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(54) **CLEANER BURNING DIESEL FUEL**

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(60) Provisional application No. 60/222,252, filed on Aug. 1, 2000.

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(57) **ABSTRACT**

An improved diesel fuel based on a blend of biodiesel and ultra-low sulfur diesel fuel, particularly with a fuel additive containing a concentrate containing fuel borne catalyst (FBC). The catalyst will preferably comprise platinum and/or cerium and/or iron, and the ultra-low sulfur diesel fuel will preferably contain less than 10% aromatics. The biodiesel is typically employed in an amount of about 20% of the blend.

CLEANER BURNING DIESEL FUEL

RELATED APPLICATIONS AND PRIORITY

[0001] This is a continuation in part of and claims priority to pending U.S. patent application Ser. No. 10/357,027 filed 3 Feb. 3, which claims priority to PCT/US01/24061, which claims priority to U.S. Provisional Patent Application 60/222,252, filed 1 Aug. 2000.

TECHNICAL FIELD

[0002] The invention provides an improved diesel fuel based on a blend of biodiesel and a low aromatic content ultra-low sulfur diesel fuel, particularly with a fuel additive containing a concentrate containing fuel borne catalyst (FBC).

BACKGROUND ART

[0003] In U.S. patent application Ser. No. 10/290,798, there is described a Low Emissions Diesel Fuel, which includes jet A and an FBC.

[0004] In U.S. patent application Ser. No. 10/357,027, there is described a Low Emissions Diesel Fuel, which includes an emulsion of jet A and an FBC.

[0005] In U.S. patent application Ser. No. 10/401,367, there is described a Low Emissions Diesel Fuel, which includes jet A, biodiesel and an FBC.

[0006] These fuels are indeed effective, but there is a continuing need for additional diesel fuels to provide yet further reductions in pollutant generation, especially NO_x and particulate emissions.

BRIEF SUMMARY OF THE INVENTION

[0007] It is an objective of the invention to provide an improved diesel fuel to reduce emissions of unburned hydrocarbons, carbon monoxide, particulates and NO_x.

[0008] It is another objective of the invention to provide a fuel employing renewable source materials having a desirable balance of hydrogen to carbon, which can decrease carbon dioxide emissions by this means and fuel economy as the emission of noxious pollutants are also controlled.

[0009] These and other objects are accomplished by the invention which provides an improved diesel fuel based on a blend of biodiesel and low aromatic content ultra-low sulfur diesel fuel, particularly with a fuel additive containing a concentrate containing fuel borne catalyst.

[0010] Several preferred aspects of the invention will be described below.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The invention provides an improved diesel fuel based on a blend of biodiesel and low aromatic content ultra-low sulfur diesel fuel, particularly with a fuel additive containing a concentrate containing fuel borne catalyst (FBC).

[0012] As a principal component of the fuel blends of the invention, there is provided a low aromatic (LA) content, ultralow sulfur diesel (ULSD) fuel. The term low aromatic content as used herein means that this component of the fuel will have an aromatic content in volume percent of less than 10%, and preferably of from 1 to 8%, particularly in the range of from 2 to 5%. The table below shows typical analyses of a No. 2 diesel and low aromatic ultralow sulfur diesel fuels LA ULSD, in addition to a preferred formulation according to the invention (LA ULSD with FBC and 20% Bio-Diesel). Equivalents which have the same essential function and those varying compositionally by up to 50%, preferably by less than 20%, e.g., no more than 10%, can also be employed.

Fuel	Typical No. 2 Diesel	Preferred Low Aromatic (LA) ULSD	Typical LA ULSD with FBC and 20% Bio-Diesel
API Gravity	36.36	35–40	35–40
Sulfur, wt %	0.0323	<0.0015	<0.0015
Cetane Number	47.7	>47	>50
Carbon, wt %	86.84	<87	<85
Hydrogen, wt %	13.16	>13	>13
Aromatics, vol %	29.9	<10	ND
Olefins, vol %	0.5	ND	ND
Saturates, vol %	69.6	ND	ND
Viscosity at 40 C. (cs)	2.3	<10, e.g. 2–3	ND
Flash Point, ° F.	157.4	>180	ND
IBP, ° F.	351.1	420–430	430
5%, ° F.	393.3	ND	449
10%, ° F.	414.0	>440	459
20%, ° F.	439.0	ND	478
30%, ° F.	459.5	ND	493
40%, ° F.	477.9	ND	509
50%, ° F.	494.6	>490	526
60%, ° F.	511.3	ND	544
70%, ° F.	529.0	ND	567
80%, ° F.	550.4	ND	592
90%, ° F.	580.3	>560	618
95%, ° F.	606.7	ND	633
EP, ° F.	641.7	<640	643

[0013] The other principal ingredient of the low-emissions diesel fuel of the invention is what is referred to in the art as "biodiesel". Biodiesel will comprise a minor proportion of the fuel blend, typically from about 1 to 35%, e.g., on the order of 15 to 25%. Blends will typically contain about 20% biodiesel, wherein this biologically-derived fuel component will be comprised of a "mono-alkyl ester-based oxygenated fuel", i.e., fatty acid esters, preferably from fatty acids derived from triglycerides such as soybean oil, Canola oil and/or tallow. As used herein, the term "fatty acid ester(s)" is intended to include any compound wherein the alcohol portion is easily removed, including polyols and substituted alcohols, etc., but are preferably esters of volatile alcohols, e.g., the C_1-C_4 alcohols (preferably methyl), 2-methoxy ethyl and benzyl esters of fatty acids containing about eight or more (e.g., 8 to 22) carbon atoms, and mixtures of such esters. Volatile alcohols are highly desirable. Methyl esters are the most highly preferred ester reactants. Suitable ester reactants can be prepared by the reaction of diazoalkanes and fatty acids, or derived by alcoholysis from the fatty acids naturally occurring in fats and oils.

[0014] Suitable fatty acid esters can be derived from synthetic or natural, saturated or unsaturated fatty acids and include positional and geometrical isomers. Suitable preferred saturated fatty acids include caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, isomyristic, isomargaric, myristic, caprylic, and anteisoarachadic. Suitable preferred unsaturated fatty acids include myristoleic, palmitoleic, ricinoleic, linoleic, oleic, elaidic, linolenic, eleasteric, arachidonic, erucic, and erythrogenic acids. Mixtures of fatty acids derived from soybean oil, palm oil, safflower oil, rapeseed oil, Canola (low ericic acid), and corn oil are especially preferred for use herein. The fatty acids can be used "as is," and/or after hydrogenation, and/for isomerization, and/for purification. For example, rapeseed provides a good source for C_{22} fatty acids; C_{16}-C_{18} fatty acids can be provided by tallow, soybean oil, or cottonseed oil; and shorter chain fatty acids can be provided by coconut, palm kernel, or babassu oils. Lard, olive oil, peanut oil, sesame seed oil, and sunflower seed oil, are other natural sources of fatty acids.

[0015] Preferred esters comprised in the biodiesel are lower alkyl esters, e.g., methyl, ethyl, propyl and butyl, particularly methyl esters of soybean and or tallow fatty acids. The following is the specification for biodiesel (B100) set by the National Biodiesel Board, December 2001, which is also adopted for the purpose of clarity and definition for the present invention. Thus, biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. This specification is for pure (100%) biodiesel prior to use or blending with diesel fuel. A considerable amount of experience exists in the US with a 20% blend of biodiesel with 80% diesel fuel (B20). Although biodiesel (B100) can be used, blends of over 20% biodiesel with diesel fuel should be evaluated on a case-by-case basis until further experience is available. Equivalents which have the same essential function and those varying compositionally by up to 25%, preferably by less than 10%, can also be employed. In some cases, as little as 2% biodiesel may be used with a blend of 98% diesel fuel of distillate origin.

Property	ASTM Method	Limits	Units
Flash Point	D93	130 min.	Degrees C.
Water & Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40 C.	D445	1.9–6.0	mm^2/sec.
Sulfated Ash	D874	0.020 max.	% mass
Sulfur	D5453		ppm
S 15 Grade		15 max.	
S 500 Grade		500 max.	
Copper Strip Corrosion	D130	No. 3 max.	
Cetane	D613	47 min.	
Cloud Point	D2500	Pref. −2° C. or Report	Degrees C.
Carbon Residue 100% sample	D4530[1]	0.050 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/gm
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus Content	D 4951	0.001 max.	% mass
Distillation Temp, Atmospheric Equivalent Temperature, 90% Recovered	D 1160	360 max.	Degrees C.

[1]To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller and manufacturer.

[0016] One product of this type is available under the trademark BioDiesel by Members of the National BioDiesel Board and is identified as "Methyl Soyate, Rapeseed Methyl Ester (RME), Methyl Tallowate". The manufacturer also refers to the fuel as "a mono-alkyl ester-based oxygenated fuel, a fuel made from vegetable oil or animal fats." It is said to contain 11% oxygen by weight. They describe the product as Methyl esters from lipid sources, CAS Number 67784-80-9.

[0017] The fuel borne catalyst (FBC) will comprise fuel-soluble platinum and/or cerium and/or iron. The cerium and/or iron are typically employed at concentrations of from 2 to 25 ppm and the platinum from 0.05 to 2 ppm, with preferred levels of cerium or iron being from 2 to 10 ppm, e.g., 3-8 ppm, and the platinum being employed at a level of from 0.1 to 0.5 ppm, e.g., 0.15 ppm. A preferred ratio of cerium and/or iron to platinum is from 75:1 to 10:1. The LA ULSD component will typically be employed at a volume ratio to the fatty acid esters of from about 2:1 to about 5:1, e.g., about 4:1. The full range of blends extends from 50:1 to 1:50 with some benefit. The LA ULSD fuel component of the blend preferably contains 50-1500 ppm detergent, up to about 500 ppm lubricity additive and 0.1-1 ppm platinum COD and 5-20 ppm cerium oleate or octoate. It is an advantage of the invention that the fatty acid esters add lubricity to the LA ULSD and decrease the need for independent lubricity additives.

[0018] The catalyzed blend of the invention is effective in lowering regulated emission pollutants, among which are NO_x, particulates, hydrocarbons and carbon monoxide. Preferably the fuel will lower NO_x and particulates at the same time, an unusual combination. Preferred blends will be effective to achieve at least a 4% or more reduction in NO_x and a particulate reduction of at least 25% as compared to a baseline of No. 2 Diesel fuel. More preferred levels will be from 5 to 25% NO_x reduction and from 20 to 60% particulate reduction. Higher reductions of particulates can be achieved by using the fuel in an engine equipped with a diesel particulate filter or diesel oxidation catalyst. These reductions are preferably obtained while reducing or not increasing NO_2 emissions.

[0019] A preferred detergent, which can be employed, comprises polyolefin amide alkyleneamine (about 65-80%) and the remainder petroleum distillate. Equivalents which have the same essential function can also be employed. One preferred form is available from Texaco as TFA-4690-C, at concentrations of from about 50 to 300 ppm, more narrowly 75-150, e.g., about 100 ppm, for which they provide the following analysis:

Properties	Method	Typical
Density @ 15° C.	D4052	0.91–0.94
Nitrogen Content, wt. %	D5291	2.3–2.4
Flash, ° C., minimum	D93	62
TBN, mgKOH/g	D2896	50–60
Kinematic Viscosity, cSt at 40° C.	D445	600–850

[0020] A preferred lubricity additive, which can be employed, comprises tall oil fatty acids, available commercially as a mixture of fatty acids including oleic, linoleic and the like. Equivalents which have the same essential function can also be employed. One preferred form is available from Texaco as TFA-4769, at concentrations of from about 25 to

500 ppm, e.g., about 150-250 ppm, for which they provide the following analysis:

Properties	Method	Typical
Specific Gravity, 60/60° F.	D1298	0.91
Pounds/Gallon, 60° F.	Calculated	7.54
Flash, ° F., minimum	D93	142
Kinematic Viscosity, cSt at 40° C.	D445	17.85

[0021] Among the specific cerium compounds are: cerium III acetylacetonate, cerium III napthenate, and cerium octoate, cerium oleate and other soaps such as stearate, neodecanoate, and octoate (2-ethylhexoate). Many of the cerium compounds are trivalent compounds meeting the formula: $Ce(OOCR)_3$ wherein R=hydrocarbon, preferably C_2 to C_{22}, and including aliphatic, alicyclic, aryl and alkylaryl. The cerium is preferred at concentrations of 2 to 15 ppm cerium w/v of fuel. Preferably, the cerium is supplied as cerium hydroxy oleate propionate complex (40% cerium by weight). Preferred levels are toward the lower end of this range.

[0022] Among the specific iron compounds are: ferrocene, ferric and ferrous acetyl-acetonates, iron soaps like octoate and stearate (commercially available as Fe(III) compounds, usually), iron pentacarbonyl Fe(CO).sub.5, iron napthenate, and iron tallate.

[0023] Any of the platinum group metal compositions, e.g., 1,5-cyclooctadiene platinum diphenyl (platinum COD), described in U.S. Pat. No. 4,891,050 to Bowers, et al., U.S. Pat. No. 5,034,020 to Epperly, et al., and U.S. Pat. No. 5,266,093 to Peter-Hoblyn, et al., can be employed as the platinum source. Other suitable platinum group metal catalyst compositions include commercially-available or easily-synthesized platinum group metal acetylacetonates, platinum group metal dibenzylidene acetonates, and fatty acid soaps of tetramine platinum metal complexes, e.g., tetramine platinum oleate. The platinum is preferred at concentrations of 0.1-2.0 ppm platinum w/v (mg per liter) of fuel, e.g., up to about 1.0 ppm. Preferred levels are toward the lower end of this range, e.g., 0.15-0.5 ppm. Platinum COD is the preferred form of platinum for addition to the fuel. The cerium or iron are typically employed at concentrations to provide from 2 to 25 ppm of the metal and the platinum from 0.05 to 2 ppm, with preferred levels of cerium or iron being from 5 to 10 ppm, e.g., 7.5 ppm, and the platinum being employed at a level of from 0.1 to 0.5 ppm, e.g., 0.15 ppm. A preferred ratio of cerium and/or iron to platinum is from 75:1 to 10:1.

[0024] In addition to utilizing the low-emissions fuel according to the invention, retarding engine timing, e.g., from 2 to 6°, can further reduce NO_x and the use of a diesel particulate filter and/or diesel oxidation catalyst can provide further reductions in carbon monoxide, unburned hydrocarbons and particulates.

[0025] The low-emissions fuel according to the invention can be employed as an emulsion with water, wherein an oil phase is emulsified with water, the water comprising from 1 to 30% water based on the weight of the aviation kerosene. In the preferred forms, the emulsion will be predominantly of the water-in-oil type and will preferably contain surfactants, lubricity additives and/or corrosion inhibitors in addition to the other components mentioned above. A discussion of suitable emulsion forms and additives is found in U.S. Pat. No. 5,743,922. An emulsion of the water-in-oil type typically provides about 1% NO_x reduction for each 1% water added. The combination of technologies will provide emissions reductions greater than either alone. The platinum/cerium fuel borne catalyst or other catalyst is preferred but optional. If desired, the combination of a blend of fatty acid esters and aviation kerosene can be employed to good effect without the fuel borne catalyst. The fuel thus formed in any of the embodiments above, can be used with timing changes, EGR, oxidation catalysts or particulate filters for enhanced emissions control.

[0026] The term "diesel particulate filter" is meant to refer to those devices known in the art as exhaust gas filters that reduce particulate emissions by trapping a portion of the particulates within a complex internal structure. They must be regenerated or replaced as deposits will accumulate. The fuel borne catalyst described above, when used with the base fuel as also described—forming the fuel of the invention—enables very reduced emissions with enhanced filter operation.

[0027] The term "diesel oxidation catalyst" is meant to refer to those devices known in the art as exhaust gas treatment catalysts that reduce particulate, hydrocarbon and carbon monoxide emissions by causing contact with catalyzed surfaces in lieu of trapping particulates as done in the diesel particulate filters. The fuel borne catalyst described above, when used with the base fuel as also described—forming the fuel of the invention—enables very reduced emissions with enhanced oxidation catalyst operation.

[0028] Retarding engine timing, e.g., by from about 2 to about 6°, is a known procedure for reducing NO_x, unfortunately it will by itself cause pollutant generation due to poor combustion. This tradeoff has been troubling the art since emissions control became important. It is an advantage of the invention, that both reduced NO_x and other pollutants can be achieved by employing the fuel of the invention in combination with one or more of the above techniques and/or exhaust gas recirculation wherein a portion of the exhaust gas is intermixed with combustion air.

[0029] In operation of the invention in one preferred form an FBC is provided, such as described in U.S. Pat. No. 6,003,303 and the references cited therein.

[0030] The invention has particular utility in the operation of fleet vehicles, which are brought to a central location for refueling at regular intervals, e.g., daily.

[0031] The concentration of FBC catalyst metal in fuel is desirably maintained between 4 and 10 ppm in this exemplary setting.

[0032] The following examples are presented to further illustrate and explain the invention and are not to be taken as limiting in any regard. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE 1

[0033] Cleaner burning biodiesel fuel blends used with the Platinum Plus® fuel borne catalyst (FBC) (added at 0.15

ppm Pt as Pt COD) and a lightly catalyzed (3-5 grams Pt) diesel oxidation catalyst (DOC) produced emission reductions of 51 percent particulates (PM) and 9 percent NOx versus baseline emissions from standard No. 2D fuel. This combination represents a reduction of over 100 lbs per year of regulated pollutants from a typical school bus and over 200 lbs per year for a local delivery vehicle. Typical biodiesel blends can increase NOx by two to four percent.

[0034] Testing was conducted over triplicate federal transient test cycles on a 1995 Navistar DT-466 engine typical of school bus, beverage and local delivery service fleets. The fuels employed are listed in the following table.

Fuel	No. 2	LA ULSD	LA ULSD	LA ULSD with FBC and 20% Bio-Diesel
API Gravity	36.36	37.84	39.30	36.0
Sulfur, wt %	0.0323	0.0001	0.00001	0.00034
Cetane Number	47.7	ND	ND	55.2
Carbon, wt %	86.84	86.02	86.0	83.7
Hydrogen, wt %	13.16	13.98	14.0	13.6
Aromatics, vol %	29.9	3.26	5.20	ND
Olefins, vol %	0.5	ND	ND	ND
Saturates, vol %	69.6	ND	ND	ND
Viscosity at 40 C. (cs)	2.3	2.94	3.00	ND
Flash Point, ° F.	157.4	198	188	ND
IBP, ° F.	351.1	423	424	430
5%, ° F.	393.3	ND	ND	449
10%, ° F.	414.0	455	456	459
20%, ° F.	439.0	ND	ND	478
30%, ° F.	459.5	ND	ND	493
40%, ° F.	477.9	ND	ND	509
50%, ° F.	494.6	500	512	526
60%, ° F.	511.3	ND	ND	544
70%, ° F.	529.0	ND	ND	567
80%, ° F.	550.4	ND	ND	592
90%, ° F.	580.3	563	586	618
95%, ° F.	606.7	ND	ND	633
EP, ° F.	641.7	601	624	643

[0035] In the first of two test sequences, a blend of 20 percent biodiesel was combined with low aromatic ultra-low sulfur diesel (LA ULSD) and the Platinum Plus® FBC (0.15% ppm Pt as Pt COD), and the engine was equipped with a lightly catalyzed (3-5 g/ft^3) DOC. Here, overall emission reductions were 66 percent HC, 63 percent CO, 9 percent NOx, 51 percent PM and 95 percent SO_x. Reductions of over 60 percent were also found in the NO_2 fraction of exhaust which is a strong lung irritant and can increase with traditional heavily catalyzed after-treatment devices. The test approach uses a lightly catalyzed DOC which reduces cost and minimizes NO_2 formation.

[0036] These tests confirm earlier test work on engines from Cummins and Detroit Diesel, which showed the ability of Cleaner Burning Biodiesel blends made with Platinum Plus® FBC and No. 1D or ULSD to reduce NO_x and PM emissions consistently.

[0037] The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading this description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is defined by the following claims. The claims cover the indicated components and steps in all arrangements and sequences which are effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

1. An improved diesel fuel blend comprising biodiesel and low aromatic content ultra-low sulfur diesel fuel.

2. A diesel fuel blend according to claim 1, which further includes a fuel borne catalyst (FBC) comprising platinum and/or iron, and/or cerium.

3. A diesel fuel blend according to claim 1, which comprises from 15 to 25% biodiesel.

4. A diesel fuel blend according to claim 1, wherein the low aromatic ultra-low sulfur diesel fuel component comprises less than 10% by volume aromatics.

5. A diesel fuel blend according to claim 1, wherein sulfur content is less than 0.0015%.

6. A diesel fuel blend according to claim 5, wherein the low aromatic ultra-low sulfur diesel fuel component comprises less than 10% by volume aromatics.

7. A diesel fuel blend according to claim 6, which further includes a fuel borne catalyst (FBC) comprising platinum and/or iron, and/or cerium.

8. A diesel fuel blend according to claim 1, which comprises from 15 to 25% biodiesel and the low aromatic ultra-low sulfur diesel fuel component comprises less than 10% by volume aromatics and a sulfur content of less than 0.0015% and the blend further includes a fuel borne catalyst (FBC) comprising platinum and/or iron, and/or cerium.

9. An improved diesel fuel blend comprising from 15 to 25% biodiesel and low aromatic content ultra-low sulfur diesel fuel comprising less than 10% by volume aromatics and a sulfur content of less than 0.0015%.

10. A diesel fuel blend according to claim 9, which further includes a fuel borne catalyst (FBC) comprising platinum and/or iron, and/or cerium.

11. A diesel fuel blend according to claim 10, wherein the FBC comprises platinum.

12. A diesel fuel blend according to claim 11, wherein the FBC comprises platinum and iron or cerium.

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