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(54) SYNERGISTIC FUEL COMPOSITION FOR ENHANCING FUEL COLD FLOW PROPERTIES

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(57) ABSTRACT

Disclosed herein is a fuel oil composition describing a synergistic blend of petroleum based fuels with renewable fuels to enhance the combined fuel's cold temperature operability properties. The oil composition comprises a petroleum based component and a renewable fuel component.

SYNERGISTIC FUEL COMPOSITION FOR ENHANCING FUEL COLD FLOW PROPERTIES

FIELD OF THE INVENTION

[0001] This invention relates generally to fuel oil compositions. The invention more specifically relates to synergistic blends of petroleum based fuels with renewable fuels and methods of using such compositions to enhance the cold temperature operability properties of fuels.

BACKGROUND OF THE INVENTION

[0002] Globally there is a significant desire to utilize "green" or "renewable fuels" as a source of energy. These fuels are gaining popularity due to various social and political factors. The effect of petroleum fuels on carbon dioxide emissions/global warming and the dependence on foreign sources of fuel are a few of the prominent factors driving popular support,

[0003] Renewable fuels are gaining greater market acceptance as a cutter stock to extend petroleum diesel market capacity. The blends of renewable fuels with petroleum diesel are being used as a fuel for diesel engines, utilized for heating, power generation, and for locomotion with ships, boats, as well as motor vehicles.

[0004] The renewable cutter stock portion of a blended fuel is commonly known as bio-diesel. Bio-diesel is defined as fatty acid alkyl esters of vegetable or animal oils. Common oils used in bio-diesel production are rapeseed, soya, palm tallow, sunflower, and used cooking oil or animal fats.

[0005] Bio-diesel is prepared by reacting whole oils with alcohols (mainly methanol) in the presence of a catalyst (acid or base), usually sodium hydroxide. This method of preparing bio-diesel, known as the CD process, is described in numerous patent applications (see, DE-A 4 209 779, U.S. Pat. No. 5,354,878, EP-A-56 25 04, the entire teachings of which are incorporated herein by reference).

[0006] Bio-diesel is a legally registered fuel and fuel additive with the U.S. Environmental Protection Agency (EPA). In order for a material to qualify as a bio-diesel, the material fuel must meet ASTM D-6751-03 (the entire teaching of which is incorporated herein by reference) specifications independent of the oil or fat used or the specific process employed to produce the additive. The ASTM D-6751 specification is intended to insure the quality of bio-diesel to be used as a blend stock for 20% and lower blend levels.

[0007] Although bio-diesel has many positive political and environmental attributes, it also has certain negative characteristics which must be taken into consideration when utilizing the material as an alternative fuel or as a blend stock for petroleum diesel.

[0008] It is well known that bio-derived fuels are inherently more sensitive to cold weather operations as compared to typical petroleum derived fuels. These fuels generally have poor handling properties as exhibited by their elevated temperatures for pour point (point at which the fuel is un-pumpable) and the relatively high Cold Filter Plugging Point (CFPP, temperature at which the material will plug fuel filters).

[0009] The inherent cold temperature sensitivity can be attributed to the abundance of linear saturated hydrocarbons (paraffin's) in the renewable fuel as compared to petroleum based fuels.

[0010] Petroleum based fuels must also meet certain handling and use requirements as described in ASTM D 975 (the entire teaching of which is incorporated herein by reference). These fuels must be pumpable and must not plug fuel filters at temperatures of use. Thus, the cold flow attributes of the fuel is a critical property which must be monitored and controlled if the product is to be considered to be fit for purpose.

[0011] In order to meet emissions and fuel efficiency goals, automotive Original Equipment Manufacturers (OEM's) are investigating the use of NOx traps, particulate traps and direct injection technologies. Such traps and catalyst systems tend to be intolerant to sulfur, this coupled with the demonstrated adverse environmental consequences of burning sulfur rich fuels has resulted in a global effort to reduce the sulfur content of fuels (Reference World-Wide Fuel Charter, April 2000, Issued by ACEA, Alliance of Automobile Manufacturers, the entire teaching of which is incorporated herein by reference). These low sulfur and ultra-low sulfur fuels are becoming increasingly necessary to ensure compliance with emissions requirements over the full useful life of the latest technological generation of vehicles. Governments are also introducing further legislation for the reduction in particulate matter and fuel emissions.

[0012] In the United States, the Environmental Protection Agency (EPA) regulations require that the sulfur content of on road fuel meet the Ultra Low Sulfur specification, specifically less than 15 ppm by mass of sulfur in the finished fuel. Similar regulations are also in place globally.

[0013] The method most commonly utilized to reduce the sulfur content of fuels is referred to as "hydro-treating". Hydro-treating is a process by which hydrogen, under pressure, in the presence of a catalyst, reacts with sulfur compounds in the fuel to form hydrogen sulfide gas and a hydrocarbon. However, hydro-treating to reduce sulfur content results not only in the removal of sulfur from the fuel but also dramatically affects the chemical composition and physical properties of petroleum fuels.

[0014] Hydro-treated fuels generally have a higher paraffin content and lower aromatic content. The increased n-paraffin's can affect the temperature and amount of crystals coming out of solution at diminished temperatures. These changes in fuel composition dramatically impact the cold flow properties of the fuel. The paraffins can form lamellar crystals when the temperature is lowered and in some cases agglomerate to inhibit fuel flow, Generally, the cold temperature handling and use characteristics hydro-treated (ULS Ultra Low Sulfur) fuels are inferior to Low Sulfur (LS) fuels.

[0015] The changes in petroleum fuel composition can be further compounded by the inclusion of renewable fuels as a blending stock for petroleum fuels. It is generally believed that the blending of modern ULS fuels with poor cold flow properties and renewable based fuels with even poorer cold flow characteristics will have a great detrimental effect on bulk fuel cold flow properties.

[0016] Problems associated with a diminished Cold Temperature Operability characteristic such as deteriorated fluidity at low temperature (i.e., increased pour point and/or cold filter plugging point) are a great concern to the fuel industry. It is anticipated, therefore, that many difficulties associated with engines, such as clogging of fuel passages or fuel filters, may occur in a normal temperature range at which the engine is operated in certain climate regions.

[0017] The present invention addresses the Cold Temperature Operability concerns of the fuel industry. Specifically, the invention discloses a novel composition having an unexpected synergy between petroleum fuel and renewable fuels, as well as the use of renewable fuel petroleum fuel blends to substantially enhance fuel of the cold flow properties. Additionally, methods are disclosed by which these compositions can be utilized.

BRIEF SUMMARY OF THE INVENTION

[0018] The present invention relates generally to fuel oil compositions. The invention more specifically relates to synergistic blends of petroleum based fuels with renewable fuels and methods of using such compositions to enhance the Cold Temperature Operability properties of fuels.

[0019] The instant invention describes compositions and methods for the preparation and use of fuel compositions with dramatically enhanced Cold Temperature Operability characteristics. The blended fuel compositions comprise (i) a petroleum based component and (ii) a renewable component.

[0020] Another aspect of the invention as described herein is the use of additives such as (a) low temperature operability/cold flow additives, (b) corrosion inhibitors, (c) cetane improvers, (d) detergents, (e) lubricity improvers, (f) dyes and markers, (g) anti-icing additives, (h) demulsifiers/antihaze additives, (i) antioxidants, (j) metal deactivators, (k) biocides, and (l) thermal stabilizers (m) antifoams and (n) static dissipater additives, in combination with a blended fuel composition of the instant invention in order to enhance other fuel properties.

[0021] Another embodiment is directed toward a method for synergistically enhancing the cold temperature operability of a fuel by employing a suitable combination of a petroleum based component and a renewable based component.

[0022] Another embodiment of the present invention is directed toward a method for operating an internal combustion engine such as a compression-ignition engine using as fuel for the engine a suitable petroleum based component and a suitable renewable based component, wherein the combination synergistically enhances cold temperature operability of said fuel.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The present invention relates generally to fuel oil compositions. The invention more specifically relates to one or more synergistic blends of petroleum based fuels with renewable fuels and methods of using such compositions to enhance the cold temperature operability properties of fuels.

[0024] The instant invention is directed to fuel compositions, comprising (i) a petroleum based component and (ii) a renewable based component wherein a synergistic combination of these fuel components dramatically enhances the Cold Temperature Operability of the fuel blend composition.

[0025] Cold Temperature Operability (CTO) of fuel is a measure of the inherent handling and use characteristics of a fuel at diminished temperatures.

[0026] A given fuel's CTO characteristics is generally considered as the lowest temperature at which the fuel can be utilized without causing operational difficulties. A fuel's CTO is estimated by its cloud point, pour point and it's CFPP. In Canada another method Low Temperature Flow Test (LTFT) is also employed.

[0027] The cloud point (CP) or wax appearance temperature (WAT) of a fuel is the point at which first visible crystals are detected in the fuel. Cloud point can be evaluated using ASTM D-2500/D-5771/D 5772/D-5773 (visible method), the entire teaching of which is incorporated herein by reference, and by IP-389 (crystal formation method), the entire teaching of which is incorporated herein by reference.

[0028] The pour point (PP) is a standardized term for the temperature at which an oil, for example, mineral oil, diesel fuel or hydraulic oil, stops flowing upon cooling. Pour point of petroleum fuels can be evaluated using ASTM D-97 (the entire teaching of which is incorporated herein by reference) and ISO-3016 (the entire teaching of which is incorporated herein by reference).

[0029] The Cold Temperature Filter Plugging Point (CFPP) of a fuel is the temperature at and below which wax in the fuel will cause severe restrictions to flow through a filter screen. CFPP is believed to correlate well with vehicle operability at lower temperatures.

[0030] CFPP of petroleum fuels in evaluated using ASTM D-6371 (the entire teaching of which is incorporated herein by reference), IP-309 (the entire teaching of which is incorporated herein by reference), and EN-116 (the entire teaching of which is incorporated herein by reference).

[0031] Low Temperature Flow Test (LTFT) is very similar in principle and function to CFPP and is evaluated using ASTM D-4539 (the entire teaching of which is incorporated herein by reference).

[0032] Synergy as defined in the present invention is the enhancement in Cold Temperature Operability characteristics of a fuel achieved by the blending of two or more fuel components which results in a blend with superior cold flow properties as compared to each individual component of the blend additively.

[0033] The synergism between the fuel components is generally evaluated by blending the renewable fuel with the petroleum fuel and measuring the CFPP response of the blends as compared to the blend fuel components

[0034] In the present embodiment, the petroleum based component is a hydrocarbon derived from refining petroleum or as a product of Fischer-Tropsch processes (well known to those skilled in the art). The hydrocarbon may also be a solvent. The fuel products are commonly referred to as petroleum distillate fuels.

[0035] Petroleum Distillate Fuels encompass a range of distillate fuel types. These distillate fuels are used in a variety of applications, including automotive diesel engines and in non on-road applications under both varying and relatively constant speed and load conditions.

[0036] Petroleum distillate fuel oils can comprise atmospheric or vacuum distillates. The distillate fuel can comprise cracked gas oil or a blend of any proportion of straight run or thermally or catalytically cracked distillates. The distillate fuel in many cases can be subjected to further processing such hydrogen-treatment or other processes to improve fuel properties. The material can be described as a gasoline or middle distillate fuel oil.

[0037] Gasoline is a low boiling mixture of aliphatic, oleinic, and aromatic hydrocarbons, and optionally, alcohols or other oxygenated components. Typically, the mixture boils in the range from about room temperature up to about 225° C.

[0038] Middle distillates can be utilized as a fuel for locomotion in motor vehicles, air planes, ships and boats as burner fuel in home heating and power generation and as fuel in multi purpose stationary diesel engines.

[0039] Engine fuel oils and burner fuel oils generally have flash points greater than 38° C. Middle distillate fuels are higher boiling mixtures of aliphatic, olefinic, and aromatic hydrocarbons and other polar and non-polar compounds having a boiling point up to about 350° C. Middle distillate fuels generally include, but are not limited to, kerosene, jet fuels, and various diesel fuels. Diesel fuels encompass Grades No. 1-Diesel, 2-Diesel, 4-Diesel Grades (light and heavy), Grade 5 (light and heavy), and Grade 6 residual fuels. Middle distillates specifications are described in ASTM D-975, for automotive applications (the entire teaching of which is incorporated herein by reference), and ASTM D-396, for burner applications (the entire teaching of which is incorporated herein by reference).

[0040] Middle distillates fuels for aviation are designated by such terms as JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1. JP-4 and JP-5. The Jet fuels are defined by U.S. military specification MIL-T-5624-N, the entire teaching of which is incorporated herein by reference, and JP-8 is defined by U.S. Military Specification MIL-T83133-D, the entire teaching of which is incorporated herein by reference. Jet A, Jet A-1 and Jet B are defined by ASTM specification D-1655 and Def. Stan. 91, the entire teachings of which are incorporated herein by reference.

[0041] The different fuels described (engine fuels, burner fuels and aviation fuels) each have further to their specification requirements (ASTM D-975, ASTM D-396 and D-1655, respectively) allowable sulfur content limitations. These limitations are generally on the order of up to 15 ppm of sulfur for On-Road fuels, up to 500 ppm of sulfer for Off-Road applications and up to 3000 ppm of sulfur for Aviation fuels.

[0042] In the present embodiment, a renewable based component is an organic material that is derived from a natural; replenishable feed stock which can be utilized as source of energy. Suitable examples of a renewable component include, but are not limited to, bio-diesel, ethanol, and bio-mass. Other renewable materials are well known to those skilled in the art.

[0043] In the present embodiment, "bio-diesel" refers to all mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats.

[0044] Bio-diesel is commonly produced by the reaction of whole oils with alcohols in the presence of a suitable catalyst. Whole oils are natural triglycerides derived from plant or animal sources. The reaction of whole oil with an alcohol to produce a fatty acid ester and glycerin is commonly referred to as trans esterification. Alternatively, bio-diesel can be produced by the reaction of a fatty acid with an alcohol to form the fatty acid ester.

[0045] The fatty acid segments of triglycerides are typically composed of C_{10}-C_{24} fatty acids, where the fatty acid composition can be uniform or a mixture of various chain lengths. The bio-diesel according to the invention may comprise single feed sourced components, or blends of multiple feed stocks derived from vegetable(s), or animal(s) origin. The commonly used single or combination feed stocks include, but are not limited to, coconut, corn, castor, linseed, olive, palm, peanut, rapeseed, safflower, sunflower, soybean, tall oil, tallow, lard, yellow grease, sardine, menhaden, herring and used cooking oils and fats.

[0046] Suitable alcohols used in either of the esterification processes can be aliphatic or aromatic, saturated or unsaturated, branched or linear, primary, secondary or tertiary, and may possess any hydrocarbon chain having lengths from about C-1 to about C-22. The industry and typical choice being identified as methanol.

[0047] Rio-diesel composition is established by specification parameters set forth in ASTM D-6751, the entire teaching of which is incorporated herein by reference. The fatty acid ester must meet and maintain the established specification parameters set forth in ASTM D-6751, regardless of the whole oil feed source or the process utilized for its production.

[0048] The ASTM4D-6751 specification outlines the requirements for bio-diesel (B100) to be considered as a suitable blending stock for hydrocarbon fuels.

[0049] During the research and development efforts to evaluate cold temperature operability properties of petroleum fuels, renewable fuels and their blends, it was discovered that a combination of petroleum fuels with renewable fuels resulted in an enhancement of the cold temperature operability of the final blended fuel

[0050] This discovery is in opposition to the commonly held belief in the petroleum industry that blending petroleum fuels with renewable fuels will have a detrimental effect on the overall cold temperature operability characteristics of the fuel. The unexpected synergistic effect described herein had heretofore been unknown in the petroleum fuel or renewable fuel industries.

[0051] The synergistic effect on Cold Temperature Operability can be achieved by blending a renewable fuel with a petroleum fuel. The renewable fuel and petroleum fuels can be blended in any proportion necessary wherein the final blend is appropriate to be utilized as a fuel.

[0052] The fuel can contain about 100% renewable components, however, in the scope of the invention, the renewable content of the blend is typically up to about 50% by volume of the finished fuel blend, more typically up to about 35% by volume of the finished fuel blend, and alternatively up to about 20% by volume of the finished fuel blend.

[0053] The invention can be practiced at high renewable fuel concentrations, wherein the renewable fuel content is greater than about 15% by volume of the finished fuel blend. The invention is also applicable at renewable fuel concentrations as low as about 15, 12.5, 12, 11, and 10% by volume of the finished fuel blend, and even at very low renewable fuel concentrations as low as about 7.5, 5, 3, 2, 1, and 0.5% by volume of the finished fuel blend.

[0054] The magnitude of the positive effect on Cold Temperature Operability as indicated by CFPP of the blended fuel is dependant on not only the volume % of renewable fuel used to make the fuel blend, but also on the specific chemical composition and physical properties of the renewable fuel utilized in the blend.

[0055] While the general positive effect on CFPP exhibited by all renewable fuels is universal, the greatest positive effect on CFPP of the blended fuel was seen where the renewable fuel utilized in the blend was derived from rapeseed as the natural, replenishable feed stock.

[0056] The effect by rapeseed derived renewable fuel on blend fuel CFPP is attributed to the substantial amount of mono unsaturated fatty chains in the rapeseed feedstock. The mono-unsaturated (eneoic—oleic type) fatty chains are desirable to polyunsaturated fatty acid chains (dieneoic—linoleic, and trieneoic linolenic type) such as those prevalent in soy bean derived feed stocks, and desirable to saturated (stearic type) fatty acid chains as those found in tallow or palm derived feeds.

[0057] It is further considered as part of the invention the blending of the described renewable feed stocks, and the utilization of these blends with petroleum fuel to enhance cold temperature operability characteristics of the final blend.

[0058] An aspect of this invention is a method of synergistically enhancing the Cold Temperature Operability of a fuel by metering into the petroleum fuel the missing synergistic renewable fuel component.

[0059] The invention described can be practiced by blending the renewable fuel with the petroleum fuel or by Mending of two or more fuels where one petroleum fuel contains the renewable fuel component.

[0060] Regardless of the order, location, or method of blending, there will be exhibited a synergistic enhancement of cold flow properties greater than that of each individual fuel.

[0061] It is additionally considered as part of the present invention the utilization of other additives in combination with the fuel blend, where these additives being present in such amounts so as to provide their normal intended functions

[0062] A non-exclusive list of additives typically used in petroleum fuel and which can be incorporated into petroleum fuel renewable fuel blends are. (a) low temperature operability/cold flow additives such as ethylene-unsaturated ester copolymers, comb polymers containing hydrocarbyl groups pendant from a polymer backbone, polar nitrogen compounds having a cyclic ring system, hydrocarbyl, hydrocarbon polymers such as ethylene alpha-olefin copolymers polyoxyethylene esters, ethers and ester/ether mixtures such as behenic diesters of polyethylene glycol, (b) corrosion inhibitors, such as fatty amines, poly amines and amides there of known as filming amines, and polymers of fatty acids known as dimmer trimer acids, (c) cetane improvers such as 2-ethyl hexyl nitrite (2EHN) and di-tert butyl peroxide (DTBP), (d) detergents such as components derived from reactions of organic acids with polyamine such as ethylenediamine, diathylene triamine, triethylene tetramine and tetraethylene pentamine, (e) lubricity improvers, such as components derived from chemical families that include: long chain fatty acid, derivatives of such fatty acids to include salts (both mineral and organic), amides and esters, dimers/trimers of fatty acids, and poly and alkyl amines (which are generally known as “filming amines”) and their derivatives such as amides, salts, and oxyalkylates, (f) dyes and markers, (g) anti-icing additives such as ethylene glycol monomethyl ether or diethylene glycol monomethyl ether (h) demulsifiers/anti-haze additives such as those produced from a phenol and an aldehyde under acidic or basic polymerization condition (industrially known as resoles or novelacs) and their alkoxylated (ethylene, propylene or butylene oxide) products, (i) antioxidant compounds such as hindered phenols exemplified by 2,6-di-t-butyl-4-methyl phenol (BHT, butylated hydroxy toluene), 2-t-butyl-4-heptyl phenol, 2-t-butyl-4-octyl phenol, 2-t-butyl-4-octyl phenol, 2-t-butyl-4-dodecyl phenol, 2,6-di-t-butyl-4-heptyl phenol, 2,6-di-t-butyl-4-dodecyl phenol, 2-methyl-6-di-t-butyl-4-heptyl phenol, and 2-methyl-6-di-t-butyl-4-dodecy-1 phenol, ortho coupled phenols to include 2,2'-bis (6-t-butyl-4-heptyl phenol), 2,2'-bis(6-t-butyl-4-octyl phenol), and 2,2'-bis(6-t-butyl-4-dodecyl phenol), where BHT is suitable, as are 2,6- and 2,4-di-t-butylphenol and 2,4,5- and 2,4,6-triisopropylphenol for use in jet fuels, (j) metal deactivators such as (1) benzotriazoles and derivatives thereof for example, 4- or 5-alkylbenzotriazoles (e.g., tolutriazole) and derivatives thereof, 4,5,6,7-tetrahyc benzotriazole and 5,5'-methylenebisbenzotriazole, Mannich bases of benzotriazole or tolutriazole, e.g., 1-[bis(2-ethylhexyl)aminomethyl]tolutriazole, 1-[bis(2-ethylhexyl)aminomethyl] benzotriazole, and alkoxyalkylbenzotriazoles such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)benzotriazole and 1-(1-cyclohexyloxybutyl)-tolutriazole, (2) 1,2,4-triazoles and derivatives thereof, for example, 3-alkyl(or aryl)-1,2,4-triazoles, and Mannich bases of 1,2,4-triazoles, such as 1-[bis(2-ethylhexyl)aminomethyl-1,2,4-triazole; alkoxyalkyl-1,2,4-triazoles such as 1-(1-butoxytheyl)-1,2,4-trizole, and acylated 3-amino-1,2,4-triazoles, (3) Imidazole derivatives, for example 4,4'-methylenebis(2-undecyl-5-methylimidazole) and bis[(N-methyl)imidazol-2-yl]carbinol octyl ether (4) Sulfur-containing heterocyclie compounds, e.g., 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole and derivatives thereof, and 3,5-bis[di(2-ethyl-hexyl) aminomethyl]-1,3,4-thiadiazolin-2-O-ne, and (5) Amino compounds and imino compounds, such as N,N'-disalicylidene propylene diamine (DMD), salicylaminoguanadine and salts thereof, (k) biocides, (l) thermal stabilizers such as those compounds containing secondary and tertiary amines, (in) anti-foams such as poly ether modified siloxanes and (n) conductivity additives such as those having components derived from chemical families that include: aliphatic amines-fluorinated polyolefins (U.S. Pat. No. 3,652,238, the entire teaching of which is incorporated herein), chromium salts and amine phosphates (U.S. Pat. No. 3,758,283, the entire teaching of which is incorporated herein), alpha-olefin-sulfone copolymer class—polysulphone and quaternary ammonium salt (U.S. Pat. No. 3,811,848, the entire teaching of which is incorporated herein), polysulphone and quaternary ammonium salt amine/epichlorhydrin adduct dinonylnaphthy]sulphonic acid (U.S. Pat. No. 3,917,466, the entire teaching of which is incorporated herein), copolymer of an alkyl vinyl monomer and a cationic vinyl monomer (U.S. Pat. No. 5,672,183, the entire teaching of which is incorporated herein), alpha-olefin-maleic anhydride copolymer class (U.S. Pat. Nos. 3,677,725 & 4,416,668, the entire teachings of which are incorporated herein), methyl vinyl ether-maleic anhydride copolymers and amines (U.S. Pat. No. 3,578,421, the entire teaching of which is incorporated herein), alpha.-olefin-acrylonitrile (U.S. Pat. Nos. 4,333,741 & 4,388,452, the entire teachings of which are incorporated herein), alpha-olefin-acrylonitrile copolymers and polymeric polyamines (U.S. Pat. No. 4,259,087, the entire teaching of which is incorporated herein), and copolymer of an alkylvinyl monomer and a cationic vinyl monomer and polysulfone (U.S. Pat. No. 6,391,070, the entire teaching of which is incorporated herein), an ethoxylated quat (U.S. Pat. No. 5,863,466, the entire teaching of which is incorporated herein), hydrocarbyl monoamine or hydrocarbyl-substituted polyalkylenieamine (U.S. Pat. No. 6,793,695, the entire teaching of which is incorporated herein), acrylic-type ester-acrylonitrile copolymers and polymeric polyamines (U.S. Pat. Nos. 4,537,601 & 4,491,651, the entire teachings of which are incorporated herein), diamine succinamide reacted with an adduct of a ketone and SO_2 (β-sutlone chemistry) (U.S. Pat. No. 4,252,542, the entire teaching of which is incorporated herein).

[0063] Low temperature operability cold/flow additives are used in fuels to enable users and operators to handle the fuel at temperatures below which the fuel would normally cause operational problems. Distillate fuels such as diesel fuels tend to exhibit reduced flow at low temperatures due in part to formation of waxy solids in the fuel. The reduced flow of the distillate fuel affects transport and use of the distillate fuels in refinery operations and internal combustion engine. This is a particular problem during the winter months and especially in northern regions where the distillates are frequently exposed to temperatures at which solid formation begins to occur in the fuel, generally known as the cloud point (ASTM D 2500) or wax appearance point (ASTM D 3117). The formation of waxy solids in the fuel will in time essentially prevent the ability of the fuel to flow, thus plugging transport lines such as refinery piping and engine fuel supply lines. Under low temperature conditions during consumption of the distillate fuel, as in a diesel engine, wax precipitation and gelation can cause the engine fuel filters to plug resulting in engine inoperability. Example of Low temperature operability/cold flow available from Innospec Inc. of Newark, Delaware is PPD 8500.

[0064] Corrosion Inhibitors are a group of additives which are utilized to prevent or retard the detrimental interaction of fuel and materials present in the fuel with engine components. The additives used to impart corrosion inhibition to fuels generally also function as lubricity improvers. Examples of corrosion inhibitors available from Innospec Inc. of Newark, Del. are DCI 6A, and DCI 4A.

[0065] Cetane Improvers are used to improve the combustion properties of middle distillates. As discussed in U.S. Pat. No. 5,482,518 (the entire teaching of which is incorporated herein by reference) fuel ignition in diesel engines is achieved through the heat generated by air compression, as a piston in the cylinder moves to reduce the cylinder volume during the compression stroke. In he engine, the air is first compressed, then the fuel is injected into the cylinder; as the fuel contacts the heated air, it vaporizes and finally begins to burn as the self-ignition temperature is reached. Additional fuel is injected during the compression stroke and the fuel burns almost instantaneously, once the initial flame has been established. Thus, a period of time elapses between the beginning of fuel injection and the appearance of a flame in the cylinder. This period is commonly called “ignition delay” and must be relatively short in order to avoid “diesel knock”. A major contributing factor to diesel fuel performance and the avoidance of “diesel knock” is the cetane number of the diesel fuel. Diesel fuels of higher cetane number exhibit a shorter ignition delay than do diesel fuels of a lower cetane number. Therefore, higher cetane number diesel fuels are desirable to avoid diesel knock. Most diesel fuels possess cetane numbers in the range of about 40 to 55. A correlation between ignition delay and cetane number has been reported in “How Do Diesel Fuel Ignition Improvers Work” Clothier, et al., Chem. Soc. Rev, 1993, pg. 101-108, the entire teaching of which is incorporated herein. Cetane improvers have been used for many years to improve the ignition quality of diesel fuels. Example of a Cetane Improvers available from Innospec Inc. of Newark, Del. is CI-0801.

[0066] Detergents are additives which can be added to hydrocarbon fuels to prevent or reduce deposit formation, or to remove or modify formed deposits, It is commonly known that certain fuels have a propensity to form deposits which may cause fuel injectors to clog and affect fuel injector spray patterns. The alteration of fuel spray patterns may cause non uniform distribution and/or incomplete atomization of fuel resulting in poor fuel combustion. The accumulation of deposits is characterized by overall poor drivability including hard starting, stalls, rough engine idle and stumbles during acceleration. Furthermore if deposit build up is allowed to proceed unchecked, irreparable harm may result which may require replacement or non-routine maintenance. In extreme cases, irregular combustion could cause hot spots on the pistons which can resulted in total engine failure requiring a complete engine overhaul or replacement. Examples of detergents available from Innospec Inc. of Newark, Del. are DDA 350, and OMA 580.

[0067] Lubricity improver ’s increase the lubricity of the fuel, to prevent wear on contacting metal surfaces in the engine. Certain diesel engine designs rely on fuel as a lubricant for their internal moving components. A potential detrimental result of poor lubricating ability of the fuel can be premature failure of engine components (e.g., fuel injection pumps). Examples of lubricity improvers available from Innospec Inc. of Newark, Del. are OLI 9070.x, and OLI 9101.x.

[0068] Dyes and Markers are materials used by the EPA (Environmental Protection Agency) and the IRS (Internal Revenue Service) to monitor and track fuels. Since 1994 the principle use for dyes in fuel is attributed to the federally mandated dying or marking of untaxed “off-road” middle distillate fuels as defined in the Code of Federal Regulations, Title 26, Part 48.4082-1(26 CFR 48.4082-1). Dyes are also used in Aviation Gasoline; Red, Blue and Yellow dyes denote octane grade in Avgas. Markers are used to identify, trace or mark petroleum products without imparting visible color to the treated product. One of the main applications for markers in fuels is in Home Heating Oil. Examples of Dyes and Markers available from Innospec Inc. of Newark, Del. are Oil Red B4 and Oil Color IAR.

[0069] Anti-Icing Additives are mainly used in the aviation industry and in cold climates. They work by combining with any free water and lowering the freeze point of the mixture that no ice crystals are formed. Examples of anti-icing additives available from Innospec Inc. of Newark, Del. are Dri-Tech and DEGME.

[0070] Demulifiers/Anti-Haze additives are mainly added to the fuel to combat cloudiness problems which maybe caused by the distribution of water in a wet fuel by dispersant used in stability packages. Examples of demulsifiers/anti-haze additives available from Innospec Inc. of Newark, Del. are DDH 10 and DDH 20.

[0071] Antioxidants are used to inhibit the degradation of fuels by interaction of the fuel with atmospheric oxygen. This process is known as “Oxidative Instability”. The oxidation of the fuel results in the formation of alcohols, aldehydes, ketones, carboxylic acids and further reaction products of these functional groups, some of which may yield polymers. Antioxidants function mainly by interrupting free radical chain reactions thus inhibiting peroxide formation and fuel degradation. Examples of antioxidants additives available from Innospec Inc. of Newark, Del. are AO 37 and AO 29.

[0072] Metal Deactivators are chelating agents that form stable complexes with specific metals. Certain metals (e.g., copper and zinc) are very detrimental to fuel stability as they catalyze oxidation processes resulting in fuel degradation (increase in gums, polymers, color, and acidity). An example of metal deactivator available from Innospec Inc. of Newark, Del. is DMD.

[0073] Biocides are used to control microorganisms such as bacteria and fungi (yeasts, molds) which can contaminate fuels. Biological problems are generally a function of fuel system cleanliness, specifically water removal from tanks and low point in the system. An example of Biocide available from Innospec Inc. of Newark, Del. is 6500.

[0074] Thermal Stabilizers are additives which help prevent the degradation of fuel upon exposure to elevated temperatures. Fuel during its use cycle is exposed to varying thermal stresses. These stresses are: 1) In storage—where temperatures are low to moderate, 0 to 49° C. (32 to 120° F.), for long periods of time, 2) In vehicle fuel systems where temperatures are higher depending on ambient temperature and engine system, 60 to 70° C. (140 to 175° F.), but the fuel is subjected to these higher temperatures for shorter periods of time than in normal storage, and 3) In (or near) the engine—where temperatures reach temperatures as high as 150° C. (302° F.) before injection or recycling, but for even shorter periods of time. Thermal stability additives protect the fuel uniformity/stability against these types of exposures. Examples of thermal stabilizers available from Innospec Inc. of Newark, Del. are FOA 3 and FOA 6.

[0075] Anti-foams additives are mainly utilized to prevent foaming of the fuel during pumping, transport and use. Examples of anti-foams available in the marketed are the TEGOPREN™ (available from Dow Corning), SAG™ (available from ex OSi—now Dow), and RHODORSIL™ (available from ex Rhone Poulene).

[0076] Canductvity Additives/Static Dissipaters/Electrical Conductivity additives are used to minimize the risk of electrostatic ignition in hydrocarbons fuels and solvents. It is widely known that electrostatic charges can be frictionally transferred between two dissimilar, nonconductive materials. When this occurs, the electrostatic charge thus created appears at the surfaces of the contacting materials. The magnitude of the generated charge is dependent upon the nature of and, more particularly, the respective conductivity of each material. Electrostatic charging is known to occur when solvents and fuels flow through conduits with high surface area or through "fine" filters. The potential for electrostatic ignition and explosion is probably at its greatest during product handling, transfer and transportation. Thus, the situations which are of greatest interest to the petroleum industry are conditions where charge is built up in or around flammable liquids, and the possibility of discharge leading to incendiary sparking, and perhaps to a serious fire or explosion. Countermeasures designed to prevent accumulation of electrostatic charges on a container being filled such as container grounding (i.e., "earthing") and bonding are routinely employed. However, it has been recognized that grounding and bonding alone are insufficient to prevent electrostatic build-up in low conductivity, volatile organic liquids. Organic liquids such as distillate fuels like diesel, gasoline,jet fuel, turbine fuels and kerosene, and relatively contaminant free light hydrocarbon oils such as organic solvents and cleaning fluids are inherently poor conductors. Static charge accumulates in these fluids because electric charge moves very slowly through these liquids and can take a considerable time to reach a surface which is grounded. Until the charge is dissipated, a high surface-voltage potential can be achieved which can create an incendiary spark, resulting in an ignition or an explosion, The increased hazard presented by low conductivity organic liquids can be addressed by the use of additives to increase the conductivity of the respective fluids. The increased conductivity of the liquid will substantially reduce the time necessary for any charges that exist in the liquid to be conducted away by the grounded inside surface of the container. Examples of conductivity additives available from Iospec Inc. of Newark, Del. are Stadis® 425, Stadis® 450.

[0077] The general chemistries and compositions of these additive families which function to impart the desired fuel characteristics are fully known in the art. A person having ordinary skill in the art to which this invention pertains can readily select an additive to achieve the enhancement of the desired fuel property.

[0078] The invention is further described by the following illustrative but non-Limiting examples. The following examples depict the synergistic enhancement of fuel cold temperature operability by the proper combination of a petroleum fuel and a renewable fuel.

EXAMPLE

[0079] Synergy Test Method: The effect on CFPP upon combining a petroleum fuel and a renewable fuel was evaluated. The base line CFPP of a series of petroleum fuels, and renewable fuels available in the fuel market were evaluated as per ASTM method D-6371. The results of the evaluation are depicted in Table 1.

TABLE 1

Middle distillate and Renewable Feedstock's		CFPP ° C.
Diesel 1		−9
Diesel 2		−34
Diesel 3		−13
Diesel 4		−4
BIO 001	Rape	−18
BIO 002	Soy	−3
BIO 003	Palm	9
BIO 004	Rape	−26
BIO 006	Tallow	3
BIO 007	Soy	2
BIO 008	Soy	−5
BIO 009	Tallow	3
BIO 010	Coconut	−8
BIO 011	Used Cooking Oil	2
BIO 012	Mixed Tank 71	3
BIO 013	Tallow	8
BIO 014	Rape	−15
BIO 015	Coconut, BD100	−8
BIO 016	Palm, BD200	11

[0080] The data indicates a wide range of CFPP performance characteristics ranging from −9° C. to −34° C. for petroleum fuels, and −26° C. to 11° C. for the renewable fuels.

[0081] These fuels were then mixed to prepare a B5 and B20 fuel blends. The CFPP of the blended fuels were measured, and the resulting data compared with the CFPP of the base petroleum fuel. The results of the evaluation are depicted in Table 2.

TABLE 2

Blends		% v/v	FAME	CFPP	Change in CFPP
Diesel 1	BIO 001	0	Rape	−9	
Diesel 1	BIO 001	5		−17	−8
Diesel 1	BIO 001	20		−22	−13
Diesel 2	BIO 001	0	Rape	−34	
Diesel 2	BIO 001	5		−43	−9
Diesel 2	BIO 001	20		−41	−7
Diesel 3	BIO 001	0	Rape	−13	
Diesel 3	BIO 001	5		−23	−10
Diesel 3	BIO 001	20		−24	−11
Diesel 4	BIO 001	0	Rape	−4	
Diesel 4	BIO 001	5		−16	−12
Diesel 4	BIO 001	20		−20	−16
Diesel 1	BIO 002	0	Soy	−9	
Diesel 1	BIO 002	5		−9	0
Diesel 1	BIO 002	20		−7	2
Diesel 2	BIO 002	0	Soy	−34	

TABLE 2-continued

Blends		% v/v	FAME	CFPP	Change in CFPP
Diesel 2	BIO 002	5		−40	−6
Diesel 2	BIO 002	20		−28	6
Diesel 3	BIO 002	0	Soy	−13	
Diesel 3	BIO 002	5		−13	0
Diesel 3	BIO 002	20		−11	2
Diesel 4	BIO 002	0	Soy	−4	
Diesel 4	BIO 002	5		−7	−3
Diesel 4	BIO 002	20		−6	−2
Diesel 1	BIO 003	0	Palm	−9	
Diesel 1	BIO 003	5		−11	−2
Diesel 1	BIO 003	20		−10	−1
Diesel 2	BIO 003	0	Palm	−34	
Diesel 2	BIO 003	5		−33	1
Diesel 2	BIO 003	20		−10	24
Diesel 3	BIO 003	0	Palm	−13	
Diesel 3	BIO 003	5		−16	−3
Diesel 3	BIO 003	20		−13	0
Diesel 4	BIO 003	0	Palm	−4	
Diesel 4	BIO 003	5		−10	−6
Diesel 4	BIO 003	20		−9	−5
Diesel 4	BIO 004	0	Rape	−4	
Diesel 4	BIO 004	5		−10	−6
Diesel 4	BIO 004	20		−15	−11
Diesel 4	BIO 006	0	Tallow	−4	
Diesel 4	BIO 006	5		−6	−2
Diesel 4	BIO 006	20		−7	−3
Diesel 3	BIO 007	0	Soy	−13	
Diesel 3	BIO 007	5		−15	−2
Diesel 3	BIO 007	20		−8	5
Diesel 4	BIO 007	0	Soy	−4	
Diesel 4	BIO 007	5		−6	−2
Diesel 4	BIO 007	20		−5	−1
Diesel 3	BIO 008	0	Soy	−13	
Diesel 3	BIO 008	5		−12	1
Diesel 3	BIO 008	20		−11	2
Diesel 4	BIO 008	0	Soy	−4	
Diesel 4	BIO 008	5		−5	−1
Diesel 4	BIO 008	20		−17	−13
Diesel 4	BIO 009	0	Tallow	−4	
Diesel 4	BIO 009	5		−5	−1
Diesel 4	BIO 009	20		−7	−3
Diesel 4	BIO 010	0	Coconut	−4	
Diesel 4	BIO 010	5		−7	−3
Diesel 4	BIO 010	20		−3	1
Diesel 4	BIO 011	0	Used	−4	
Diesel 4	BIO 011	5	Cooking Oil	−6	−2
Diesel 4	BIO 011	20		−8	−4
Diesel 4	BIO 012	0	Mixed Tank	−4	
Diesel 4	BIO 012	5	71	−6	−2
Diesel 4	BIO 012	20		−9	−5
Diesel 4	BIO 013	0	Tallow	−4	
Diesel 4	BIO 013	5		−7	−3
Diesel 4	BIO 013	20		−8	−4
Diesel 4	BIO 014	0	Rape	−4	
Diesel 4	BIO 014	5		−8	−4
Diesel 4	BIO 014	20		−18	−14

[0082] Data clearly indicates that there is a positive influence on cold temperature operability characteristics of a petroleum fuel by blending the fuel with a renewable fuel. At the B5 blend level, 79% of the petroleum/renewable fuel blends had a CFPP enhancement of 2° C. or more as compared to the base petroleum fuel, and at the B20 level, 58% of the blends exhibited 2° C. or more CFPP enhancement.

[0083] The greatest magnitude of effect was seen with Rapeseed based material as the renewable fuel feed. The average CFPP enhancement by the Rapeseed material at B5 blend level was 8.1° C., and at the B20 level was 12° C.

[0084] These results were a great surprise as the commonly held belief in the petroleum industry is tat renewable fuelers will have a great detrimental effect on cold temperature operability characteristics of petroleum fuels. It is evident that by a proper choice of the type and volume % of a renewable fuel, a fuel blend can be produced with enhanced Cold Temperature Operability characteristics.

[0085] While certain embodiments of the present invention have been disclosed in detail, it is to be understood tat various modifications may be adopted without departing from the spirit of the invention or scope of the following claims.

What is claimed is;

1. A composition for enhancing cold temperature operability of a fuel comprising a petroleum based component and a renewable based component.

2. The composition of claim **1**, wherein said petroleum based component is selected from the group consisting of a middle distillate fuel, a jet fuel, and a Fischer-Tropsch fuel.

3. The composition of claim **1**, wherein said petroleum based component comprises less then about 500 ppm by mass of sulfur.

4. The composition of claim **3**, wherein said petroleum based component comprises less then about 15 ppm by mass of sulfur.

5. The composition of claim **1**, wherein said renewable based component is selected from the group consisting of a product derived from the trans esterification of naturally occurring whole oils of plants or animals with an alcohol, the ester of a fatty acid derived from naturally occurring oils, and an alcohol.

6. The composition of claim **5**, wherein said natural oils are selected from the group consisting of Soy, Palm, Rapeseed, Linseed, Coconut, Corn, Cotton, Cooking, Sunflower, Safflower, Tallow, Lard, Yellow Grease, Fish Oils and blends thereof.

7. A method of synergistically enhancing cold temperature operability of a fuel, comprising employing a combination of a petroleum based component and a renewable based component.

8. The method of claim **7**, wherein said petroleum based component is selected from the group consisting of a middle distillate fuel, a jet fuel, and a Fischer-Tropsch fuel.

9. The method of claim **7**, wherein said petroleum based component comprises less then about 500 ppm by mass of sulfur.

10. The method of claim **9**, wherein said Petroleum Based Component comprises less then about 15 ppm by mass of sulfur.

11. The method of claim **7**, wherein said renewable based component selected from the group consisting of product derived from the trans esterification of naturally occurring whole oils of plants or animals with an alcohol, or the ester of a fatty acid derived from naturally occurring oils, and an alcohol.

12. The method of claim **11**, wherein said natural oils are selected from the group consisting of Soy, Palm, Rapeseed, Linseed, Coconut, Corn, Cotton, Cooking, Sunflower, Safflower, Tallow, Lard, Yellow Grease, Fish Oils, and blends thereof.

13. The method of claim **12**, wherein said natural oil is Rapeseed ad blends thereof.

14. The method of claim **12**, wherein said natural oil is Soy and blends thereof.

15. The method of claim **11**, wherein said alcohol is selected from the group consisting of linear, branched, alkyl, aromatic, primary, secondary, tertiary, and polyols.

16. The method of claim **7**, wherein said renewable based component is present in the fuel blend between about 0.1% to about 99.9% v/v of fuel blend.

17. The method of claim **16**, wherein said renewable based component is present in the fuel blend between about 1% to about 50% v/v of fuel blend.

18. The method of claim **17**, wherein said renewable based component is present in the fuel blend between about 2% to about 25% v/v of fuel blend.

19. The method of claim **1**, wherein the synergistic fuel blend combination of a further comprise one or more additives selected from the group consisting of: (a) low temperature operability/cold flow additives, (b) corrosion inhibitors, (c) cetane improvers, (d) detergents, (e) lubricity improvers, (f) dyes and markers, (g) anti-icing additives, (h) demulsifiers/anti haze additives, (i) antioxidants, (j) metal deactivators, (k) biocides, (l) thermal stabilizers (m) antifoams, (n) static dissipater additives, and combinations thereof.

20. A method for operating an internal combustion engine such as a compression-ignition engine using as fuel for the engine a petroleum based component and a renewable based component, wherein said combination synergistically enhances cold temperature operability of said fuel.

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