in the range of 30 to 65 cetane number.

[0021] The term "flash point" generally refers to how easily a substance or composition, typically a fluid, may ignite or burn. The measurement of flash point is defined in test methods that are maintained by standardization bodies such as the Energy Institute in the UK, ASTM in the USA, CEN in Europe and ISO internationally. For example, for diesel fuel the procedure is defined in ASTM D975. The flash point of a fuel is essentially the lowest temperature at which vapors from a test portion combine with air to give a flammable mixture and "flash" when an ignition source is applied. Materials with higher flash points are less likely to ignite than those with lower flash points. For example, a flash point of 66 °C to 93 °C (150 °F to 200 °F) is considered to present a moderately low ignition hazard and a flash point of 38 °C to 66 °C (100 °F to 150 °F) is considered to present a moderate to high ignition hazard. For reference purposes diesel fuel has a flash point of about 38 °C to 54 °C (100 °F to 130 °F) and gasoline a flash point of about -40 °C to -46 °C (-40 °F to -50 °F). The flash point of a fuel is one property that needs to be considered in determining the suitability of a fuel composition for practical use.

[0022] The term "mixing" when used generically or without a modifier includes each of the processes described herein for dispersing one ingredient in another.

[0023] The term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: (1) hydrocarbon
substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical); (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy); (3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thiienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0024] The term "lower" when used in conjunction with terms such as alkyl, alkenyl, and alkoxy, is intended to describe such groups that contain a total of up to 7 carbon atoms.

[0025] Reference in the disclosures that follow to "oil" in general refers to vegetable oils, animal derived oils and mixtures of vegetable and animal derived oils, including recycled versions thereof. Unless the context of the description requires otherwise, reference to "vegetable oil" should be understood to include a reference to animal derived oils and mixtures of both vegetable and animal derived oils.

[0026] The terms "stability" or "stable" when used in reference to an emulsion refer to the dispersed or hydrophilic
phase remaining substantially dispersed in the lipophilic phase (vegetable and/or animal oil and/or fat). In other words, substantially no phase separation occurs as indicated by visual observation after a period following preparation of the emulsion of at least about 24 hours; preferably at least about 48 hours, more preferably at least about 72 hours; for example, substantially no phase separation is observable after about 4 days or more, at ambient temperatures suitable for use of the emulsified fuel composition in its directed application, for example, use in burners, motor vehicles and the like. Alternatively, stability can be characterized by measuring sediment formation according to the test method ASTM D96.

[0027] Compositions of the present invention, characterized for purposes of the present invention as fuel compositions, and referred to as "biofuel," are suitable for use in internal combustion engines, preferably diesel engines of various configurations as well as in equipment that combusts fuels to generate heat, such as furnaces, boilers, power generating equipment and the like, including gas or combustion turbines. Diesel engines that may be operated with compositions of the present invention include all compression-ignition engines for both mobile (including locomotive and marine) and stationary power plants. These include diesel engines of the two-stroke-per-cycle and four-stroke-per-cycle types. The diesel engines include but are not limited to light and heavy duty diesel engines and on and off-highway engines, including new engines as well as in-use engines. The diesel engines include those used in automobiles, trucks, buses including urban buses, locomotives, stationary generators, and the like. For example, with regard to use in burners, the compositions are useful in different types of oil burners for domestic and other heating purposes including sleeve burners, natural-draft pot burners, force-draft pot burners, rotary wall flame
burners, and air-atomizing and pressure-atomizing gun burners; with the latter type of burner being the most commonly used burner for home heating, particularly in the United States. In particular, such compositions are useful fuels for diesel motors (both new and old generation) and/or boilers and single- or multi-step burners, also referred to in the art as staged burners.

[0028] Various mixing devices well known in the art can be employed to facilitate formation of an emulsified composition of the instant embodiment as well as the present invention generally including, for example, mixer-emulsifiers, which typically utilize a high speed rotor operating in close proximity to a stator (such as a type made by Charles Ross & Sons Co., NY), paddle mixers utilizing paddles having various design configurations including, for example, reverse pitch, anchor, leaf, gate, finger, double-motion, helix, etc., including batch and in-line equipment, and the like. Other methods of mixing useful in this embodiment as well as generally in the present invention are further described hereinbelow. The processes of various embodiments of the present invention can be carried out at a convenient temperature, including, for example, at ambient or room temperature, such as about 20 °C to about 22 °C or even as high as 25 °C. The time and temperature of mixing can be varied provided that the desired emulsified composition is achieved and, based on subsequent observation and/or testing, it is suitably stable until it is used, as well as during use. Under conditions wherein sediment may form following mixing of the components of the fuel composition, it can be desirable to wait for a period of time in order to allow for sedimentation, if any, to occur, such material to subsequently be removed or separated from the emulsified fuel composition. Typically, such time period is at least about 4 minutes; preferably about 5 minutes; more preferably about 6 minutes or more. The
preferred amount of time can readily be determined with limited and simple experiments and such time can be adjusted, based on, for example, the type, quality and composition of the vegetable oil employed, as well as the other components of the mixture, including emulsifier(s). [0029] Mixing methods in additions to those described above are suitable for use in the present invention and in some instances are particularly preferred. Mixtures can be prepared with traditional mixing or blending equipment such as vats or tank equipped with motor driven stirrers having various configurations, e.g., paddle, helix, etc. Mixing carried out in such equipment is time consuming, often requiring greater than 10 minutes of mixing, for example, about 10 to about 30 minutes, alternately about 15 to about 20 minutes in order to achieve a uniform and stable emulsion. However, such emulsions contain dispersed particles having an average particle size, e.g., diameter or average dimension on the order of greater than about 20 microns, for example, about 20 to about 50 microns; alternatively about 20 to about 35 microns. Emulsions having an average particle size of about 20 microns or greater are referred to herein as "macroemulsions." A fuel composition having macroemulsion characteristics will typically exhibit properties that differ from the same fuel composition having an average particle size that is significantly smaller, in other words, a microemulsion or one in which the particle size is less than about 20 microns, such as 19 microns or less. For example, a given composition in macroemulsion form may exhibit a higher viscosity, lower flash point and poorer stability in a process requiring extended recirculation of the fuel composition as well as requiring a greater amount of emulsifier in order to produce a satisfactory and stable emulsion compared to the same composition in microemulsion form.
In a preferred method, fuel mixtures of the present invention are prepared using ultrasonic mixing equipment, which equipment is particularly advantageous for preparing stable emulsions having a small particle size, for example less than about 10 microns, or about 0.01 to about 5 microns on average, in other words embodiments of a microemulsion. Preferred equipment of this type is available commercially as "Sonolator" ultrasonic homogenizing system, Sonic Corp., Conn. Such microemulsions can be prepared at ambient temperature, for example about 22 °C, and at pressures of about 500 psi to about 1500 psi, although pressures as high as 5000 psi can also be used to produce stable microemulsions. The Sonolator system is particularly useful in that it can be operated in alternative, useful modes, including semi-continuous, continuous, single-feed or multiple-feed. In particular, such a system operated in multiple-feed mode can utilize feed tanks containing, for example, vegetable oil, water, emulsifier and other components, such as alcohol, cetane enhancer, alkyl glycol or alkyl glycol derivative, etc. Such a system allows feeding of one or more of the components simultaneously, sequentially or intermittently in order to achieve a particularly desirable result, including but not limited to a specific emulsion particle size, particle size distribution, mixing time, etc. As noted above, fuel compositions prepared using ultrasonic emulsification can be accomplished using a lower concentration of emulsifier for the same concentration of other components, particularly the vegetable oil(s) and water. For example, where a composition prepared without ultrasonic mixing requires about 1.0 wt% emulsifier to obtain a satisfactory emulsion, it may only require less than about 0.5 wt% emulsifier with the same composition in order to obtain a satisfactory emulsion, preferably an enhanced emulsion in that the particle size is smaller, resulting in a microemulsion. Typically the amount of emulsifier is about
10% less than would be required in the absence of ultrasonic emulsification; preferably about 20% less; more preferably about 30% less; still more preferably about 40% less; for example, about 50%, 60%, 70%, 80% or even 90% less than the amount of emulsifier required for a satisfactory emulsion without the use of ultrasonic energy input. For example, an emulsified fuel composition requiring 1 wt% emulsifier to obtain an average emulsion particle size of about 20 microns can be replaced with 0.2 wt% of the same emulsifier in the same composition to obtain an emulsion having a particle size of about 5 microns. For purposes herein, the use of a device that introduces ultrasonic energy for mixing and emulsification is referred to as a "high shear" method, regardless of the physical processes that may occur on a microscopic or molecular scale.

[0031] Emulsification using high shear such as imparted by an ultrasonic device results in an emulsion having a mean particle or droplet size in the range of about 0.01 microns to less than about 20 microns; such as about 0.01 microns to about 15 microns; or about 0.1 microns to about 10 microns; about 0.1 microns to about 8 microns; about 0.2 microns to about 6 microns; about 0.5 microns to about 5 microns; about 0.5 microns to about 4 microns; about 0.5 microns to about 3 microns; about 0.5 microns to about 3 microns; about 0.1 microns to about 2 microns; about 0.1 microns to about 1 micron; or about 0.1 microns to about 1 micron or less, for example about 0.8 microns. According to a preferred embodiment of the invention, the dispersed phase or the water-containing phase of the fuel composition comprises droplets having a mean diameter, or major dimension, of 5 microns or less. Thus emulsification is conducted under conditions sufficient to provide such a mean droplet particle size.

[0032] High-shear devices that may be used include but are not limited to the Sonic Corporation Sonolator Homogenizing
System, in which pressure can be varied over a wide range, for example about 500 to about 5,000 psi; IKA Work Dispax, and shear mixers including multistage, for example, three stage rotor/stator combinations. The tip speed of the rotor/stator generators may be varied by a variable frequency drive that controls the motor. Silverson mixer two-stage mixer, which also incorporates a rotor/stator design and the mixer employs high-volume pumping characteristics similar to a centrifugal pump. Inline shear mixers employing a rotor-stator emulsification approach (Silverson Corporation); Jet Mixers, venturi-style/cavitation shear mixers; Microfluidizer shear mixers, high-pressure homogenization shear mixers (Microfluidics Inc.); and any other available high-shear generating mixer capable of producing the desired microemulsion, including high shear mixers selected from the group consisting of Aquashear mixers (Flow Process Technologies Inc.), pipeline static mixers, hydraulic shear devices, rotational shear mixers, ultrasonic mixing, and combinations thereof.

[0033] Mixing of the components is preferably conducted at ambient, or substantially ambient, temperature conditions. It has been observed that in some instances mixing to obtain the emulsified fuel composition is accompanied by a slight exothermic response. Mixing can be satisfactorily conducted at temperatures in the range of about 5 °C to about 75 °C; for example about 10 °C to about 65 °C; or about 15 °C to about 55 °C; or about 20 °C to about 45 °C; such as 22 °C to about 35 °C.

[0034] The water used in the compositions of the present invention can be from any source. The water employed in preparing the fuel compositions of the present invention can be deionized, purified for example using reverse osmosis or distillation, and/or demineralized and have a low content of dissolved minerals, for example, salts of calcium, sodium and
magnesium, and will similarly include little, if any, chlorine and/or fluorine as well as being substantially free of undissolved particulate matter. Preferably the water has been substantially demineralized by methods well known to those skilled in the art of water treatment in order to remove dissolved mineral salts and has also been treated to remove other additives or chemicals, including chlorine and fluorine. The substantial absence of such materials is expected to lead to improvements in the condition of metal surfaces in engines and burners, particularly the inner surfaces of cylinders and nozzles. The water may be present in the water–vegetable oil fuel emulsions at a concentration of about 1% to about 50% by weight; alternatively about 2% to about 50% by weight; about 3% to about 40% by weight; about 4% to about 35% by weight; and about 5% to about 30% water.

[0035] The fuels useful in the present invention are based on animal derived oils and fats as well as on vegetable oils and fats, including mixtures thereof. Vegetable oils and fats are substances that are present, in variable percentages, in the seeds or in the fruits of various plants. In addition to those that are typically available in nature, the present invention can also utilize vegetable oils and fats that are obtained from genetically engineered plants, including algae, and including those that may be developed to yield particularly high levels of oils and fats so that they are particularly preferred sources of such materials for use as fuels. Since the fats and oils are to be used in the compositions of the present invention and burned as fuel, it is not necessary that such fats and oils be edible. At the present time, the most common, commercially available vegetable oils, such oils being particularly useful herein, are obtained from the seeds of peanuts, sunflowers, soy, sesame, colza (similar in its properties to rapeseed oil, but obtained from the seeds of Brassica campestris, var.
oleifera), rape or canola, corn and cotton and from the fruits of palm, olive, and coconut. The fatty substance can be obtained from treatment of the entire fruit (for example, olive oil), the pulp (palm oil), or just the kernel (palm seed oil). All of these vegetable based or derived oils are examples of oils suitable for use in the present invention. Other vegetable oils that may be useful in the present invention include crambe oil, jatropha oil, linseed oil, tung oil, as well as other so-called minor oil crops as described in "Minor Oil Crops," FAO Agricultural Services Bulletin No. 94, Food and Agricultural Organization of the United Nations, Rome, 1992, incorporated herein by reference, such oils generally including: among the minor edible oil crops, argan; avocado; babassu palm; balanites; borneo tallow nut; brazil nut; caryocar spp; cashew nut; Chinese vegetable tallow; cohune palm; the cucurbitaceae family including gourd, buffalo gourd, fluted pumpkin, and marrow; smooth loofah; grapeseed; illipe; kusum; macadamia nuts; mango seed; noog abyssinia; nutmeg; perilla; pili nut; rice bran; sacha inche; seje; shea nut; and teased. Among the minor non-edible oil crops are: allanblackia; almond; chaulmoogra; cuphea spp.; jatropha curcas; karanja seed; neem; papaya; tonka bean; tung; and ucuuba. Vegetable oils are obtained from their vegetable plants, seeds, etc. by methods well known in the art, including mechanical extraction or pressing as well as chemical or solvent extraction, and are typically filtered to remove extraneous matter in order to deliver a substantially clean product. However, it is within the scope of the present invention that used vegetable oil or fat from commercial sources can also be used, including, for example, food frying operations.

[0036] Furthermore, oils and fats useful in the present invention can be obtained from animal derived sources. Such animal derived or extracted oils include animal tissue
extract, piscine oil, cod-liver and shark-liver oil, fish oil in general, including oil from a wide variety of oil bearing fish some of which may be farmed for that purpose including fish oil currently being promoted by the Alaskan fish industry, tallow and mixtures thereof. For purposes herein, tallow refers to fat obtained from parts of the bodies of cattle, sheep, oxen, horses, chickens and other birds raised for food purposes, and the like as well as similar fats, such as those obtained from plants and also referred to as tallow. Large quantities of animal derived fats and oils can be obtained as byproducts from meat rendering facilities. Mixtures of oils and fats obtained from vegetable and animal sources are also useful in the present invention. [0037] In addition to or as part of the categories of vegetable and animal derived oils and fats are those oils and fats obtained from recycled oil and grease usually from restaurants and food processing plants. Such fats and oils may originally be from vegetable or animal sources. It is to be understood that oils and fats from these sources can still be useful even though they may require some pretreatment in order to remove food and other particulate matter as well as to reduce acidity from free fatty acids or sulfur-containing compounds that may be present, using methods well known to those skilled in the art. [0038] Surfactants are known to enhance the stability of an emulsion. A surfactant may be employed in accordance with the present invention to enhance the stability of fuel-water emulsion, particularly over time. The following tabulation provides examples of surfactants contemplated by the invention, although useful surfactants are not limited to those in the table. For example, also useful are surfactants disclosed in a comprehensive listing of surfactants that can be found in the spectral database of Bio-Rad Laboratories (www.informatics.bio-rad.com), including infrared spectra and.
in a number of cases, chemical composition and chemical and physical properties and sources, incorporated herein by-reference. The compounds are generally characterized as alcohols, nitrogen-containing compounds, esters of long chain carboxylic acids, hydrocarbons, various esters and salts of long chain carboxylic acids, sulfated and sulfonated compounds including alkylaryl sulfonates isothionates, lignosulfonates, sulfated and sulfonated alcohols, amines, amides, carboxylic acids, carboxylic acid esters, sulfated and sulfonated polyalkoxylated materials such as esters, ethers, nitrogen compounds, aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA), in other words EDTA, DTPA, NTA acids and salts, phosphates, silicates and silicones. To the extent that a particular surfactant includes atoms, groups or compounds that may unnecessarily contribute to pollution, e.g., sulfur, its use can be limited to the amount necessary for producing and/or maintaining a stable emulsion or fuel composition. Particularly preferred surfactants include cetyl alcohol, hydrogenated castor oil and mixtures of cetyl alcohol and hydrogenated castor oil. The following materials, referred to as surfactants herein, can be employed in accordance with the water-fuel composition of the present invention.

[0039] Tabulation of Useful Surfactants
[0040] (A) Nonionic surfactants:
Esters of polyhydric alcohols,- alkoxylated amides,- esters of polyoxyalkylene, polyoxypropylene and of polyoxyethylene-polyoxypropylene glycols,- ethers of polyoxyalkylene glycols; tertiary acetylenic glycols; and polyoxyethylated alkyl phosphates.
[0041] (B) Anionic surfactants:
Carboxylic acids and soaps, sulfated esters, amides, alcohols, ethers and carboxylic acids (all salts); sulfonated petroleum, aromatic hydrocarbons, aliphatic hydrocarbons, esters, amides, amines, ethers, carboxylic acids, phenols and lignins (all salts); acylated polypeptides (salts); and phosphates.

[0042] The following specific compounds are also included. In the list that follows, the abbreviation "P.O.E." refers to polyoxyethylene (polyethylene glycol) and the abbreviation "P.O.P." refers to polyoxypropylene.

[0043] (C) Fatty Acids:
Caprylic acid, abietic acid, pelargonic acid, coconut oil fatty acids, capric acid, corn oil fatty acids, lauric acid, cottonseed oil fatty acids, myristic acid, soya oil fatty acids, palmitic acid, tallow fatty acids, stearic acid, hydrogenated fish oil fatty acids, behenic acid, tall oil fatty acids, undecylenic acid, dimer acids, oleic acid, trimer acids, erucic acid, castor oil, linoleic acid, hydrogenated castor oil, ricinoleic acid, lanolin, naphthenic acid, and lanolin fatty acids.

[0044] (D) Fatty Acid Salts:
Lithium stearate, ammonium oleate, cadmium stearate, sodium caprate, ammonium linoleate, calcium stearate, sodium laurate, ammonium ricinoleate calcium oleate, sodium myristate, ammonium naphthenates, calcium linoleate, sodium palmitate, ammonium abietate, calcium ricinoleate, sodium stearate, morpholine laurate, calcium naphthenates, sodium undecylenate, morpholine myristate, cobalt stearate, sodium oleate, morpholine palmitate, cobalt naphthenates, sodium linoleate, morpholine stearate, copper stearate, sodium ricinoleate, morpholine undecylenate, copper oleate, sodium naphthenates, morpholine olate, copper naphthenates, sodium abietate, morpholine linoleate, iron stearate, sodium polymerized carboxylates, morpholine ricinoleate, iron naphthenate.
morpholine napthenate, lead stearate, sodium salt of tall oil, morpholine abietate, lead oleate, potassium caprate, triethanolamine caprate, lead naphthenate, potassium laurate, triethanolamine laurate, magnesium stearate, potassium myristate, triethanolamine myristate, magnesium oleate, potassium palmitate, manganese stearate, potassium stearate, triethanolamine palmitate, manganese naphthenate, potassium undecylenate, triethanolamine stearate, nickel oleate, potassium oleate, strontium stearate, potassium linoleate, triethanolamine undecylenate, tin oleate, potassium ricinoleate, zinc laurate, potassium naphthenate, triethanolamine oleate, zinc palmitate, potassium abietate, triethanolamine linoleate, zinc stearate, ammonium caprate, triethanolamine ricinoleate, zinc oleate, ammonium laurate, zinc linoleate, ammonium myristate, triethanolamine naphthenates, zinc naphthenate, ammonium palmitate, zinc resinate, ammonium stearate, triethanolamine abietate, ammonium undecylenate, aluminum palmitate, aluminum stearate, aluminum oleate, bari um stearate, and barium naphthenate.

[0045] (E) Olefins:
Linear C\textsubscript{14} alpha-olefin, and linear C\textsubscript{16} alpha-olefin.

[0046] (F) Phosphorous Compounds and Mercaptans:
POE octyl phosphate, sodium phosphated castor oil, ammonium phosphated castor oil, 2-ethylhexyl polyphosphate sodium salt, capryl polyphosphate sodium salt, sodium di(2-ethylhexyl) phosphate, lecithin (soy phosphatides), and POE tert-dodecyl mercaptoethanol.

[0047] (G) Polyethylene and Propylene Glycol Esters:
Hydroxyethyl laurate, PEG monooleate, propylene glycol monolaurate, hydroxyethoxyethyl laurate, PEG dioleate, ethylene glycol monoricinoleate, propylene glycol monostearate, hydroxy ethoxyethoxy ethyl laurate, diethylene glycol monoricinoleate, propylene glycol dilaurate, PEG monolaurate, PEG monoricinoleate, propylene glycol distearate,
PEG dilaurate, diethylene glycol coconate, ethylene glycol monostearate, dipropylene glycol monostearate, POE coco fatty acids ester, diethylene glycol monostearate, propylene glycol monooleate, POE castor oil, triethylene glycol monostearate, ethylene glycol hydroxystearate, propylene glycol monoric inoleate, PEG monostearate, PEG trihydroxy stearate, propylene glycol monoisostearate, ethylene glycol distearate, POE hydrogenated castor oil, propylene glycol monohydroxystearate, PEG distearate, POE tall oil, PEG monoisostearate, POE abietic acid, propylene glycol dipelargonate, PEG diisostearate, POE lanolin, hydroxyethyl oleate, acetylated lanolin, isopropylester of lanolin fatty acids, hydroxyethoxyethyl oleate, POE lanolin acetylated, methoxy PEG monooleate, POE propylene glycol monostearate, and hydroxy ethoxyethoxy ethyl oleate.

[0048] (H) Alcohols, Phenols and Polyoxyethylene Derivates:
Stearyl alcohol, oleyl alcohol, octyl phenol, nonyl phenol, tert-octylphenoxy ethanol, p-dodecyl phenol, dinonyl phenol, tridecyl alcohol, tetradecyl alcohol, lanolin alcohols, cholesterol, dimethyl hexynol, dimethyl octynediol, tetramethyl decynediol, POE tridecyl phenyl ether, POE lanolin alcohol ether, POE cholesterol, POE n-octylphenol, POE tert-octylphenol, POE nonylphenol, POE dinonyl phenol, POE dodecyl phenol, POE lauryl alcohol ether, POE cetyl alcohol ether, POE stearyl alcohol ether, POE tetramethyldecynediol, POE oleyl alcohol ether, POP EtO, POE isohexadecyl alcohol ether, 2,6,8-trimethyl-4-nonyloxypolyethylenoxyethanol, polyoxypropylene-polyoxyethylene block copolymer, alkyl ether of POE/POP, and POE tridecyl alcohol ether.

[0049] (J) Glycerol Esters:
Glycerol monocaprylate, glycerol monolaurate, glycerol mono/dicocoate, glycerol dilaurate, glycerol monostearate, glycerol monostearate distilled, glycerol distearate, glycerol
monooleate, glycerol dioleate, glycerol trioleate, glycerol monoisostearate, glycerol monoricinoleate, glycerol monohydroxystearate, POE glycerol monostearate, acetylated glycerol monostearate, succinylated glycerol monostearate, diacetylated glycerol monostearate tartrate, modified glycerol phthalate resin, triglycerol monostearate, triglycerol monooleate, triglycerol monoisostearate, decaglycerol tetraoleate, decaglycerol decastearate, pentaerythritol monolaurate, pentaerythritol monostearate, pentaerythritol distearate, pentaerythritol tetrastearate, pentaerythritol monooleate, pentaerythritol dioleate, pentaerythritol trioleate, pentaerythritol tetracicinoleate, sorbitan monolaurate, POE sorbitan monolaurate, sorbitan monopalmitate, POE sorbitan monopalmitate, sorbitan monostearate, POE sorbitan monostearate, sorbitan tristearate, POE sorbitan tristearate, sorbitan monooleate, POE sorbitan monooleate, sorbitan trioleate, POE sorbitan trioleate, POE sorbitol hexaoleate, POE sorbitol oleate laurate, POE sorbitol polyoleate, POE sorbitol, beeswax-ester, sucrose monolaurate, sucrose cocoate, sucrose monomyristate, sucrose monopalmitate, sucrose dipalmitate, sucrose monostearate, sucrose distearate, sucrose monooleate, sucrose dioleate, lauryl lactate, cetyl lactate, sodium lauryl lactate, sodium stearoyl lactate, sodium isostearoyl-2-lactylate, sodium stearoyl-2-lactylate, calcium stearoyl-2-lactylate, sodium capryl lactate, lauryl alcohol, and cetyl alcohol.

[0050] **(K)** Amides and amide derivatives:
Stearamide, oleamide, erucamide, behenamide, lauric acid monoethanolamide, tallow monoethanolamide, POE lauric amide, myristic acid diethanolamide, stearic acid diethanolamide, oleic acid diethanolamide, POE oleic amide, coco acid diethanolamide, POE coco amide, POE hydrogenated tallow amide,
lauric acid monoisopropanolamide, and oleic acid monoisopropanolamide.

[0051] (L) Sulfates:
Sodium n-octyl sulfate, sodium 2-ethylhexyl sulfate, sodium decyl sulfate, sodium lauryl sulfate, sodium tridecyl sulfate, sodium sec-tetradecyl sulfate, sodium cetyl sulfate, sodium sec-heptadecyl sulfate, sodium oleyl sulfate, sodium oleyl stearate sulfate, sodium tridecyl ether sulfate, potassium lauryl sulfate, magnesium lauryl sulfate, triethanolamine lauryl sulfate, ammonium lauryl sulfate, diethanolamine lauryl sulfate, triethanolammonium lauryl sulfate, POE octylphenol sodium salt, alkylaryl polyether sulfate sodium salt, sulfated POE nonylphenol sodium salt, sulfated nonylphenyl ether of tetraethyleneglycol ammonium salt, sulfated lauryl ether of tetraethyleneglycol sodium salt, POE sodium lauryl monoether sulfate, POE sodium lauryl ether sulfate, POE ammonium lauryl sulfate, sulfated oleic acid sodium salt, sulfated castor oil-fatty acids sodium salt, sulfated propyloleate sodium salt, sulfated isopropyloleate sodium salt, sulfated butyloleate sodium salt, sulfated glycerol monolaurate sodium salt, sulfated glycerol trioleate sodium salt, sulfated castor oil sodium salt, sulfonated marine oil, sulfated neatsfoot oil sodium salt, sulfated rice bean oil sodium salt, sulfated soya bean oil sodium salt, sulfated synthetic sperm oil, and sulfated tallow sodium salt.

[0052] (M) Miscellaneous Surfactant Compounds:
Perfluoro surfactant-anionic, perfluoro surfactant-cationic, ethylenediamine tetraacetic acid disodium salt, ethylenediaminetetraacetic acid tetrasodium salt, sodium dihydroxyethyl glycinate, trisodium nitrilotriacetate, sodium citrate, silicone defoamer-oil, silicone defoamer-water dispersible, sodium tetraborate, sodium carbonate, sodium phosphate-tribasic, sodium silicate, and alkyl benzene sulfonic acid-propylene tetramer.
[0053]  (N) Sulfonates:
Sodium toluene sulfonate, sodium xylene sulfonate, sodium
cumene sulfonate, sodium dodecylbenzene sulfonate, sodium
tridecylbenzene sulfonate, sodium kerylbenzene sulfonate,
calcium dodecylbenzene sulfonate, ammonium xylene sulfonate,
triethanolammonium dodecylbenzene sulfonate, alkylammonium
dodecylbenzene sulfonate, aliphatic hydrocarbons-sulfonic
acid, sodium petroleum sulfonate, calcium petroleum sulfonate,
Bryton barium sulfonate, magnesium petroleum sulfonate,
ammonium petroleum sulfonate, isopropylamine petroleum
sulfonate, ethylenediamine petroleum sulfonate,
triethanolamine petroleum sulfonate, sulfonated naphthalene
sodium diisopropyl naphthalene sulfonate, sodium dibutyl
naphthalene sulfonate, sodium benzyl naphthalene sulfonate,
sodium naphthalene formaldehyde-condensate sulfonate, sodium
polymerized alkynaphthalene sulfonate, potassium polymerized
alkynaphthalene sulfonate, ammonium dibutynaphthalene
sulfonate, ethanolamine dibutynaphthalene sulfonate, sodium
sulfooleate, sodium monobutylphenylphenol monosulfonate,
disodium dibutylphenylphenol disulfonate, potassium
monoethylphenylphenol monosulfonate, ammonium
monoethylphenylphenol monosulfonate, guanidinium
monoethylphenylphenol monosulfonate, sodium decylidendiphenylether
disulfonate, sodium dodecylidendiphenylether disulfonate, calcium
polymerized alkyl-benzene sulfonate, sulfonated polystyrene,
sulfonated aliphatic polyester, sodium-2-sulfoethyl olate,
sodium amyl sulfooleate, sodium lauryl sulfoacetate, sodium
diisobutyl sulfosuccinate, sodium diamyl sulfosuccinate,
sodium dihexyl sulfosuccinate, sodium dioctyl sulfosuccinate,
sodium ditridecyl sulfosuccinate, sodium alkylarylpolyether
sulfonate, and sodium lignosulfonate.

[0054]  (O) Amines and Amine Derivatives:
tert-\text{C}_{1x}\text{C}_{14} amine, n-dodecylamine, n-tetradecylamine, n-
hexadecylamine, n-octadecylamine, C_{x8}-C_{24} amine, oleylamine,
cocoamine, hydrogenated tallow amine, tallow amine, POE tert-
amine, POE stearyl amine, POE oleyl amine, C\textsubscript{i2}-C\textsubscript{i4} tert-
alkylamines, ethoxylated POE cocoamine, POE tallow amine, POE
soya amine, POE octadecylamine, N-b-hydroxyethyl stearyl
imidazoline, POE (3) N-tallow trimethylene diamine, N-b-
hydroxyethyl cocoimidazoline, N-b-hydroxyethyl oleyl
imidazoline, n-dodecylamine acetate, hexadecyl amine acetate,
octadecylamine acetate oleylamine acetate, cocoamine acetate,
hydrogenated tallow amine acetate, tallow amine acetate, soya
amine acetate, N-stearyl-N\textsuperscript{1}.N\textsuperscript{1}-diethylethylene-
diamine acetate, N-oleylethylenediamine formate, cocoamidopropyl
dimethyl amine oxide, lauryl dimethylamine oxide, myristyl
dimethylamine oxide, soya amine, diococoamine, dihydrogenated
tallow amine, dimethyl hexadecylamine, dimethyl
octadecylamine, dimethyl cocoamine, dimethyl soyaamine, N-
coco-1,3-diaminopropane, N-soya-1,3-diaminopropane, N-tallow-
1,3-diaminopropane, N-coco-b-aminobutyric acid,
stearamidoethyl diethylamine, sodium-N-coco-b-aminopropionate,
N-tallow trimethylene diamine diacetate, disodium-
N-tallow-b-imino dipropionate, disodium-N-lauryl-b-imino
dipropionate, cetyl betaine, coco betaine, myristamidopropyl
betaine, oleyl betaine, coconut amido betaine, oleyl amido
betaine, coconut oil acid ester of sodium isethionate,
cocoamido alkyl dimethylamine, behenic amido alkyl
dimethylamine, isostearic amido alkyl dimethylamine, oleic
amido alkyl dimethylamine, sodium-N-methyl-N-palmitoyl
taurate, sodium-N-methyl-N-oleyl taurate, sodium-N-coconut
acid N-methyl taurate, sodium-N-methyl-N-tall oil taurate, N-
lauryl sarcosine, cocoyl sarcosine, N-oleyl sarcosine, sodium-
N-lauryl sarcosinate, sodium carboxymethylnonyloxyhydroxy-ethy
imidazolinium hydroxide, sodium carboxymethylundecyloxyhydroxy-
ethyl imidazolinium hydroxide, sodium carboxymethylcocoxyhydroxy-
ethyl imidazolinium hydroxide, sodium carboxyethylolenyloxyhydroxy-
ethyl imidazolinium hydroxide, sodium carboxyethylolenyloxyhydroxy-
ethyl imidazolinium hydroxide, sodium
carboxymethylstearylhydroxy-ethyl imidazolinium hydroxide, and sodium carboxymethylsodiumcarboxyethyl cocoether imidazolinium.

[0055] (P) Quaternary Amine Salts:
Dodecyltrimethyl ammonium chloride, hexadecyltrimethyl ammonium chloride, octadecyltrimethyl ammonium chloride, cetyltrimethyl ammonium bromide, cetyltrimethyl ammonium bromide, coco trimethyl ammonium chloride, tallow trimethyl ammonium chloride, soya trimethyl ammonium chloride, dicoco dimethyl ammonium chloride, dimethyl 80% behenyl benzyl ammonium chloride, methyl bis (2-hydroxyethyl) coco ammonium chloride, dihydrogenated tallow dimethyl ammonium chloride, methylcetylbenzyl trimethyl ammonium chloride, n-alkyl dimethyl benzyl ammonium chloride, alkylidimethyl-3 -4-dichloro-
benzyl ammoniumchloride, octylphenoxylmethoxyethyl dimethyl-
benzyl ammonium chloride, octylcresoxyethoxyethyl dimethyl-
benzyl ammonium chloride, cocoamidopropyl PG-dimonium chloridediphosphate, 2-hydroxyethylbenzyl stearyl imidazolinium chloride, 2-hydroxyethylbenzyl coco imidazolinium chloride, ethyl bis (pulethoxyethanol) alkyl ammonium chloride, diethyl heptadecyl imidazolinium ethylsulfate, lauryldimethylbenzyl ammonium chloride, stearyldimethylbenzyl ammonium chloride, laurlylpyridinium chloride, 1-hexadecylpyridinium chloride, cetylpyridinium bromide, lauryl isoquinolinium bromide, and substituted oxazoline.

[0056] In one embodiment the emulsifier or surfactant comprises at least one sorbitan ester. The sorbitan esters include sorbitan fatty acid esters wherein the fatty acid component of the ester comprises a carboxylic acid of about 10 to about 100 carbon atoms, and in one embodiment about 12 to about 24 carbon atoms. Sorbitan is a mixture of anhydrosorbitols, principally 1,4-sorbitan and isosorbide (Formulas I and II):
Sorbitan, (also known as monoanhydrosorbitol, or sorbitol anhydride) is a generic name for anhydrides derivable from sorbitol by removal of one molecule of water. The sorbitan fatty acid esters of this invention are a mixture of partial esters of sorbitol and its anhydrides with fatty acids. These sorbitan esters can be represented by the structure below which may be any one of a monoester, diester, triester, tetraester, or mixtures thereof (Formula III):

\[
\text{(III)}
\]

In formula (III), each Z independently denotes a hydrogen atom or C(O)R\text{--}, and each R mutually independently denotes a hydrocarbyl group of about 9 to about 99 carbon atoms, more preferably about 11 to about 23 carbon atoms. Examples of sorbitan esters include sorbitan stearates and sorbitan oleates, such as sorbitan stearate (i.e., monostearate), sorbitan distearate, sorbitan tristearate, sorbitan monoleate and sorbitan sesquioleate. Sorbitan esters are available commercially under the trademarks "Span" and "Arlacel" from ICI. The sorbitan esters also include polyoxyalkylene sorbitan esters wherein the alkylene group has about 2 to about 30 carbon atoms. These polyoxyalkylene sorbitan esters can be represented by Formula IV:
wherein in Formula IV, each R independently is an alkylene group of about 2 to about 30 carbon atoms; R\(^1\) is a hydrocarbyl group of about 9 to about 99 carbon atoms, more preferably about 11 to about 23 carbon atoms, and w, x, y and z represent the number of repeat oxyalkylene units. For example ethoxylolation of sorbitan fatty acid esters leads to a series of more hydrophilic surfactants, which is the result of hydroxy groups of sorbitan reacting with ethylene oxide. One principal commercial class of these ethoxylated sorbitan-esters are those containing about 2 to about 80 ethylene oxide units, and in one embodiment from about 2 to about 30 ethylene oxide units, and in one embodiment about 4, in one embodiment about 5, and in one embodiment about 20 ethylene oxide units. They are available from Calgene Chemical under the trademark "POLYSORBATE" and from ICI under the trademark "TWEEN". Typical examples are polyoxyethylene (hereinafter "POE") (20) sorbitan tristearate (Polysorbate 65; Tween 65), POE (4) sorbitan monostearate (Polysorbate 61; Tween 61), POE (20) sorbitan trioleate (Polysorbate 85; Tween 85), POE (5) sorbitan monooleate (Polysorbate 81; Tween 81), and POE (80) sorbitan monooleate (Polysorbate 80; Tween 80). As used herein the number within the parentheses refers to the number of ethylene oxide units present in the composition.

[0057] The following is a list of emulsifiers that may be particularly useful:

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<th>Product Name*</th>
<th>Synonym</th>
<th>HLB</th>
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<tr>
<td>2,4,7,9-Tetramethyl-5-decyne-4,7-diol</td>
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<td>PEG-block-PPG-block-PEG, Mn=4400</td>
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<td>Triton X-100</td>
<td>Polyoxyethylene(10) isoctylphenyl ether</td>
<td>13.5</td>
</tr>
<tr>
<td>Igepal CO-720</td>
<td>Polyoxyethylene(12) nonylphenyl ether</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>Polyoxyethylene(12) tridecyyl ether</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>Polyoxyethylene(18) tridecyyl ether</td>
<td>14.5</td>
</tr>
<tr>
<td>Igepal CA-720</td>
<td>Polyoxyethylene(12) isoctylphenyl ether</td>
<td>14.6</td>
</tr>
<tr>
<td>Tween 80</td>
<td>Polyoxyethylene(20) sorbitan monooleate</td>
<td>14.9</td>
</tr>
<tr>
<td>Tween 60</td>
<td>Polyoxyethylene(20) sorbitan monostearate</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>PEG-block-PPG-block-PEG, Mn=2900</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>PPG-block-PEG-block-PPG, Mn=2000</td>
<td>15.0</td>
</tr>
<tr>
<td>Brij 78</td>
<td>Polyoxyethylene(20) stearyl ether</td>
<td>15.3</td>
</tr>
<tr>
<td>Brij 98</td>
<td>Polyoxyethylene(20) oleyl ether</td>
<td>15.3</td>
</tr>
<tr>
<td>Merpol HCS surfactant</td>
<td>Polyoxyethylene(20) sorbitan monopalmitate</td>
<td>15.5</td>
</tr>
<tr>
<td>Tween 40</td>
<td>Polyoxyethylene(20) sorbitan monopalmilate</td>
<td>15.6</td>
</tr>
<tr>
<td>Brij 58</td>
<td>Polyoxyethylene(20) cetyl ether</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>Polyoxyethylene(20) hexadecyl ether</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>Polyethylene-block-poly(ethylene glycol), Mn=2250</td>
<td>16.0</td>
</tr>
<tr>
<td>Tween 20</td>
<td>Polyoxyethylene(20) sorbitan monolaurate</td>
<td>16.7</td>
</tr>
<tr>
<td>Brij 35</td>
<td>Polyoxyethylene(23) lauryl ether</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>2,4,7,9-Tetramethyl-5-decyne-4,7-diol ethoxylate (15 EO/OH)</td>
<td>17.0</td>
</tr>
<tr>
<td>Igepal CO-890</td>
<td>Polyoxyethylene(40) nonylphenyl ether</td>
<td>17.8</td>
</tr>
<tr>
<td>Triton X-405</td>
<td>Polyoxyethylene(40) isoctylphenyl ether</td>
<td>17.9</td>
</tr>
<tr>
<td>Brij 700</td>
<td>Polyoxyethylene(100) stearyl ether</td>
<td>18.8</td>
</tr>
<tr>
<td>Igepal CO-990</td>
<td>Polyoxyethylene(100) nonylphenyl ether</td>
<td>19.0</td>
</tr>
<tr>
<td>Igepal DM-970</td>
<td>Polyoxyethylene(150)</td>
<td>19.0</td>
</tr>
</tbody>
</table>
Useful emulsifiers of the types listed in the above table can be generically represented by the following classes of chemical compounds, members of which are commercially available and are suitable provided that they are used in accordance with the teachings herein such that stable emulsified compositions are produced:

(a) sorbitol esters of the general formula

\[
\text{X} \quad \text{H} \quad \text{H} \quad \text{X} \\
\text{H} \quad \text{C} \quad \text{C} \quad \text{X} \\
\text{X} \quad \text{H} \quad \text{H} \quad \text{X}
\]

in which: the radicals X are identical to or different from one another and are each OH or R\textsuperscript{1}COO\textsuperscript{"}, where R\textsuperscript{1} is a linear or branched, saturated or unsaturated, aliphatic hydrocarbon radical optionally substituted by hydroxyls and having from 7 to 22 carbon atoms, provided that at least one of said radicals X is R\textsuperscript{1}COO\textsuperscript{"},

(b) fatty acid esters of the general formula

\[
\text{R}^2 \quad \text{C} \quad \text{O} \quad (\text{R}^\text{3} \text{O})_n \quad \text{R}^4
\]

in which: R\textsuperscript{2} is a linear or branched, saturated or unsaturated, aliphatic hydrocarbon radical optionally substituted by hydroxyl groups and having from 7 to 22 carbon atoms, R\textsuperscript{3} is a linear or branched C\textsubscript{1}-C\textsubscript{10} alkylene,
n is an integer greater than or equal to 6, and
\( R^4 \) is \( H \), linear or branched \( \text{Ci-Ci}_0 \) alkyl or
\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{R}^5
\end{array}
\]
where \( R^5 \) is as defined above for \( R^2 \); and

[0061] (c) polyalkoxylated alkylphenol of the general formula

\[
\begin{array}{c}
\text{R}^6 \\
\text{O} \\
\text{R}^7 \quad \text{O}_m \quad \text{R}^8
\end{array}
\]

in which: \( R^8 \) is a linear or branched \( \text{Ci-C}_2\text{O} \) alkyl,
\( m \) is an integer greater than or equal to 8, and
\( R^7 \) and \( R^8 \) are respectively as defined above for \( R^3 \) and \( R^4 \) of
formula (II).

[0062] Particularly useful emulsifiers include compounds exhibiting a hydrophilic- lipophilic balance (HLB, which refers to the size and strength of the polar (hydrophilic) and non-polar (lipophilic) groups that comprise the emulsifier or surfactant molecule) typically in the range of about 1 to about 40; in another embodiment about 5 to about 20. HLB is a well-known parameter utilized by those skilled in the art for characterizing emulsifiers. It is defined in detail, for example, in the references "Emulsions: Theory and Practice, P. Becher, Reinhold Publishing Corp., ACS Monograph, ed. 1965", in the chapter "The chemistry of emulsifying agents" (pg. 232 et seg.); and also in Handbook of Applied Surface and Colloid Chemistry, K. Holmberg (Ed.), "Chapter 11, Surface Chemistry in the Petroleum Industry," J.R. Kanicky et al., 251-267, which also describes a method for calculating HLB values based on chemical structure; these references incorporated herein by reference to the extent permitted. A well established empirical procedure for determining HLB
values for a given emulsifier may be determined experimentally by the method of W.C. Griffin, J. Soc. Cosmetic Chem., 1, 311 (1949), incorporated herein by reference to the extent permitted. Examples of suitable compounds are included in the above table and are also disclosed in McCutcheon's Emulsifiers and Detergents, 1998, North American Edition (pages 1-235) & International Edition (pages 1-199), incorporated herein by reference for their disclosure of compounds having an HLB in the range of about 1 to about 40; in one embodiment about 1 to about 30; in one embodiment about 1 to 20; and in another embodiment about 4 to about 18; alternatively, greater than about 8, for example about 8.5 or about 9 to about 18. Various useful compounds include those identified in the above table, including for example, sorbitan monolaurate, polyoxyethylene (20) sorbitan monooleate, and polyoxyethylene (20) sorbitan monolaurate.

[0063] It is also possible to obtain stable emulsified fuel compositions using a combination of emulsifiers. For purposes of explanation and not limitation, for example instead of a single emulsifier having an HLB value of about 12 an emulsified fuel composition can be prepared using a mixture of emulsifiers, such as a 50/50 mixture two emulsifiers, one having an HLB value of about 16 and the other an HLB value of about 8. Similarly combinations of three or more emulsifiers can also be used, provided that the HLB value of the mixture exhibits the desired overall value and the effect of the mixture is to provide a stable emulsion. For purposes of a mixed emulsifier composition, the HLB value of the emulsifier mixture is calculated as a linear sum weighted average based on the weight fraction that each of the emulsifiers represents compared to the total amount of emulsifier present:

\[
\text{HLB}_m = \Sigma [(\text{HLB}_n) (\text{wtn/WT\text{tot}})]
\]

where:

\[\Sigma = \text{Sum of the values shown in brackets}\]
the HLB value of one or a mixture of emulsifiers; n = number of emulsifiers present in the mixture, wherein any number of emulsifiers can be used; typically n = 1 to about 5; more typically 1 to about 4; or 1 to about 3 or 1 to about 2. For example, it is suitable to use mixtures of 2, 3 or 4 emulsifiers to obtain a stable emulsion;

\[ \text{HLB}_n = \text{HLB value of a single emulsifier if } n = 1 \text{ or the HLB value of each emulsifier in a mixture of emulsifiers; } \]

\[ \text{wt}_n = \text{the weight, for example in grams, of each emulsifier in a mixture of emulsifiers; and } \]

\[ \text{wt}_{\text{tot}} = \text{the total weight of all emulsifiers present in a mixture of emulsifiers.} \]

[0064] In a preferred embodiment a mixture of two emulsifiers is used wherein one emulsifier has an HLB value of equal to or less than about 6, for example about 1 to about 6.0, or about 2 to about 5.9, or about 3 to about 5.5, or about 4 to about 5.9, and the like; and the second emulsifier has an HLB value of greater than about 6, for example about 6 to about 20; or about 6.1 to about 18, or about 6.5 to about 16, or about 7 to about 15, and the like,—provided that both emulsifiers do not have an HLB value of 6. Alternatively, one emulsifier comprising a bimodal distribution of chemical species exhibiting each of the HLB properties can be used.

[0065] The use of multiple emulsifiers in the same emulsified fuel composition can be advantageous in compositions in which the total concentration of hydrophilic components is low. For example, compositions in which the water concentration is less than about 5 wt%, such as about 1 wt% to about 5 wt%, or about 1 wt% to about 4 wt%, or 1 wt% to about 3 wt%, or 1 wt% to about 2 wt%. Alternatively, the concentrations of various hydrophilic or substantially hydrophilic components can be added together for consideration of the above recited concentrations, including water, hydroxyl-containing component (8) such as one or more alcohols
or glycols and the like. In particular, if the ratio of the total amount of such hydrophilic components to the total amount of lipophilic components, the latter including but not limited to the animal and vegetable fats and oils, is equal to or less than about 0.25, for example, about 0.05 to about 0.25 or any specific value therebetween, including, for example, about 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22 or 0.24, it is desirable to use a mixture of emulsifiers as described above; in other words, emulsifier mixtures wherein at least one emulsifier has an HLB value of equal to or less than about 6 and at least one emulsifier has an HLB value of greater than about 6 (subject to the provisos expressed above). For example, a composition comprising, in wt%, 80 of vegetable oil, 4 of water and 14 of ethanol (e.g., 95 wt% ethanol containing 5 wt% water and/or denaturants) results in a calculated ratio of 18/80 = 0.225. To prepare a stable emulsion using such components it is preferable to employ a mixture of emulsifiers, for example, a 50/50 mixture of an emulsifier having an HLB value of, for example, about 4 and one having an HLB value of about 15. In contrast, a stable emulsified composition can be prepared using a single emulsifier where the lipophilic and hydrophilic components comprise 75 wt% vegetable oil, 1 wt% water, and 23 wt% alcohol. Alternatively, a mixture of emulsifiers can be used even where the calculated ratio is greater than 0.25, particularly if the value is only slightly greater, for example about 5% to about 10% greater. Optionally, a mixture of emulsifiers can be used if desired; particularly if it is anticipated that the user of such a fuel composition may subsequently introduce an additive into the composition that might have the effect of changing the calculated ratio.

[0066] Alcohols useful in the present invention include hydroxyl-containing organic compounds selected from the group consisting of (A) monohydrlic (one OH group) alcohols
characterized as (1) aliphatic, including straight and branched chain, and sub-characterized within this group as paraffinic (for example, ethanol) and olefinic (for example, allyl alcohol); (2) alicyclic (for example, cyclohexanol); (3) aromatic (for example, phenol, benzyl alcohol); (4) heterocyclic (for example, furfuryl alcohol); and (5) polycyclic (for example, sterols); (B) dihydric (two OH groups), including glycols and derivatives (for example, diols); (C) trihydric (three OH groups), including glycerol and derivatives; and (D) polyhydric (polyols), having three or four or more OH groups). In particular, useful alcohols include alcohols selected from the group consisting of C1 to C4 straight and branched chain monoalcohols, C2 to C4 mono- and polyalkylene glycols including ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, derivatives of C2 to C4 mono- and polyalkylene glycols provided that the molecular weights of such polyalkylene glycols are suitable for use in the fuel compositions of the present invention, and mixtures thereof. Fuel compositions in which a monoalcohol is included also preferably include at least one of tert-butyl alcohol, at least one C2-C4 alkylene glycol or a mixture of both. Ethyl alcohol or ethanol and propylene glycol are particularly preferred in the compositions of the present invention. Ethanol is available commercially in the anhydrous form (also referred to as absolute alcohol or 100% ethanol) and as various proofs or percentages of ethanol where the additional component in the ethanol is water, the most common being 190 proof or 95 vol%. If ethanol is used for purposes other than as a beverage, it is denatured by addition of substances, such as methanol, 2-propanol, ethyl acetate, methyl isobutyl ketone, heptane or kerosene, to make the product undesirable for human consumption, but allows for its use for industrial purposes, including as a component in fuel or as a fuel. As
noted, ethanol other than absolute ethanol is typically identified by use of the term "proof," where the conversion between proof and the concentration of ethyl alcohol is that 2 proof equals 1% by volume, typically measured at 20 °C, although measurements at other temperatures are also accepted, including e.g., 15.6 °C. While various denaturants are available that can render ethanol (with or without the presence of moisture or water) unsuitable for human consumption, certain of such denaturants may not be suitable for use in connection with fuels because of their adverse effects on fuel stability, vehicle engines and fuel systems and emissions. A list of denaturants used in connection with ethyl alcohol for various purposes can be found in The Merck Index, Thirteenth Edition, 2001, entry 3796, page 670, incorporated herein by reference. Physical properties of ethanol can vary depending on whether ethanol is anhydrous, mixed with water to various concentrations, and whether it is denatured and the type of denaturant used. Denaturants that may be unsuitable for use in connection with fuels are known to those skilled in the art and are often specified by various governmental agencies. For example, the Indian government prohibits the use of methanol, pyrroles, turpentine, ketones and tars (high molecular weight pyrolysis products of fossil or non-fossil vegetable matter). The standards in ASTM D4806 and ASTM D5798, incorporated herein by reference, describe the amount and types of denaturants typically permitted for use in fuels and also identifies others that should not be used in view of their potentially adverse effects, as noted above. Furthermore, ASTM D5798 also describes the standards for fuels for use in engines that are designed to utilize ethanol as a substitute for petroleum, i.e., that include substantially high percentages of ethanol. Absolute ethyl alcohol is ordinarily understood to mean ethyl alcohol containing no more than 0.5 vol.% water, although for purposes of the present
invention, such a moisture limitation has little significance. When used in the vegetable oil emulsion fuel composition of the present invention, alcohol or a mixture of the alcohols identified herein as useful, are included at a concentration of about 1 wt% to about 25 wt% based on the total weight of the fuel composition; or about 2 wt% to about 22 wt%; or about 3 wt% to about 20 wt%; or about 4 wt% to about 18 wt%; or about 5 wt% to about 20 wt%; or about 1 wt% to about 15 wt%; or about 1 wt% to about 10 wt%; or about 1 wt% to about 5 wt%; or about 2 wt% to about 6 wt%; alternatively, about 3 wt% to about 8 wt%.

[0067] Alternatively, the C4 alcohol butyl alcohol is also useful in the present invention. Where butyl alcohol is used it is preferred to use tert-butyl alcohol because it is more readily soluble in water. However, since n-butyl alcohol and sec-butyl alcohol are not completely soluble in water, their use can require a further adjustment in the type and amount of emulsifier in the fuel composition in order to obtain a stable emulsion. Tert-butyl alcohol can be used in place of or in combination with ethanol, for example including mixtures in which the relative amount, by weight, of ethanol to tert-butyl alcohol is about 95/5 to 5/95; including useful amounts therebetween such as about 85/15, 80/20, 75/25, 70/30, 65/35, 60/40, 55/45, 50/50, 45/55, 40/60, 35/65, 30/70, 25/75, 20/80, 15/85, and about 10/90.

[0068] The water-vegetable oil fuel emulsions comprise: a continuous vegetable oil fuel phase; a discontinuous water or aqueous phase being comprised of aqueous droplets preferably having a mean diameter of about 10 microns or less, for example, 5 microns; and an emulsifying amount of at least one emulsifier. The emulsions may be prepared by various steps or sequences of addition as described herein, including for example, (1) mixing the vegetable oil, emulsifier and other desired additives using standard mixing techniques to form a
vegetable oil-emulsifier mixture; and (2) mixing the vegetable oil-emulsifier mixture with water (and optionally additional additives, including for example ethanol, propylene glycol, cetane improver, or mixtures thereof) under emulsifying mixing conditions to form the desired water-vegetable oil fuel emulsion.

[0069] Optionally, additives may be added to the emulsifier, the vegetable oil, the water or combinations thereof. The additives include but are not limited to cetane improvers, organic solvents, other fuels such as diesel fuel, glycols, surfactants or emulsifiers, other additives known for their use in fuel and the like. The additives are added to the emulsifier, vegetable oil or the water prior to and in the alternative at the emulsification device(s) depending upon the solubility or other fluid properties of the additive. The additives are generally in the range of about 1% to about 40% by weight, in another embodiment about 5% to about 30% by weight, and in another embodiment about 7% to about 25% by weight of the fuel mixture.

[0070] The vegetable oil fuel emulsifier mixtures contain about 50% to about 95% by weight, in another embodiment about 55% to about 90% by weight; and in another embodiment about 60% to about 85% by weight vegetable oil fuel, and it further contains about 0.05% to about 10%, in another embodiment about 0.1% to about 10%, and in another embodiment about 1% to about 5% by weight of at least one emulsifier.

[0071] The water, which can optionally include but is not limited to one or more alkylene glycol, alcohol, cetane improver or mixtures thereof. In one embodiment the water, alcohol and/or alkylene glycol and/or the cetane improver are mixed with one another and fed continuously to the fuel additives stream. In another embodiment the water, alcohol and/or alkylene glycol and/or the cetane improver or mixtures thereof flow out of separate tanks and/or combinations thereof.
into or mixed prior to the emulsification device. In one embodiment the water, alcohol and/or alkylene glycol and/or the cetane improver mixture meets the vegetable oil fuel additives mixture immediately prior to or in the emulsification device.

[0072] Alternative methods are available for preparing one embodiment the emulsified fuel of the present invention. For example, vegetable oil or a vegetable oil mixture and a major proportion, or all, of the desired amount of C1-C4 alcohol, such as ethanol, are mixed with one another to form a two phase composition with the alcohol as the upper phase. When the water and remaining component (s), including emulsifier (s), are added with agitation, a stable, emulsified composition is produced. Alternatively, the C1-C4 alcohol, or a proportion thereof, including a major proportion, e.g., greater than 50 wt%, can be mixed with the components other than the water, to which the vegetable oil is added, which results in a two phase mixture with the oil as the upper phase. If a split addition of alcohol is used, any convenient fraction can be used as a two-phase mixture results until the water is added. Addition of water to this mixture with agitation produces a stable, emulsified composition. If desired, either of the described two phase mixtures can be produced and stored until such time as it is desired to add the water component, with the additional component (s) if required, to form the stable, emulsified composition. Furthermore, the two-phase mixtures can be shipped to a desired location before addition of the water in order to reduce the burden of shipping water in the mixture.

[0073] An optional component of the fuel mixture referred to as supplementary combustible liquid can be "paint thinner," turpentine or mineral spirits. Materials of this type are generally described in U.S. 5,609,678, incorporated herein by reference in its entirety. Alternatively, the use of this
component in the present invention can be characterized as a low viscosity, low density supplementary combustible liquid additive. Such an optional component can be useful for the purpose of modifying one or more properties of the fuel composition, including, for example, the cetane number, density and viscosity. Consequently, the amount and type of such component can be selected based on its combustion properties as measured by the cetane number of the resulting fuel composition, by the density of the resulting composition and by its viscosity as well as its effect on the phase distribution of the microemulsion in view of the amount and type of surfactant used. In each instance the amount of the liquid added can be suitably adjusted to produce a fuel composition having the overall balance of properties suitable for the end use of the fuel product, for example, as a fuel for a diesel engine, a furnace, etc., or for adjusting the properties of the fuel composition for the ambient temperature environment in which it is intended to be used, for example, as an automotive diesel fuel for winter or summer use.

Useful supplementary combustible liquid additives of the paint thinner type include products identified as hydrotreated, light steam cracked naphtha residuum (petroleum), also referred to as naphtha, petroleum, hydrotreated heavy, and identified as CAS 64742-48-9. This product has also been described as a complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It typically comprises hydrocarbons having carbon numbers predominantly in the range of C6 through C13 and boiling in the range of approximately 65 °C to 230 °C (149 °F to 446 °F). Several of its characteristic physical properties include the following: boiling point, 155-217 °C; melting point, 0 °C; density, 0.76-.0.79 g/cm³; vapor pressure, 0.1-0.3 kPa @ 20 °C; flash point, 40-62 °C; auto-ignition temperature, 255-270 °C. - explosive
limits, 0.7-6.0 vol% in air. A suitable material is available commercially from Italchimica Lazio S.r.l. (Monterotondo Scalo, Italy). A particularly useful product is one that is treated such that it is further described as "odorless," as that term is understood in the art. This product has a viscosity of 1.23 mm²/s (ASTM D445) and a density of 0.772 kg/DM³ (ASTM D4052). It corresponds to the product used in the examples hereinbelow.

[0075] For purposes of the present invention it is to be understood that a supplementary combustible liquid component useful in the present invention can be generally understood by those skilled in the art to include a broad range of petroleum distillate materials as well as supplementary combustible liquids from other sources, for example, plant or vegetable sources. Useful products generally boil in the range of about 145 °C to about 200 °C. Turpentine is a supplementary combustible fluid that could be used. Specifications for "gum spirit of turpentine" (natural, organic or vegetable-based turpentine) have been published by several national bodies including the American Society for Testing and Materials (ASTM D 13-92) and the Bureau of Indian Standards (IS 533:1973). These standards were devised largely for the quality assessment of turpentine intended for use as a solvent, i.e., in whole form rather than as a chemical feedstock in which the composition is of prime importance. They generally specify parameters such as relative density or specific gravity, refractive index, distillation and evaporation residues. The International Organization for Standardization (ISO), which is a world-wide federation of national standards institutes, has issued a standard, the main requirements of which are shown in the following Table. A draft ISO standard for "oil of turpentine, Portugal type, Pinus pinaster (1994)" includes physical data very similar to that in the following Table, but with the addition of a range for optical rotation (20 °C) of
-28° to -35°. Compositional ranges are also given for a number of constituents of the turpentine including alpha-pinene (72-85%) and beta-pinene (12-20%).

[0076]

Table

Physical Property Requirements for Gum Spirit of Turpentine
(ISO Specification 412-1976)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative density (20/20°C)</td>
<td>0.862-0.872</td>
</tr>
<tr>
<td>Refractive index (20°C, D line)</td>
<td>1.465-1.478</td>
</tr>
<tr>
<td>Distillation (% v/v)</td>
<td>max 1 below 150°C; min 87 below 170°C</td>
</tr>
<tr>
<td>Evaporation residue (% m/m)</td>
<td>max 2.5</td>
</tr>
<tr>
<td>Residue after polymerization (% v/v)</td>
<td>max 12</td>
</tr>
<tr>
<td>Acid value</td>
<td>max 1</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>Min 32</td>
</tr>
</tbody>
</table>

[0077] "Turpentine substitute" is a "mineral oil" based replacement for the vegetable-based organic solvent turpentine and it is suitable for use herein. It is a hydrotreated light distillate of petroleum, which forms a clear transparent liquid at ambient or room temperature. It is a complex mixture of highly refined hydrocarbon distillates mainly in the C9-C16 range. The liquid is highly volatile and the vapours are flammable. It is a widely available as a less costly substitute for turpentine. It is commonly used as an organic solvent in painting and decorating, for thinning oil based paint and cleaning brushes. Also known as turps substitute, mineral turpentine, or simply turps, which can cause confusion with vegetable-based turpentine.

[0078] White spirit, also known as Stoddard solvent is also suitable for use herein. It is a paraffin-derived clear, transparent liquid which is a common organic solvent used in painting and decorating. It is a mixture of saturated aliphatic and alicyclic C7 to C12 hydrocarbons with a maximum content of 25% of C7 to C12 alkyl aromatic hydrocarbons. White spirit typically is used as an extraction solvent, as a cleaning solvent, as a degreasing solvent and as a solvent in
aerosols, paints, wood preservatives, lacquers, varnishes, and asphalt products. In western Europe about 60% of the total white spirit consumption is used in paints, lacquers and varnishes. White spirit is the most widely used solvent in the paint industry.

[0079] Three different types and three different grades of white spirit are available. The type refers to whether the solvent has been subjected to hydrodesulfurization (removal of sulfur) alone (Type 1), solvent extraction (Type 2) or hydrogenation (Type 3). Each type comprises three different grades: low flash grade, regular grade, and high flash grade. The grade is determined by the crude oil used as the starting material and the conditions of distillation. In addition there is Type 0, which is referred to as distillation fraction with no further treatment, comprising predominantly saturated C9 to C12 hydrocarbons with a boiling range of 140-200 °C.

[0080] The physical properties of the three types of white spirit are shown in the following table:

<table>
<thead>
<tr>
<th>Property</th>
<th>Type 1: Low flash</th>
<th>Type 2: Regular</th>
<th>Type 3: High flash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial boiling point (IBP) (°C)</td>
<td>130-144</td>
<td>145-174</td>
<td>175-200</td>
</tr>
<tr>
<td>Final boiling point (°C)</td>
<td>IBP+21, max. 220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average relative molecular mass</td>
<td>140</td>
<td>150</td>
<td>160</td>
</tr>
<tr>
<td>Relative density (15°C)</td>
<td>0.765</td>
<td>0.780</td>
<td>0.795</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>21-30</td>
<td>31-54</td>
<td>&gt; 55</td>
</tr>
<tr>
<td>Vapor pressure (kPa, 20°C)</td>
<td>1.4</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Volatility (n-butyl acetate=1)</td>
<td>0.47</td>
<td>0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>Autoignition temperature (°C)</td>
<td>240</td>
<td>240</td>
<td>230</td>
</tr>
<tr>
<td>Explosion limits (% by volume in air)</td>
<td>0.6-6.5</td>
<td>0.6-6.5</td>
<td>0.6-8</td>
</tr>
<tr>
<td>Vapor density (air=1)</td>
<td>4.5-5</td>
<td>4.5-5</td>
<td>4.5-5</td>
</tr>
<tr>
<td>Refractive index (at 20°C)</td>
<td>1.41-1.44</td>
<td>1.41-1.44</td>
<td>1.41-1.44</td>
</tr>
<tr>
<td>Viscosity (cps, 25°C)</td>
<td>0.74-1.65</td>
<td>0.74-1.65</td>
<td>0.74-1.65</td>
</tr>
<tr>
<td>Solubility (% by weight in water)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Kauri-butanol value</td>
<td>29-33</td>
<td>29-33</td>
<td>29-33</td>
</tr>
</tbody>
</table>
The various fluids identified as "mineral spirits" are suitable for use as a supplementary combustible fluid in the present invention. Mineral spirits is commonly used as a paint thinner and mild solvent and it is suitable for use herein. In Europe, it is referred to as petroleum spirit. They are especially effective in removing oils, greases, carbon and other material from metal. Mineral spirits is derived from the light distillate fractions during crude oil refining and comprise C6 to C11 compounds, with the majority being C9 to C11. There are many different substances generally referred to as mineral spirits and each generally has a different CAS number. One common type is mineral oil spirits identified as CAS 64475-85-0. Stoddard solvent, referred to above is a particular type, subcategory or subset of mineral spirits, identified as CAS 8052-41-3 and contains 30-62 wt% alkanes, 27-40 wt% cycloalkanes, 0.3-20 wt% alkylbenzenes, 0.007-0.1 wt% other benzenes, 0.2 wt% naphthalenes and 0.3 wt% acenaphthalenes. Commercial Stoddard Solvent products are available under the tradenames Varsol 1 and Texsolve S. Similarly, benzine is another, subset of mineral spirits comprising C5 to C9 hydrocarbons and boiling at about 154 °C to about 204 °C. Mineral spirits on the other hand comprise 20-65 wt% alkanes, 15-40 wt% cycloalkanes and 10-30 wt% aromatics; the specific amount of each varying depending on the particular "mineral spirit" being considered. General properties for mineral spirits include vapor pressure of 2.53 mtt/Hg; API gravity of about 48 to about 51; density of about 0.793 at 15 °C and about 0.779 at 20 °C; kinematic

<table>
<thead>
<tr>
<th>Property</th>
<th>T1: Low flash</th>
<th>T2: Regular</th>
<th>T3: High flash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline point (°C)</td>
<td>60-75</td>
<td>60-75</td>
<td>60-75</td>
</tr>
<tr>
<td>Reactivity</td>
<td>reaction with strong oxidizing agents</td>
<td>-</td>
<td>0.5-5</td>
</tr>
<tr>
<td>Odor threshold (mg/m3)</td>
<td>-</td>
<td>0.5-5</td>
<td>4</td>
</tr>
</tbody>
</table>
viscosity of 1.43 cSt (or mm2/sec) at 150°C and 1.78 cSt at 0°C.

[0082] Another supplementary combustible liquid that can be used is kerosene. Kerosene is typically defined as a refined petroleum solvent (predominantly C_9-C_15 hydrocarbon, which is typically a mixture of 25% normal paraffins, 11% branched paraffins, 30% monocycloparrafins, 12% dicycloparafins, 1% tricycloparafins, 16% mononuclear aromatics and 5% dinuclear aromatics. (NIOSH Pocket Guide, www.cdc.gov) Alternatively, a product known as hydrotreated kerosene (CAS No. 64742-47-8) can be used. As its name suggests, it is derived from kerosene, or straight run kerosene, by hydrogenation in order to saturate the double bonds present in various molecules of kerosene. Its physical properties are not unlike kerosene. Common physical properties and other characteristics are shown in the following table.

[0083] Physical properties and descriptive information*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS number:</td>
<td>8008-20-6</td>
</tr>
<tr>
<td>molecular weight:</td>
<td>170 (approximately, C_9 to C_15 hydrocarbons)</td>
</tr>
<tr>
<td>melting point:</td>
<td>-51°C</td>
</tr>
<tr>
<td>boiling point:</td>
<td>175-325°C</td>
</tr>
<tr>
<td>appearance:</td>
<td>colorless to pale straw</td>
</tr>
<tr>
<td>density:</td>
<td>about 0.8g/mL</td>
</tr>
<tr>
<td>specific gravity</td>
<td>0.95 (30°C)</td>
</tr>
<tr>
<td>kinematic viscosity:</td>
<td>2.7 cSt (20°C)</td>
</tr>
<tr>
<td>odor:</td>
<td>Odorless</td>
</tr>
<tr>
<td>flash point:</td>
<td>65-85°C</td>
</tr>
<tr>
<td>molecular formula:</td>
<td>C_9 to C_15 hydrocarbons and others</td>
</tr>
<tr>
<td>synonyms:</td>
<td>kerosine; coal oil; fuel oil no.1; range oil</td>
</tr>
<tr>
<td>solubility:</td>
<td>Insoluble in water, miscible in all petroleum solvents</td>
</tr>
<tr>
<td>structural composition:</td>
<td>composition varies greatly and includes C_9 to C_15 hydrocarbons (aliphatic and aromatic) with a boiling range of about 175 to 325°C</td>
</tr>
</tbody>
</table>

[0084] In one embodiment an additive composition of the present invention comprises at least one alcohol and at least one surfactant or emulsifier and, optionally, a low viscosity, low density supplementary combustible liquid, such as paint thinner as well as other components described herein. The various embodiments of the fuel compositions of the present invention are generally prepared according to the methods described herein. In one embodiment an additive composition, the components of which are described herein, is added gradually to water, or vice versa, in order to prepare a mixture, preferably with mixing during the addition, although mixing can be carried out after the components are added to one another. Alternatively, the individual components of the additive mixture and the water can be combined in any convenient order provided that a uniform mixture is obtained. Mixing is continued until a satisfactory distribution, dispersion or emulsion of components is achieved. Typically the additive composition is used in an amount of about 20% by weight based on the amount of the vegetable oil that will be present in the final mixture. The amount of additive used can be suitably varied. Typically, the additive is used at about 2 wt% to about 30 wt% based on the weight of the oil present; preferably about 20 wt% to about 28 wt%; more preferably about 10 wt% to about 30 wt% for engines and about 10 wt% to about 20 wt% for burners and heaters. Furthermore, higher amounts of the additive can be used, for example, about 35 wt% or about 40 wt% or up to about 45 wt%, keeping cost in mind so that a suitable amount is used to achieve the desired effect and at a cost consistent with economic requirements. Alternatively, useful amounts may include specific concentrations of about 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27,
28, 29 and 30 wt% or more, as well as ranges of values based on any two of the individual values recited; for example, 2-30%, 5-25%, etc. In this embodiment the additive is used in an amount sufficient to obtain a substantially complete emulsion of water and oil present in the composition. The mixture comprising water and additive is added to an oil or a fat of vegetable origin, for example, colza or canola oil. The weight ratio of water to oil typically can be varied over a range and still be useful in the present invention, for example, from about 4:1 to about 1:4; a preferred ratio of water to oil is about 3:1 to about 1:3; more preferably about 2:1 to about 1:2; still more preferably about 1:1. Mixing of the water-additive combination with the vegetable oil is continued until a substantially complete, or suitable, emulsion of the components is obtained.

[0085] Cetane number or CN is to diesel fuel what octane rating is to gasoline, it is generally recognized as a measure of the fuel's combustion quality. Cetane is an alkane molecule, specifically \( \text{C}_{14}\text{H}_{22} \), that ignites very easily under compression, so it is assigned a cetane number of 100. All other hydrocarbons in diesel fuel, as well as other fuels intended for use in diesel engines, including biodiesel and the biofuel compositions of the present invention, are indexed to cetane as an indicator of how well they ignite under compression. The cetane number therefore measures how quickly the fuel starts to burn (auto-ignites) under a standardized set of diesel engine conditions. Typical hydrocarbon-based diesel fuel contains many hydrocarbon compounds and there can be more than one compound susceptible to ignition in other fuels, including the fuels of the present invention. Since each component can exhibit a different cetane number or modify the cetane number of the fuel of which it is a component, the overall cetane number of the fuel is an indicator of the average cetane quality of all of the components present. A
fuel with a high cetane number starts to burn shortly after it is injected into the cylinder; it has a short ignition delay period. Conversely, a fuel with a low cetane number resists auto-ignition and has a longer ignition delay period. A typical diesel engine has acceptable performance with a fuel having a CN between about 45 to about 50. Typically, there is no performance or emission advantage when the CN is greater than about 50; after this point, the fuel's performance reaches a plateau. Hydrocarbon diesel fuel sold commercially is said to be available in two CN ranges: 40-46 for regular diesel, and 45-50 for premium. In addition to a higher CN, premium diesel includes additives to improve the effective CN and lubricity of the fuel as well as detergents to clean the fuel injectors and minimize carbon deposits, water dispersants (since water in hydrocarbon diesel fuel is considered objectionable), and other additives depending on geographical and seasonal needs. Cetane number can be determined using standardized tests, including ASTM D613 and EN ISO 5165. The cetane number rating in this test compares the diesel fuel's performance in a standard engine with that of a mixture of cetane and alpha-methyl-naphthalene. The cetane number is the percentage by volume of cetane in the mixture that has the same performance as the fuel being tested. Suitable fuels typically will have CN values of at least about 35 to about 55; preferably about 40 to about 50; more preferably about 45 to about 50; for example at least about 45, 46, 47, 48, 49, 50, 51, 52, 53, 54 or 55. Alternatively, cetane number can be estimated by calculating the value according to the procedures specified in ASTM D976, using the density of the fuel and its mid-distillation temperature, or in ASTM D4737 using a four variable equation. When an estimated cetane number is determined in this manner, it is sometimes referred to as cetane index to distinguish it from the value determined according to the engine test, as in ASTM 613. It is
understood by those skilled in the art that where a cetane index is calculated, the value is dependent on the fuel properties and is not affected by additives that may be included to improve cetane number. Such additives will, of course, affect the cetane number determined by use of an engine test since the overall fuel composition affects the value measured in that test. Cetane index values can also be useful for characterizing a fuel composition of the present invention. When used, a cetane number improving additive or mixture of additives can be present in an amount effective to improve the CN of the fuel compositions of the present invention to the extent desired; in other words, to a level suitable for the particular application or use to which the emulsified vegetable fuel will be put. In one embodiment, the concentration of the cetane improver is at a level of up to about 10% by weight; in another embodiment about 0.05 to about 10% by weight; in a further embodiment about 0.05 to about 5% by weight; in a still further embodiment about 0.05 to about 1% by weight; alternatively, about 0.1 to about 1% by weight.

[0086] Various chemical compounds have been identified that have the ability to improve the cetane number of diesel fuel. Where necessary or desired to meet specific performance requirements in certain applications, one embodiment of the vegetable oil-based water-fuel emulsion compositions of the present invention can optionally include one or more compounds having the ability to increase cetane number. Useful cetane improvers include but are not limited to one or more of peroxides, nitrates, nitrites, nitrocarbamates, mixtures thereof and the like. Useful cetane improvers include but are not limited to nitropropane, dinitropropane, tetranitromethane, 2-nitro-2-methyl-1-butanol, 2-methyl-2-nitro-1-propanol, and the like. Also included are nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric.
These compounds include substituted and unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and in one embodiment about 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Examples of such compounds include 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, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylvicyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also useful are the nitrate esters of alkoxy-substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-[(2-ethoxy-ethoxy) ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. A useful cetane improver is 2-ethylhexyl nitrate.

[0087] Organic peroxides can also be useful as cetane improvers in the fuel compositions herein. Generally useful compounds are dialkyl peroxides of the formula R1OOR2 wherein R1 and R2 are the same or different alkyl groups having 1 to about 10 carbon atoms. Suitable peroxide cetane improver compounds should be soluble in the fuel composition and thermally stable at typical fuel temperatures of operating engines. Peroxides wherein R1 and R2 are tertiary alkyl groups having about 4 or about 5 carbon atoms are especially useful. Examples of suitable peroxides include di-tertiary butyl peroxide, di-tertiary amyl peroxide, diethyl peroxide, di-n-propyl peroxide, di-n-butyl peroxide, methyl ethyl peroxide, methyl-tert-butyl peroxide, ethyl-tert-butyl peroxide, propyl-tert-amyl peroxide, mixtures thereof and the like. Preferred peroxides generally exhibit one or more and
preferably most of the following characteristics: good solubility in the fuel, suitable water partition coefficient characteristics, good thermal stability and handling characteristics, have no impact on fuel quality or fuel system components, and have low toxicity. A useful peroxide is di-tertiary butyl peroxide, also sometimes referred to as tertiary butyl peroxide.

[0088] The biofuel of the present invention typically has a density suitable for its use as a fuel in diesel engines and in other applications where diesel fuel would otherwise be useful, including in furnaces, gas or combustion turbines and other combustion equipment. Density can be measured according to the standard test method, EN ISO 3675, at 15 °C and suitable fuels have a density of about 850 kg/m³ to about 950 kg/m³; preferably about 860 kg/m³ to about 910 kg/m³; for example about 870 kg/m³ to about 890 kg/m³. Alternatively, in the United States, diesel fuel density is characterized by the standard developed by the American Petroleum Institute, referred to as API gravity. Typical API gravity values for fuels of the present invention useful as fuels for diesel engines range from about 25 API to about 40 API, corresponding to specific gravity values of about 0.904 to about 0.825 (at 60 °F or 15.6 °C); preferably about 26 API gravity to about 38 API gravity; more preferably about 27 API gravity to about 37 API gravity; for example, about 35 API gravity, corresponding to a specific gravity of about 0.850. The accepted formula relating API gravity to specific gravity is:

\[
\text{API} = \left(\frac{141.5}{\text{Sp.Gr.}}\right) - 131.5
\]

(with the abbreviation Sp.Gr. meaning specific gravity and wherein it is determined at 60 °F or 15.6 °C, as noted above.

[0089] Biofuel compositions of the present invention typically have a viscosity so that they are suitable for use as a fuel in diesel engines and in other applications where diesel fuel would otherwise be useful, including furnaces and
other combustion equipment. Viscosity can be measured according to the standard test methods, EN ISO 3104 or ASTM D445 (kinematic viscosity at 40 °C), wherein potentially useful values can be about 3 mm\(^2\)/s to about 60 mm\(^2\)/s; alternatively about 3.5 mm\(^2\)/s to about 50 mm\(^2\)/s; or for example about 3.6 mm\(^2\)/s to about 40 mm\(^2\)/s; about 3 mm\(^2\)/s to about 40 mm\(^2\)/s; about 3 mm\(^2\)/s to about 30 mm\(^2\)/s; about 1 mm\(^2\)/s to about 25 mm\(^2\)/s; about 2 \(\text{m}\)\(^2\)/s to about 12 mm\(^2\)/s; about 3 mm\(^2\)/s to about 10 mm\(^2\)/s; about 4 mm\(^2\)/s to about 8 mm\(^2\)/s; about 2 mm\(^2\)/s to about 6 \(\text{m}\)\(^2\)/s; and including viscosity values that, upon testing are suitable for use in the application or environment of a suitable biofuel composition.

[0090] Other suitable optional ingredients can be included in the compositions of the present invention provided that they do not substantially adversely affect performance of the composition and its intended use. Included in the category of such other optional ingredients would be, for example, thermal and aging stabilizers; coloring agents, dyes and markers, particularly those permitted in the European Union as set forth in EN 14214:2003-5.1; agents to modify the odor of the mixture in order to prevent inadvertent ingestion, including, for example, alkyds; etc. Alternatively, and if necessary, agents can be added in a suitable amount, typically at a low concentration, that are capable of modifying or masking an unpleasant odor or smell, if any, of the exhausted gas after combustion. Other conventional additives and blending agents for fuel compositions of the present invention may be present. For example, the fuels of this invention may contain conventional quantities of such conventional additives as rust inhibitors such as alkylated succinic acids and anhydrides, inhibitors of gum formation, metal deactivators, upper cylinder lubricants, friction modifiers, detergents, antioxidants, heat stabilizers, bacteriostatic agents, microbiocides, fungicides and the like. Such conventional
additives can be present in the fuel composition at concentrations of up to about 1 wt% based on the total weight of the water-vegetable oil fuel emulsion; for example about 0.01 wt% to about 1 wt%.

[0091] The practice of the present invention, including in particular the above described additive composition, results in the preparation of a fuel composition based on animal or vegetable fats or oils and water in an emulsion that is stable for an extended time and over a wide range of temperatures, for example about -10 °C to about +50 °C. Furthermore, in a test conducted at -25 °C, a composition of the present invention, for example compositions as shown in Examples 1 and 2, including paint thinner and 30 grams of cetyl alcohol, did not exhibit any evidence of freezing, cloudiness or phase separation. The fuel produced according to the compositions and methods of the present invention can be used without modification to the tanks and/or piping systems of the motors and burners in common use. Thus another advantage of the present invention is that it permits the return at any moment to the use of traditional fuels without modification of the systems in which the fuel is used.

[0092] Further advantages can be realized with certain preferred methods and compositions of the present invention, including:

[0093] (a) Product and manufacturing costs are low and competitive with other fuels, particularly due to the presence of water in the composition;

[0094] (b) The present compositions do not exhibit the high solvent power of methyl esters that are present in traditional biodiesel, which can cause problems with polymeric materials present in the storage systems, burners and engines, including linings, packing rings and seals;
The fuel of the present invention does not leave deposits in the storage tanks and fuel lines, thus reducing the need for frequent maintenance;

The fuel of the invention is renewable since it is based on vegetable and animal products that can be regularly replaced. Furthermore, not only is the energy source renewable, but the amount of carbon dioxide emitted during combustion corresponds very closely to the amount of carbon dioxide used by the plants in generating the vegetable matter which is the source of the oils or fats. This, of course, cannot occur in the case of petroleum based fuels;

Emission of nitrogen oxides, particularly undesirable pollutants, is reduced with respect to traditional biodiesel-based fuels, especially in view of the water and additive mixture. In a test using a diesel engine operating at 1500 rpm, traditional biodiesel produced 196 mg/Nm³, whereas a composition of the present invention under the same conditions resulted in 160 mg/Nm³, more than an 18% reduction (where Nm³ refers to "normal" cubic meters, defined as volume at temperature T = 20.0 °C (68 °F), and pressure P = 1.01 bar (14.72 psia));

Incombustible hydrocarbons produced during the combustion of a fuel composition of the present invention are less than those produced by traditional biodiesel-based fuels and CO emissions and are believed typically to be about 15%-20% less. In a test of a fuel composition similar to that shown in Example 1 (including 30 grams of cetyl alcohol, but without paint solvent) in a diesel engine operating at 1500 rpm, CO emissions were observed to be reduced by 37 wt% (838 versus 1248 mg/Nm³);

The chemical composition and average size of particulate matter resulting from combustion of traditional biodiesel-based fuels and the fuels of the present invention are subject to variability. Limited testing for smoke has
been conducted using the Bacharach Scale (values 0 to 9, with 0 indicating the lowest level) and employing the Zambelli Emicont 50 test instrument and a 3 meter long exhaust pipe connected to a diesel engine (the Bacharach scale may also be referred to in test method ASTM D 2156 which measures smoke density in flue gases from burning petroleum distillate heating fuels). A comparative value of 6 was observed using a fuel composition of the present invention as described in subparagraph (f) above. While particulate matter generated during combustion of traditional biodiesel based fuels is thought to serve a useful function by absorbing some of the undesirable and polluting aromatic compounds produced during combustion of that fuel, the fuel of the present invention is believed to produce very little of such aromatic compounds in the first place. Moreover, it has been found that particulate matter produced during combustion of the fuel of the present invention is up to about 70% less than that produced by petroleum-based fuels and are, on average, larger than those produced by such petroleum-based fuels. Additionally, it is generally believed that larger particles are less dangerous since they are less likely to be permanently retained in the lungs than smaller particles. Particulates, measured according to UNICHIM 494 (Association for Unification in the Field of the Chemical Industry, a standards setting organization in Italy) resulted in 0.16 mg/Nm³, well below the levels observed with gasoil (0.30 mg/Nm³) and biodiesel (0.24 mg/Nm³).

[0100] (h) Emission of SO₂ does not constitute a problem for the fuels of the present invention since there is no sulfur present in the vegetable oil or fat and the amount and type of other components present can be controlled in order to limit, reduce or eliminate the presence of sulfur (as well as nitrogen).
It has been observed that the biofuel compositions of the present invention exhibit anti-microbial, anti-bacterial and anti-mold characteristics, especially compositions comprising hydrogenated castor oil and/or cetyl alcohol as well as ethanol. Three different tests were performed, one each against bacteria, spores and mould/fungi, to confirm this activity of the novel, formulated biofuel of Example 1, containing 30 grams hydrogenated castor oil and 500 grams paint solvent and Example 2, containing 25 grams cetyl alcohol. The biofuel compositions exhibited successful results in the following tests:

Test for activity against spores: Successful disinfection according to the British Standard (BS EN 1276) occurs when there is a five log reduction in cell number within 5 minutes, meaning that the reduction of spore number must be at least of 95% in an assigned period of time. Based on this, the biofuel composition was tested against germs (spores) of the following strains: Mycobacterium smegmatis and Bacillus Stearothermophilus.

Test for activity against fungi: The tests against mold and fungi followed the guidelines of the European standard 1275 that requires a minimum of a four log reduction in cell number within five minutes. The strain used was Candida albicans, strain ATCC number 10231.

Biofuel compositions made according the methods and components previously described include those useful, for example, in multi-jet new generation diesel engines as well as traditional diesel engines. Such compositions can comprise for example, about 25 to about 30 wt% water, about 40 to about 60 wt% vegetable oil and about 15 to about 30 wt% additive.

The following aspects of the invention represent possible alternative embodiments:

1. A fuel mixture prepared from the following components: (A) 1500 parts vegetable oil or fat; and (B) 900 parts water;
and (C) 400 parts denatured ethanol 90 wt% (180 proof); axid,
(D) 30 parts of at least one component selected from the group
consisting of (1) hydrogenated castor oil; (2) cetyl alcohol;
and (3) a mixture of (1) and (2).
2. The fuel mixture of aspect 1 further comprising 500 parts
of odorless paint solvent.
3. A fuel mixture prepared from the following components:
(A) 1500 parts vegetable oil or fat; and (B) 900 parts water;
and (C) 400 parts denatured ethanol 90 wt% (180 proof); and,
(D) 30 parts of at least one component selected from the group
consisting of (1) hydrogenated castor oil; (2) cetyl alcohol;
and (3) a mixture of (1) and (2) according to the following
method: (I) components (C) and (D) are mixed with one another
to form an additive; (II) the additive is mixed with component
(B) to form a mixture (II); (III) mixture (II) is added with
concurrent mixing, at a suitable rate to (A) in order to
produce a substantially emulsified mixture.
4. A fuel additive comprising a mixture of: (A) 400 parts
denatured ethanol 90 wt% (180 proof) and, (B) 30 parts of at
least one component selected from the group consisting of (1)
hydrogenated castor oil; (2) cetyl alcohol; and (3) a mixture
of (1) and (2).

[0106] The following examples are provided as specific
illustrations of embodiments of the claimed invention. It
should be understood, however, that the invention is not
limited to the specific details set forth in the examples.
All parts and percentages in the examples, as well as in the
specification, are by weight unless otherwise specified.
Furthermore, any range of numbers recited in the specification
or claims, such as that representing a particular set of
properties, units of measure, conditions, physical states or
percentages, is intended to literally incorporate expressly
herein by reference or otherwise, any number falling within
such range, including any subset of numbers within any range
so recited. For example, whenever a numerical range with a lower limit, \( R_L \), and an upper limit \( R_U \), is disclosed, any number \( R \) falling within the range is specifically disclosed. In particular, the following numbers \( R \) within the range are specifically disclosed:

\[ R = R_L + k(R_U - R_L) \]

where \( k \) is a variable ranging from 1% to 100% with a 1% increment, e.g., \( k \) is 1%, 2%, 3%, 4%, 5%, ..., 50%, 51%, 52%, ..., 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range represented by any two values of \( R \), as calculated above is also specifically disclosed.

[0107] For purposes of the present invention, unless otherwise defined with respect to a specific property, characteristic or variable, the term "substantially" as applied to any criteria, such as a property, characteristic or variable, means to meet the stated criteria in such measure such that one skilled in the art would understand that the benefit to be achieved, or the condition or property value desired is met.

[0108] Throughout the entire specification, including the claims, the word "comprise" and variations of the word, such as "comprising" and "comprises," as well as "have," "having," "includes," "include" and "including," and variations thereof, means that the named steps, elements or materials to which it refers are essential, but other steps, elements or materials may be added and still form a construct within the scope of the claim or disclosure. When recited in describing the invention and in a claim, it means that the invention and what is claimed is considered to be what follows and potentially more. These terms, particularly when applied to claims, are inclusive or open-ended and do not exclude additional, unrecited elements or methods steps.

[0109] As used throughout the specification, including the described embodiments, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates
otherwise. Thus, for example, reference to "a surfactant" includes a single surfactant as well as two or more different surfactants in combination, reference to "a vegetable oil or fat" includes mixtures of two or more vegetable oils or fats as well as a single vegetable oil or fat, and the like.

[0110] The term "about" encompasses greater and lesser values than those specifically recited provided that the value of the relevant property or condition facilitates reasonably meeting the technologic objective (s) of the present invention as described in detail in the specification and claims. More specifically, the term "about" when used as a modifier for, or in conjunction with, a variable, is intended to convey that the numbers and ranges disclosed herein are flexible and that practice of the present invention by those skilled in the art using, for example, concentrations, amounts, contents, carbon numbers, temperatures, properties such as density, purity, etc., that are outside of a stated range or different from a single value, will achieve the desired result, namely, a biofuel additive composition or a fuel composition or mixture comprising such an additive.

EXAMPLES

[0111] Example 1. New Generation Hi-Pressure Injection Diesel

A fuel mixture is prepared from the following components:

1500 grams vegetable oil or fat; and
900 grams water (e.g., tap water); and
400 grams denatured ethanol 90° (180 proof); and,

(a) 30 grams hydrogenated oil of ricin (castor oil).
Alternatively, a mixture using (b) 30 grams cetanol (cetyl alcohol) is prepared; and (c) a further alternative mixture using (a) + (b) together (30 grams total) is also prepared; and optionally,

500 grams odorless paint solvent is also included in one or more of the above described mixtures.
[0112] The mixture is suitable for use with a new generation high pressure injection diesel engine. Based on current raw material costs it is estimated that the above composition costs about 204 €/1000L (about $0.94/gal at current exchange rates). It is expected that the cost for producing the composition on a commercial scale will be lower. For comparison purposes, the raw material cost of commercial biodiesel fuel is about 492 €/1000L (about $2.26/gal at current exchange rates).

[0113] Example 2. Traditional Tractor-Type Low-Pressure Injection Diesel

[0114] A fuel mixture is prepared from the following components:

[0115] 1100 grams vegetable oil; and
500 grams water; and
250 grams ethyl alcohol (180 proof); and
25 grams hydrogenated castor oil; or cetalol (cetyl alcohol); or mixture of castor oil and cetalol; and
25 grams paint thinner.

[0116] The mixture is suitable for use with a traditional tractor-type low-pressure injection diesel engine. Based on current raw material costs it is estimated that the above composition costs about 243 €/1000L (about $1.12/gal at current exchange rates). It is expected that the cost for producing the composition on a commercial scale will be lower.

[0117] Example 3. Modified Traditional Tractor-Type Low-Pressure Injection Diesel

[0118] A fuel mixture is prepared from the following components:

1100 grams vegetable oil;
900 grams water;
250 grams ethyl alcohol (180 proof);
25 grams (a) hydrogenated castor oil; or (b) cetalol or a mixture of (a) and (b);
300 grams odorless paint thinner.

[0119] The mixture is suitable for use with a modified traditional tractor-type low pressure injection diesel engine.

[0120] Example 4. Fuel for Use in Oil Burners

[0121] A fuel mixture is prepared from the following components:

- 900 grams oil;
- 500 grams water;
- 25 grams (a) castor oil; or (b) cetalol; or (c) a mixture of (a) and (b);
- 250 grams ethyl alcohol.

[0122] The mixture is suitable for use in oil burners.

[0123] Example 5. Fuel for Use in Modified Oil Burners

[0124] A fuel mixture is prepared from the following components:

- 1100 grams oil;
- 900 grams water;
- 375 grams ethyl alcohol;
- 30 grams (a) hydrogenated castor oil; or (b) cetalol.

[0125] The mixture is suitable for use in modified oil burners.


[0127] Fuel mixtures of the present invention were prepared as follows: the water and ethanol were first mixed with one another. The vegetable oil was then added slowly to the alcohol-water mixture with stirring and finally the emulsifier or surfactant was added to the mixture containing the oil. For the composition in which a cetane improver was used, that component was added to the mixture at the end. The mixtures were all prepared at about ambient or room temperature, 22 °C. Corresponding mixtures have been prepared using ultrasonic mixing equipment, which equipment particularly advantageous for preparing stable emulsions having a small particle size.
for example less than about 5 microns on average ("Sonolator" ultrasonic homogenizing system, Sonic Corp., Conn.). The compositions described herein are amenable to preparing such emulsions, also referred to herein as microemulsions. The microemulsions could also be prepared at 22 °C and at pressures of about 500 psi to about 1500 psi, although pressures as high as 5000 psi also produced stable microemulsions. The fuel components and amounts are shown in the following table:

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Vegetable oil**</th>
<th>Water</th>
<th>Ethanol</th>
<th>Emulsifier†</th>
<th>Cetane additive*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofuel 1</td>
<td>1200g 72.95 wt%</td>
<td>335g  20.36 wt%</td>
<td>105g     6.38 wt%</td>
<td>HCO: 5g 0.31 wt%</td>
<td></td>
</tr>
<tr>
<td>Biofuel 2</td>
<td>1200g 80.53 wt%</td>
<td>225g  15.11 wt%</td>
<td>53g      3.56 wt%</td>
<td>HCO: 5g 0.33 wt%</td>
<td>7g 0.47 wt%</td>
</tr>
<tr>
<td>Biofuel 3</td>
<td>900g 59.40 wt%</td>
<td>350g  23.10 wt%</td>
<td>250g     16.50 wt%</td>
<td>Tween: 15g 1.00 wt%</td>
<td></td>
</tr>
</tbody>
</table>

** Refined soybean oil  
† HCO=hydrogenated castor oil, 98% pure; Tween 80  
* 2-ethylhexyl nitrate

[0128] The above mixtures were tested for various properties and performance characteristics under different test conditions and using various standard fuels for comparison.

[0129] Specifically, Biofuel 3 was tested in a stationary burner and its performance compared to gas oil, biodiesel and BTZ fuel oil and water emulsion mixture. Descriptions and properties of the reference fuels can be found in a published report titled, "Sperimentazione Combustibili Analisi comparativa di combustibili per uso civile" (Fuel Experimentation. Comparative analyses of fuels for civic use) December 5, 2005, by Stazione Sperimentale per i Combustibili (SSC) and Consorzio Ingegneria per l'Ambiente e Io Sviluppo Sostenibile (IPASS); and reported at http://www.ssc.it/, incorporated herein by reference. Biofuel 3 was tested using an experimental thermal plant consisting of a reversed flame Ravasio Model TRM 150 boiler with a nominal thermal capacity
of 175 kW and a Elco Klockner Model EK 3.50 S-Z burner for fuel oil. Heat generated is discharged to a heat exchanger for measurement of performance and exhaust gasses are also analyzed for emissions. The following conditions were used: fuel tank temperature about 16 °C; burner warm-up temperature about 60 °C; atomization pressure, 28 bar; fuel feed, 23 kg/h; thermal power, 160 kW; excess oxygen in exhaust, 6%. BTZ fuel oil was blended with water at 13 wt% and it was blended with biodiesel (standard mixture of fatty acid methyl esters) at 20 wt%. Test results are reported in the following table.

<table>
<thead>
<tr>
<th>Fuel Tests*</th>
<th>BTZ</th>
<th>BTZ+Water</th>
<th>BTZ+Biodiesel</th>
<th>Biofuel 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM, mg/Nm3</td>
<td>21.1</td>
<td>10.0</td>
<td>11.1</td>
<td>13.4</td>
</tr>
<tr>
<td>PM10, mg/Nm3</td>
<td>20.9</td>
<td>10.0</td>
<td>11.1</td>
<td>10.8</td>
</tr>
<tr>
<td>NOx, mg/A/m3</td>
<td>560.4</td>
<td>469.3</td>
<td>543.7</td>
<td>122</td>
</tr>
<tr>
<td>CO, mg/Nm3</td>
<td>10.7</td>
<td>37.7</td>
<td>10.5</td>
<td>138</td>
</tr>
<tr>
<td>UHC, mg/Nm3</td>
<td>&lt;0.4</td>
<td>0.9</td>
<td>&lt;0.4</td>
<td>17.5</td>
</tr>
<tr>
<td>Organics</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Formaldehyde, µg/Nm3</td>
<td>20</td>
<td>10</td>
<td>30</td>
<td>6.44</td>
</tr>
<tr>
<td>Acetaldehyde, pg/Nm3</td>
<td>20</td>
<td>60</td>
<td>-</td>
<td>1.93</td>
</tr>
<tr>
<td>Propionaldehyde, pg/Nm3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.41</td>
</tr>
<tr>
<td>Combustion Yield, %</td>
<td>93.4</td>
<td>94.4</td>
<td>92.8</td>
<td>92</td>
</tr>
</tbody>
</table>

* Abbreviations and tests: PM=total particulate matter, UNI 13284-1; PM10=fine particulates, <10µM, EPA 201A; NOx, nitrogen oxides, UNI 10878; CO, carbon monoxide, UNI 9969; UHC=unburned hydrocarbons, UNI EN 12619; Organics, SSC test method; combustion yield or energy efficiency, UNI 10389.

In other laboratory tests Biofuel 3 exhibited an excellent flow point of -42 °C (measured according to ISO 3016-94) as well as viscosity and lower heating capacity values (ASTM D 240-02) typical of the class of fuel oils. As shown above, Biofuel 3 also resulted in low NOx and other emissions. It was also observed that Biofuel 3 exhibited a regular, stable, deep yellow flame at the burner. An increase in density of the recirculated fuel was observed, which response can
probably be mitigated by further improvements in emulsion particle size as well as adjustments to the composition, according to the methods described above.

[0131] Heat capacity and low temperature characteristics of Biofuel 2 and Biofuel 3 were measured using standard thermogravimetric analysis (TGA) and the new technique of modulated differential scanning calorimetry (MTDSC). For TGA a heating rate of 10 °C/min is used until 100 °C, after which the sample is heated isothermally for one hour and then the same heating rate is resumed until 1000 °C, after which the sample is thoroughly degraded. MTDSC superimposes a sinusoidal heating wave (±0.5 °C, 60 sec. period) on the normally linear ramp (5 °C/min.); temperature interval -20 °C to +250 °C in an inert nitrogen atmosphere. The heating tests reflected the stability of the emulsifier(s) since the solvents and water are evaporated at 100 °C. The laboratory test showed that Biofuel 1 was stable until 200 °C whereas Biofuel 2 was stable until about 165 °C. Heat capacity (J/g*°C) was about 1.6 for Biofuel 1 and about 1.8 for Biofuel 2, similar to that of gas oil. Furthermore, both Biofuel 1 and Biofuel 2 did not exhibit thermal effects or freezing at -20 °C.

[0132] Further testing was conducted at the "Centro Universitario di Ricerca per Io Sviluppo sostenibile" near Rome, Italy (University Center for Research and Sustainable Development, CIRPS). Biofuel 1 and Biofuel 2 were tested and compared to traditional diesel fuel for power performance and emissions using two different automobile engines, Fiat Multipla 1.9 jtd (common rail engine) and Fiat Punto 1.7 td (aspirated engine, also called Fiat Punto TD 70 ELX). Power tests were performed using a dynamometer, Cartec LPS 2510, with the following results:
Compared to traditional diesel, in the Fiat Multipla power decreased about 3% with Biofuel 1 and about 15% with Biofuel 2. In the Fiat Punto, the power decreased about 4% with Biofuel 2 and about 11% with Biofuel 1 compared to traditional diesel. However, it has also been reported that when traditional biodiesel is compared to traditional diesel power decreases about 11%. (Energy Information Administration, www.eia.doe.gov/oiaf/analysispaper/biodiesel).

Emissions tests were conducted with Biofuel 2 using the same vehicles according to the various standards and criteria of UNICHIM 422, 467 and 494 methods; ONI 10169 regulation; and DM 25/08/00 for sulfur and nitrogen oxide measurements. The test results are summarized in the following table:

<table>
<thead>
<tr>
<th>Test</th>
<th>Fuel Type</th>
<th>Vehicle</th>
<th>Power (kW)</th>
<th>Torque (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diesel</td>
<td>Multipla</td>
<td>84.3</td>
<td>215</td>
</tr>
<tr>
<td>2</td>
<td>Biofuel 1</td>
<td></td>
<td>71.7</td>
<td>160</td>
</tr>
<tr>
<td>3</td>
<td>Biofuel 2</td>
<td></td>
<td>81.5</td>
<td>209</td>
</tr>
<tr>
<td>4</td>
<td>Diesel</td>
<td>Punto</td>
<td>47.7</td>
<td>123</td>
</tr>
<tr>
<td>5</td>
<td>Biofuel 1</td>
<td></td>
<td>42.5</td>
<td>117</td>
</tr>
<tr>
<td>6</td>
<td>Biofuel 2</td>
<td></td>
<td>45.8</td>
<td>127</td>
</tr>
</tbody>
</table>

*Lower values indicate better performance

The results of these tests indicate very good performance for Biofuel 2 compared to traditional diesel fuel.

Example 7

A composition of the present invention, referred to as a biofuel composition, having components that provided a
composition particularly useful in stationary burners or furnaces; for example, burners used for generating heat and power. The components are shown in the following table:

<table>
<thead>
<tr>
<th>Biofuel 7A</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component</strong></td>
<td><strong>Amount, grams</strong></td>
<td><strong>Amount, weight%</strong></td>
<td><strong>Useful Range, weight%</strong></td>
</tr>
<tr>
<td>Vegetable Oil</td>
<td>900</td>
<td>63.649</td>
<td>55-70</td>
</tr>
<tr>
<td>Water</td>
<td>300</td>
<td>21.216</td>
<td>15-30</td>
</tr>
<tr>
<td>Ethyl Alcohol, 95%</td>
<td>200</td>
<td>14.144</td>
<td>5-20</td>
</tr>
<tr>
<td>Emulsifier*</td>
<td>14</td>
<td>0.990</td>
<td>0.1-5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1414</td>
<td>100.000</td>
<td>100.000</td>
</tr>
</tbody>
</table>

* Polyoxyethylene (20) sorbitan monooleate (Tween 80)

[0136] The composition represented by Biofuel 7A was evaluated in several standard fuel tests. The tests and results are summarized in the following table:

<table>
<thead>
<tr>
<th>Test</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity@60°F</td>
<td>ASTM D4052</td>
<td>21.04 Deg. API</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ASTM D4294</td>
<td>0.0206 Wt%</td>
</tr>
<tr>
<td>Flash Point</td>
<td>ASTM D93A</td>
<td>72°F</td>
</tr>
<tr>
<td>Sediment &amp; Water</td>
<td>ASTM D1796</td>
<td>0.05 Vol%</td>
</tr>
<tr>
<td>Viscosity, Kin@100°F</td>
<td>ASTM D445</td>
<td>22.93 cSt</td>
</tr>
<tr>
<td>Carbon Residue 10% bottom</td>
<td>ASTM D4530</td>
<td>&lt;0.05 Wt%</td>
</tr>
<tr>
<td>Sulfated Ash</td>
<td>ASTM D874</td>
<td>&lt;0.001 Wt%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>ASTM D5291</td>
<td>12.27 Wt%</td>
</tr>
<tr>
<td>Copper Corrosion</td>
<td>ASTM D130</td>
<td>1a Rating</td>
</tr>
<tr>
<td>Total Acidity</td>
<td>ASTM D664</td>
<td>0.040 mg KOH/g</td>
</tr>
<tr>
<td>Stability (BS&amp;W)</td>
<td>ASTM D96</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>Specific Gravity@60°F/60°F</td>
<td>AOCSS Cc 10a-25</td>
<td>0.9341</td>
</tr>
<tr>
<td>Bomb Calorimetry</td>
<td>ASTM D240</td>
<td>11,900 BTU/lb</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>ASTM D1091</td>
<td>3.4 ppm</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ASTM D129</td>
<td>18 ppm</td>
</tr>
<tr>
<td>Cloud point (gel point)</td>
<td>EN ISO 6245</td>
<td>-28°F</td>
</tr>
<tr>
<td>Potassium</td>
<td>EPA 258.1</td>
<td>&lt;0.1 ppm</td>
</tr>
<tr>
<td>Sodium</td>
<td>EPA 273.1</td>
<td>&lt;0.1 ppm</td>
</tr>
<tr>
<td>Calcium</td>
<td>EPA 215.1</td>
<td>3.6 ppm</td>
</tr>
<tr>
<td>BTU/gal*</td>
<td></td>
<td>92,600</td>
</tr>
</tbody>
</table>

* Calculated from density and bomb calorimetry data

[0137] Another biofuel composition particularly useful in vehicles, for example, cars, trucks, farm equipment, etc., preferably having diesel engines or engines suitable for burning diesel fuels or their equivalent, was also prepared according to the following formula:
A further Biofuel composition of the present invention was prepared as follows: the water and propylene glycol were first mixed with one another. Small amounts of the vegetable oil were then added slowly to the alcohol-water mixture with stirring after each addition and finally the emulsifier or surfactant was added to the mixture containing the oil. The mixture was prepared at about room temperature, 22 °C. Alternatively the mixture was prepared using ultrasonic mixing equipment also as described above. However, using such equipment it was possible to add all ingredients simultaneously and still obtain a stable emulsion, a microemulsion, having a small particle size, for example less than about 5 microns on average. As above, the microemulsion could also be prepared at 22 °C and at pressures of about 500 psi to about 1500 psi, as well as pressures as high as 5000 psi. The fuel composition of this example utilized components resulting in a composition particularly useful in applications requiring an elevated flashpoint compared to the compositions identified above, including but not limited to uses such as diesel engines for vehicles and burners. The fuel components are shown in the following table:
The composition represented by Biofuel 8 was evaluated in several standard fuel tests. The tests and results are summarized in the following table:

<table>
<thead>
<tr>
<th>Test</th>
<th>Method</th>
<th>Result</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity @ 60°F</td>
<td>ASTM D4052</td>
<td>15.7</td>
<td>Deg. API</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ASTM D4294</td>
<td>0.0202</td>
<td>Wt%</td>
</tr>
<tr>
<td>Flash Point</td>
<td>ASTM D93 A</td>
<td>167-205</td>
<td>°F</td>
</tr>
<tr>
<td>Sediment &amp; Water</td>
<td>ASTM D 1796</td>
<td>1-4</td>
<td>Vol%</td>
</tr>
<tr>
<td>Viscosity, Kin @ 100°F</td>
<td>ASTM D445</td>
<td>11-52.4</td>
<td>cSt</td>
</tr>
<tr>
<td>Carbon Residue 10% bottom</td>
<td>ASTM D4530</td>
<td>&lt;0.05</td>
<td>Wt%</td>
</tr>
<tr>
<td>Sulfated Ash</td>
<td>ASTM D 874</td>
<td>&lt;0.001</td>
<td>Wt%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>ASTM D 5291</td>
<td>12.23</td>
<td>Wt%</td>
</tr>
<tr>
<td>Copper Corrosion</td>
<td>ASTM D130</td>
<td>1a</td>
<td>Rating</td>
</tr>
<tr>
<td>Total Acidity</td>
<td>ASTM D664</td>
<td>0.039</td>
<td>mg KOH/g</td>
</tr>
</tbody>
</table>

Clearly, the flash point of Biofuel 8 is significantly higher than that of Biofuel 7A. Furthermore, mixtures of up to 25 wt% Biofuel 8 with traditional diesel fuel, biodiesel fuel and ethanol can be prepared and the two fuel mixtures can be readily dispersed in one another and are stable, in other words they do not separate into different phases.

In another experiment, adding 0.5 wt% of a cetane improver, 2-ethyl hexyl nitrate, to the composition of Biofuel 8 produced a stable biofuel composition within the scope of the invention and exhibiting an increased cetane number.
Example 10

Additional formulations were prepared and tested in order to evaluate stability of vegetable oil based emulsion compositions. The formulations are shown in the table below:

<table>
<thead>
<tr>
<th>Component, wt%</th>
<th>Example 10-1</th>
<th>Example 10-2</th>
<th>Example 10-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable Oil</td>
<td>75.9</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Water</td>
<td>18.5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Ethyl alcohol (95%)</td>
<td>4.5</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Emulsifier(s)*</td>
<td>0.6</td>
<td>1</td>
<td>0.5+0.5</td>
</tr>
<tr>
<td>Cetane Improver**</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
<tr>
<td>Emulsion Stability</td>
<td>&lt;0.1</td>
<td>5</td>
<td>Nil</td>
</tr>
</tbody>
</table>

* 10-1 and 10-2: Polyoxylethylene (20) sorbitan monooleate (Tween 80); 10-3: mixture of Tween 80 and sorbitan monooleate (Span 80)
** 2-ethyl hexyl nitrate

Based on the amount of sediment that could be separated, Example 10-1 in the table above is characterized as a stable emulsion fuel whereas Example 10-2 is considered unstable. However, by utilizing a blend of emulsifiers with an effective HLB of 9.6 ((0.5x14.9) + (0.5x4.3)) it was possible to modify the properties of the composition sufficiently so that a stable emulsified fuel could be obtained.

Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made to the illustrative embodiments and that other arrangements may be devised without departing from the spirit and scope of the present invention as defined by the appended claims.
CLAIMS

1. A biofuel composition comprising an aqueous emulsion having:
   (A) a continuous phase comprising about 50 wt% to about 95 wt% of at least one liquid oil of vegetable or animal origin or mixtures thereof;
   (B) a water-containing dispersed phase comprising about 1 wt% to about 50 wt% of water;
   (C) about 1 wt% to about 25 wt% of a hydroxyl-containing organic compound selected from the group consisting of monohydric, dihydric, trihydric and polyhydric alcohols, provided that when a monohydric alcohol is present there is also present at least one of tert-butyl alcohol, at least one C2-C4 alkylene glycol or a mixture of both;
   (D) about 0.05 wt% to about 10 wt% of at least one emulsifier;

   wherein the dispersed phase comprises water-containing droplets having an average particle size of less than about 20 microns and wherein all amounts are expressed based on the total weight of the composition.

2. The biofuel of claim 1 wherein the at least one emulsifier exhibits a hydrophilic-lipophilic balance, HLB, of about 8.5 to about 18.

3. The biofuel of claim 2 wherein the at least one emulsifier is selected from the group consisting of polyethylene glycol-polypropylene glycol block copolymers, sorbitan monooleate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monolaurate, polyoxyethylene (20) sorbitan trioleate, polyethylene (20) sorbitan monooleate, polyethylene (20) sorbitan monolaurate, and mixtures thereof.
4. The biofuel of claim 1 further comprising an effective amount of an additive to increase the cetane number of the biofuel composition.

5. The biofuel of claim 4 wherein the cetane additive is selected from the group consisting of peroxides, nitrates, nitrites, nitrocarbamates, and mixtures thereof.

6. The biofuel of claim 5 wherein the cetane additive is selected from the group consisting of substituted or unsubstituted, linear, branched or mixed linear or branched, alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and mixtures thereof.

7. The biofuel of claim 5 wherein the cetane additive is selected from the group consisting of dialkyl peroxides of the formula R1OR2 wherein R1 and R2 are the same or different alkyl groups having 1 to about 10 carbon atoms, and mixtures thereof.

8. The biofuel of claim 5 wherein the cetane additive is selected from the group consisting of 2-ethylhexyl nitrate, di-tertiary-butyl peroxide and mixtures thereof.

9. The biofuel of claim 1 wherein the hydroxyl-containing organic compound includes at least one member selected from the group consisting of C1 to C4 straight and branched chain monoalcohols, C2 to C4 mono- and poly-alkylene glycols, derivatives of C2 to C4 mono- and poly-alkylene glycols provided that the molecular weights of such polyalkylene glycols are suitable for use in the fuel compositions, and mixtures thereof.

10. The biofuel of claim 9 wherein the alcohol is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, and mixtures thereof.

11. The biofuel of claim 1 further comprising a supplementary low viscosity, low density combustible liquid selected.
from the group consisting of hydrocarbon solvents, paint
thinner, turpentine, mineral spirits and mixtures thereof.

12. A method of preparing an emulsified fuel composition
comprising:
(A) providing the following components in the amounts
based on the total weight of the composition:
(1) about 50 wt% to about 95 wt% of at least one
liquid oil of vegetable or animal origin or
mixtures thereof;
(2) water in an amount sufficient to produce a
water-containing dispersed phase comprising
about 1 wt% to about 50 wt% of water;
(3) about 1 wt% to about 25 wt% of a
hydroxyl-containing organic compound selected
from the group consisting of monohydric,
dihydric, trihydric and polyhydric alcohols,
provided that when a monohydric alcohol is
present there is also present at least one of
tert-butyl alcohol, at least one C2-C4 alkylene
glycol or a mixture of both; and
(4) about 0.05 wt% to about 10 wt% of at least one
emulsifier;
(B) mixing components (A) (I)-(A) (4) with one another
under conditions of high shear, thus producing a
dispersed phase comprising water-containing droplets
having an average particle size of less than about
20 microns.

13. The method of claim 12 wherein said dispersed phase
comprises water-containing droplets having an average
particle size of about 0.1 to about 10 microns.

14. The method of claim 13 wherein the at least one
emulsifier exhibits a hydrophilic-lipophilic balance,
HLB, of about 8.5 to about 18.
15. The method of claim 14 wherein the at least one emulsifier is selected from the group consisting of polyethylene glycol-polypropylene glycol block copolymers, sorbitan monooleate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monolaurate, polyoxyethylene (20) sorbitan trioleate, polyethylene (20) sorbitan monooleate, polyethylene (20) sorbitan monolaurate, and mixtures thereof.

16. The method of claim 13 including further providing an effective amount of an additive to increase the cetane number of the biofuel composition.

17. The method of claim 14 wherein the cetane additive is selected from the group consisting of peroxides, nitrates, nitrites, nitrocarbamates, and mixtures thereof.

18. The method of claim 12 wherein the hydroxyl-containing organic compound includes at least one member selected from the group consisting of C1 to C4 straight and branched chain monoalcohols, C2 to C4 mono- and poly-alkylene glycols, derivatives of C2 to C4 mono- and poly-alkylene glycols provided that the molecular weights of such polyalkylene glycols are suitable for use in the fuel compositions, and mixtures thereof.

19. The method of claim 12 wherein the components are provided and mixed substantially simultaneously.

20. The method of claim 16 wherein the water is premixed with the components other than the vegetable oil to produce an aqueous mixture and the aqueous mixture is thereafter mixed with the vegetable oil.

21. The method of claim 13 using high shear generating mixing equipment.

22. The method of claim 21 wherein high shear is generated using mixing equipment capable of generating and introducing ultrasonic energy into the mixture.
23. The method of claim 22 wherein the amount of emulsifier is from about 20% to about 90% of the amount emulsifier required to obtain the dispersed particle size in the absence of the use of ultrasonic energy.

24. Emulsified fuel according to claim 1 wherein the average droplet particle size is selected from the group consisting of about 0.01 to about 15 microns; 0.1 to about 10 microns; 0.5 to about 5 microns, and mixtures thereof.

25. Emulsified fuel according to claim 24 further comprising an effective amount of an additive to increase the cetane number of the biofuel composition.

26. Emulsified fuel according to claim 25 wherein the cetane additive is selected from the group consisting of peroxides, nitrates, nitrites, nitrocarbamates, and mixtures thereof.

27. Emulsified fuel according to claim 1 further comprising at least one member selected from the group consisting of thermal stabilizers, aging stabilizers, antioxidants, coloring agents, dyes, markers, odor modifying agents, rust inhibitors, inhibitors of gum formation, metal deactivators, upper cylinder lubricants, friction modifiers, detergents, bacteriostatic agents, fungicides, microbiocides and mixtures thereof.

28. The emulsified fuel according to claim 25 wherein the emulsifier is selected from the group consisting of polyethylene glycol-polypropylene glycol block copolymers, sorbitan monooleate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monolaurate, polyoxyethylene (20) sorbitan trioleate, polyethylene (20) sorbitan monooleate, polyethylene (20) sorbitan monolaurate, and mixtures thereof and wherein the alcohol is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol,
propylene glycol, dipropylene glycol, tripropylene glycol, and mixtures thereof.

29. The emulsified fuel according to claim 28, further comprising a supplementary low viscosity, low density combustible liquid selected from the group consisting of hydrocarbon solvents, paint thinner, turpentine, mineral spirits and mixtures thereof.

30. The biofuel composition of claim 1 comprising oil obtained from the seeds or fruits of plants or mixtures thereof.

31. The method of claim 12 comprising oil obtained from the seeds or fruit of plants or mixtures thereof.

32. The biofuel of claim 2 wherein the at least one emulsifier comprises a mixture of at least two emulsifiers wherein at least one of the two emulsifiers exhibits a low HLB value of about 1 to about 6 and at least one of the two emulsifiers exhibits a high HLB value of about 6 to about 20, provided that the low HLB value and the high HLB value are not both equal to 6.

33. The biofuel of claim 32 wherein: (I) the sum of (a) the weight of water and (b) the weight of hydroxyl-containing organic compound; divided by (II) the weight of vegetable and animal fat and oil is lower than about 0.25.

34. The method of claim 14 wherein the at least one emulsifier comprises a mixture of at least two emulsifiers wherein at least one of the two emulsifiers exhibits a low HLB value of about 1 to about 6 and at least one of the two emulsifiers exhibits a high HLB value of about 6 to about 20, provided that the low HLB value and the high HLB value are not both equal to 6.

35. The method of claim 34 wherein: (I) the sum of (a) the weight of water and (b) the weight of hydroxyl-containing organic compound; divided by (II) the weight of vegetable
and animal fat and oil is equal to or less than about 0.25.

36. An emulsified fuel mixture prepared from the following components: (A) 1500 parts vegetable or animal oil or fat; and (B) 900 parts water; and (C) 400 parts denatured ethanol 90 wt% (180 proof); (D) 30 parts of at least one component selected from the group consisting of (1) hydrogenated castor oil; (2) cetyl alcohol; and (3) a mixture of (1) and (2); and optionally further comprising 500 parts of a supplementary combustible liquid.

37. A method for preparing an emulsified fuel mixture comprising: (I) mixing (A) 400 parts denatured, water-containing ethanol 90 wt% (180 proof); and, (B) 30 parts of at least one component selected from the group consisting of (1) hydrogenated castor oil; (2) cetyl alcohol; and (3) a mixture of (1) and (2) to form an additive; (II) mixing the additive with component (B) 900 parts water, to form a mixture (II); (III) adding mixture (II) with concurrent mixing to (D) 1500 parts vegetable or animal oil or fat to produce a substantially emulsified mixture.