Reduced-Emissions Combustion Utilizing Multiple-Component Metallic Combustion Catalyst

Description

Background of The Invention

[0001] The invention concerns new compositions and a new process for improving the efficiency of fossil fuel combustion sources. Utilizing a fuel containing a fuel-soluble catalyst comprised of platinum and at least one additional metal reduces production of pollutants of the type generated by incomplete combustion, *e.g.*, particulates, unburned hydrocarbons and carbon monoxide.

[0002] Diesel engines have a number of important advantages over engines of the Otto type. Among them are fuel economy, ease of repair and long life. From the standpoint of emissions, however, they present problems more severe than their spark-ignition counterparts. Emission problems relate to particulates, nitrogen oxides (NO_x), unburned hydrocarbons (HC) and carbon monoxide (CO). As engine operation modifications are made to reduce particulates and unburned hydrocarbons on diesel engines, the NO_x emissions tend to increase.

[0003] After treatment devices, such as diesel particulate filters (DPFs) and diesel oxidation catalysts (DOCs), have been proposed to reduce the emission of particulates and gaseous hydrocarbons and carbon monoxide from diesel engines. These devices are greatly stressed in older engines and are in need of efficiency improvements in newer engines. In all cases, they are expensive due in significant part to the cost of precious metals used required to be effective. It would be desirable to reduce the cost of DOC or DPF devices or eliminate them altogether.

[0004] It has been believed that one way to achieve this is to employ fuel borne catalysts (FBCs); however, they have not been fully effective at the relatively high levels employed. FBCs produce ash and data published under the European VERT program show that at high FBC dose rates of 20 ppm, or 100 ppm, cerium the number of ultra fine particles increases dramatically above baseline. However, for a bimetallic used at 0.5/7.5 or 0.25/4 ppm there is no significant increase in the ultra fine particle number. It has been found that

at low levels of FBC there is not a separate ultrafine oxide particle peak and metal oxides are contained in the soot over the entire particle size distribution. It would be desirable to reduce the contribution of metal ash to overall engine emissions. For an engine meeting 1998 US emission standards, particulate emissions are limited to 100,000 μg/hp-hr (0.1 gram/hp-hr). A cerium FBC used at 30 ppm in fuel represents a metal catalyst input loading to the engine of 6000 μg/hp-hr of metal or roughly 6% of untreated engine emissions.

[0005] There is a need to provide diesel fuels containing FBCs at lower than current levels, yet which have high effect, such that after treatment devices might be eliminated or reduced in size, catalyst loading or frequency of cleaning of soot, by lowering emissions of particulates, HC and CO directly from diesel engines.

Summary Of The Invention

[0006] It is an advantage of the invention that improvements can be achieved without the use of after treatment devices, such as filters or catalysts, *e.g.*, diesel particulate filters (DPF's) or diesel oxidation catalysts (DOC's) in the case of diesel engines.

[0007] It is a further advantage of the invention that improvements can be achieved for engine out emissions from diesel engines to an extent that if after treatment devices, such as DOCs or DPFs, are applied the devices can use less precious metals with improved performance.

[0008] The fuel employed according to the invention comprises carbonaceous fuel, *e.g.*, fossil fuel, containing low or ultra low levels of catalyst metal additives. The catalyst metal additives will preferably be soluble or dispersible in the fuel and contain platinum and cerium and/or iron compositions.

[0009] In one aspect, the invention provides a diesel fuel for powering a diesel engine with reduced emission of particulates without the need for an after treatment device, comprising: a base fuel comprising distillate, and a fuel borne catalyst comprising platinum and cerium and/or iron, wherein the platinum is employed at a level of from 0.05 to 0.5 ppm, *e.g.*, 0.1 to 0.5 ppm, and the levels of cerium or iron being from 5 to 10 ppm.

Preferably, the diesel fuel contains less than 0.05% sulfur. In a preferred aspect, the cerium and/or iron are present at total concentrations of from 0.5 to less than 8 ppm.

[0010] In another aspect the invention provides a method for reducing the emissions of particulates, hydrocarbons and carbon monoxide from a diesel engine directly out of the engine prior to contact with an oxidizer or particulate trap comprising: adding a fuel-soluble platinum group metal composition and at least one other catalytic compound comprising fuel-soluble compounds of cerium and/or iron to a diesel fuel to lower the emissions of particulates, unburned hydrocarbons and carbon monoxide, wherein the platinum is employed at a level of from 0.05 to 0.5 ppm, *e.g.*, 0.1 to 0.5 ppm, and the levels of cerium and/or iron being from 5 to 10 ppm; and operating a diesel engine with the fuel.

[0011] From another perspective, the invention can be described as providing a process for improving combustion of pilot fuel in a dual-fuel diesel engine, which operates principally on natural gas, comprising: adding to a pilot fuel, a multi catalyst composition comprising platinum at concentrations of from only 0.0005 to less than 0.15 ppm and cerium and/or iron at total concentrations of from only 0.5 to less than 8 ppm.

[0012] From yet another perspective the invention is seen as providing a process for combusting a carbonaceous fuel comprising: mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels reduced to as low as 0.0005 ppm for platinum and levels as low as 0.5 ppm for the cerium and iron; and combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements.

[0013] In another aspect of the invention there is provided a process for combusting a carbonaceous fuel comprising: mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels of from about 0.0005 to 2 ppm for platinum and levels of from about 1 to 25 ppm for the cerium and iron; combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements; then, for at

least a period of time changing the amount of catalyst utilized by mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels reduced to as low as 0.0005 ppm for platinum and levels as low as 0.5 ppm for the cerium and iron; and combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements.

[0014] Yet further, the invention provides a process for combusting a carbonaceous fuel comprising: for at least a part of a treatment regimen utilizing higher catalyst concentrations, *e.g.*, platinum at 0.5 to 2.0 ppm and cerium at 7.5 to 15 ppm; mixing with fuel a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels of 0.0005 to less than 0.15 ppm for platinum and levels of 0.05 to less than 1.0 ppm for the cerium and iron; and combusting the fuel with air in a regimen of treatment that will achieve one or more of the noted improvements.

[0015] Many of the preferred aspects of the invention are described below. Equivalent compositions are contemplated.

Description Of The Drawings

[0016] The invention will be better understood and its advantages will become more apparent from the following written description, especially when read in light of the accompanying drawings wherein:

[0017] **Fig. 1** is a graph summarizing the data from Example 3, wherein a platinum/cerium fuel borne catalyst (FBC) at low concentrations was evaluated on several fuels on a diesel engine.

[0018] **Fig. 2** is a graph summarizing the data from Example 6, wherein a platinum/cerium fuel borne catalyst (FBC) at low concentrations was evaluated on several fuels on a diesel engine.

[0019] **Fig. 3** is a graph summarizing the data from Example 7, wherein a platinum/cerium fuel borne catalyst (FBC) at low concentrations was evaluated on several fuels on a diesel engine.

Detailed Description of the Invention

[0020] In addition to the other advantages and improvements of the invention, the use of low and ultra-low individual and combined catalyst levels is significant in several regards, including the great reduction in catalyst solids which can accumulate within a system or are exhausted. The invention can reduce pollutants without the use of after-treatment devices and can enhance after treatment due to the reduced production of particulates and the increased ability to burn off carbon deposits. Cerium and iron levels are reduced to levels as low as 0.05 ppm and platinum levels are reduced to levels as low as 0.0005 ppm. A regimen of treatment will utilize effective levels within the low and ultra-low ranges for a time and under conditions, which will achieve one or more of the noted improvements.

[0021] As noted above, the invention relates to improving combustion of diesel fuels, which typically comprise a fossil fuel, such as any of the typical petroleum-derived fuels including distillate fuels. The diesel fuel can be of any of those formulations disclosed in the above priority patent applications, which are incorporated by reference herein in their entireties. A fuel can be one or a blend of fuels selected from the group consisting of distillate fuels, including diesel fuel, *e.g.*, No. 2 Diesel fuel, No. 1 Diesel fuel, jet fuel, e.g., Jet A, or the like which is similar in boiling point and viscosity to No. 1 Diesel fuel, ultra low sulfur diesel fuel (ULSD) and biologically-derived fuels, such as those comprising a "mono-alkyl ester-based oxygenated fuel", *i.e.*, fatty acid esters, preferably methyl esters of fatty acids derived from triglycerides, e.g., soybean oil, Canola oil and/or tallow.

[0022] Jet A and Diesel No. 1 are deemed equivalent for applications of the invention, but are covered by different American Society For Testing and Materials (ASTM) specifications. The diesel fuels are covered by ASTM D 975, "Standard Specification for Diesel Fuel Oils". Jet A has the designation of ASTM D 1655, "Standard Specification for Aviation Turbine Fuels". The term ultra low sulfur diesel fuel (ULSD) means No. 1 or No. 2 diesel fuels with a sulfur level no higher than 0.0015 percent by weight (15 ppm) and some jurisdictions require a low aromatic hydrocarbon content *e.g.*, less than ten percent by volume.

[0023] The term low aromatic content ultralow sulfur diesel (LA ULSD) fuel. 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 formulation also containing a biodiesel component (LA ULSD with FBC and 20% Bio-Diesel).

Fuel	Typical No.2 Diesel	LA ULSD	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 40C (cs)	2.3	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

[0024] Biologically-derived fuels are referred to in the art as "biodiesel". Biodiesel typically comprises a minor proportion of a diesel 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.

[0025] 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 erucic 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.

[0026] 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 50 %, preferably by less than 20%, can also be employed. In some cases as little as 2% biodiesel may be used with a blend of 98% diesel fuel from one of the other sources identified above.

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 S 15 Grade S 500 Grade	D5453	15 max. 500 max.	ppm
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

[0027] 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

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

contain 11% oxygen by weight. They describe the product as Methyl esters from lipid sources, CAS Number 67784-80-9.

[0028] The process of the invention employs a fuel-soluble, multi-metal catalyst, preferably comprising fuel-soluble platinum and either cerium or iron or both cerium and iron. The cerium and/or iron are typically employed at concentrations of from 0.5 to 20 ppm and the platinum from 0.0005 to 2 ppm, with preferred levels of cerium and/or iron being from 5 to 10 ppm, e.g., 7.5 ppm, and the platinum being employed at a level of from 0.0005 to 0.5 ppm, e.g., less than 0.15 ppm, and in some cases less than 0.1 ppm, say 0.01 to 0.09 ppm. In some embodiments, the treatment regimen can call for the utilizing higher catalyst concentrations initially or at defined intervals or as needed--but not for the whole treatment as has been necessary in the past. In some cases, platinum concentrations can be as high as 1 ppm or even up to 2 ppm, as needed. The cerium and/or iron are preferred at levels of cerium and/or iron being from 2 to 10 ppm, e.g., 3-8 ppm, and the platinum being employed at a level of from 0.05 to 0.5 ppm, e.g., from 0.1 to 0.5ppm, e.g., 0.15 ppm, for typical operations. The tests below, run at these levels show surprising results in terms of engine out emissions.

[0029] A preferred ratio of cerium and/or iron to platinum is from 100,000:1 to 3:1, e.g., in the range of from 100:1 to 20,000:1, but more typically will be from 50,000:1 to 500:1. A preferred ratio within the above ranges and shown surprisingly effective by testing will have a ratio of cerium and/or iron to platinum at from 75:1 to 10:1. A formulation using 0.15 ppm platinum with 10 ppm of cerium and 5 ppm of iron is exemplary. Another, preferred formulation will contain 0.15 ppm platinum and 7.5 ppm cerium. Another advantage of low levels of catalyst (about 3 to 15 ppm total), preferably below 12 ppm and more preferably below 8 ppm, is the reduction in ultra fine particles resulting from metal oxide emissions. Data published under the European VERT program show that at high FBC dose rates of 20 ppm, or 100 ppm, cerium the number of ultra fine particles increases dramatically above baseline. However, for a bimetallic used at 0.5/7.5 or 0.25/4 ppm there is no significant increase in the ultra fine particle number. It has been found that at low levels of FBC there is not a separate ultrafine oxide particle peak and metal oxides are contained in the soot over the entire particle size distribution. A further advantage of the low dose rates prescribed by the current invention is a reduction in the contribution of metal ash to overall engine emissions. For an engine meeting 1998 US emission

standards, particulate emissions are limited to 100,000 μg/hp-hr (0.1 gram/hp-hr). A cerium FBC used at 30 ppm in fuel represents a metal catalyst input loading to the engine of 6000 μg/hp-hr of metal or roughly 6% of untreated engine emissions. Therefore, low levels of catalyst used in the present invention of less than 8 ppm and preferably 4 ppm as a bimetallic or trimetallic FBC will, for example, contribute only 800 – 1600 μg/hp-hr of catalyst loading to the engine or 0.8 – 1.6% of baseline soot emissions. This has the advantage of reduced metal ash emissions and reduces the contribution of the FBC to overall particulate mass emissions or loading of metal ash to downstream emission control devices.

[0030] The fuel can contain detergent (*e.g.*, 50-300 ppm), lubricity additive (e.g., 25 to about 500 ppm), other additives, and suitable fuel-soluble catalyst metal compositions, *e.g.*, 0.1-2 ppm fuel soluble platinum group metal composition, *e.g.*, platinum COD or platinum acetylacetonate and/or 2-20 ppm fuel soluble cerium or iron composition, *e.g.*, cerium as a soluble compound or suspension, cerium octoate, ferrocene, iron oleate, iron octoate and the like. The fuel as defined, is combusted without the specific need for other treatment devices although they can be used especially for higher levels of control on diesels.

[0031] A combination of platinum with iron and/or cerium at low concentrations in fuels is as effective as much higher concentrations of cerium, iron or other metals without platinum in reducing carbon or soot deposits or emissions. Concentrations of a few ppm metals in combination are as effective as 30-100 ppm of iron and/or cerium used alone.

[0032] In one aspect, the process of the invention will comprise: mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels reduced to as low as 0.0005 ppm for platinum and levels as low as 0.5 ppm for the cerium and iron; and combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements. In one aspect, low catalyst levels can be employed for at least a portion of a treatment regimen, which can also include employing a higher initial dose and/or intermittently using higher catalyst levels.

[0033] The invention also has significant beneficial use in the area of dual-fuel diesel engines, which although they operate principally on natural gas, utilize a more smoke-producing pilot fuel such as regular diesel fuel. In some cases the catalyst concentrations according to the invention can be the above-noted low catalyst levels for at least a part of a treatment regimen, with platinum concentrations of from only 0.0005 to less than 0.15, *e.g.*, less than 0.1, ppm and cerium and/or iron at total concentrations of from only 0.5 to less than 8 ppm. In some cases, it will be useful to utilize less than 0.05 ppm platinum and a total catalyst level of less than 5 ppm.

[0034] These bimetallic and trimetallic platinum combinations are compatible with standard additive components for distillate and residual fuels such as pour point reducers, antioxidant, corrosion inhibitors and the like.

[0035] 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 other C_6 to C_{24} alkanoic acids, and the like. 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 1 to 15 ppm cerium w/v of fuel, *e.g.*, 4 to 15 ppm. Preferably, the cerium is supplied as cerium hydroxy oleate propionate complex (40% cerium by weight) or a cerium octoate (12% cerium by weight). Preferred levels are toward the lower end of this range.

[0036] 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 napthenate, iron tallate and other C_6 to C_{24} alcanoic acids, iron penta carbonyl $Fe(CO)_5$ and the like.

[0037] 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. 5,266,083 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, including substituted (*e.g.*, alkyl, aryl, alkyaryl substituted) and

unsubstituted 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 0.05-2.0 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 0.5 to 25 ppm of the metal and the platinum from 0.0005 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 100,000:1 to 10:1, e.g., from 50,000:1 to 500:1. A formulation using 0.0015 ppm platinum with 10 ppm of cerium and 5 ppm of iron is exemplary, with a ratio of cerium plus iron to platinum of about 10,000:1. An alternative exemplary composition will contain 0.0015 ppm platinum with 10 ppm of iron and 5 ppm of cerium. Another will contain from 3 to 10 ppm of a combination of Ce and Fe along with 0.1 to 0.5 ppm platinum. Another fuel of preference will contain from 0.05 to 0.5 ppm platinum and the levels of cerium and/or iron of from 0.5 to 10 ppm, especially wherein the cerium and/or iron are present at total concentrations of from 3 to 8 ppm.

[0038] The combustion according to the invention can be of 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 diesel fuel. 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. Combustion can improve combustion efficiency and reduce particulates without the use of oxidation catalysts or particulate filters for enhanced emissions control on diesel engines. Also, better carbon burn out in open flame combustion sources will lead to lower carbon deposits on heat transfer surfaces and lower soot oxidation temperatures on downstream heat recovery devices.

[0039] The fuels of the invention, comprising a base fuel and low levels of fuel borne catalysts based on platinum and cerium and/or iron compounds, provide better engine out emissions than the prior art, yet further provide unexpectedly good results in terms of PM, HC, CO, NO_x and NO_2 as a percentage of NO_x when used with an after treatment device

such as a diesel oxidation catalyst (DOC) or diesel particulate filter (DPF). Other devices including particulate reactors, partial filters or NO_x adsorbers can also be used and benefit from reduced engine out emissions of the current invention. 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. They can be of any suitable construction, for example of ceramic, metal, SiC or wire mesh. 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. See the examples below, for the engine out results and the benefits of the FBC with catalyzed after treatment devices to reduce NO_2 and particulate emissions. While not wishing to be bound by any theory, the unexpectedly good results with after treatment devices as well as for engine out emissions, this may be because the platinum is not present in amounts sufficient to produce excessive amounts of NO_2 and yet produces some NO_2 or other chemical species which is sufficient to foster oxidation of the carbon in the particulates in the presence of low levels of cerium and/or iron. NO2 is a strong lung irritant and can be generated in large quantities by traditional use of heavily catalyzed aftertreatment devices such as DOCs, DPFs or combinations. The net result of the limited NO_2 production due to low platinum concentrations and the cerium and/or iron being present in low but sufficient amounts to produce greater than expected reductions in particulates (as well as other species resulting from incomplete oxidation) and at the same time control the amount of NO_2 generated and released. Unlike the prior art, then, the invention has found that high NO_2 production rates are not necessary and, indeed, has found a way to provide emissions less irritating to humans.

[0040] The following examples are presented to further explain and illustrate 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

[0041] This example describes the preparation of a low-emissions diesel fuel according to a preferred aspect of the invention a fuel is blended using the Colonial Pipeline Company

fungible aviation kerosene grade 55 analyzed above (Jet A, and similar in boiling and viscosity to No. 1 Diesel), with additives (100 ppm of the TFA 4690-C detergent, 225 ppm of the noted Texaco lubricity additive) and a fuel borne catalyst (FBC) containing 0.15 ppm platinum supplied as platinum COD and 7.5 ppm cerium supplied as cerium hydroxy oleate propionate complex (solution containing 40% cerium by weight). These ppm values are, again weight of metal in mg per volume of fuel in liters The fuel was used in a test of a 1998 DDC Detroit Diesel Series 60, 400 hp engine and showed remarkably improved results as compared to a reference on highway No 2 or a CARB ULSD (California Air Resources Board Ultra Low Sulfur Diesel) fuel.

[0042] Test data is summarized in the following table, wherein the test results of the FTP transient--composite results are given for the various fuels tested.

[0043]

		Emissions (g/bhp-hr)				
Fuel	**Sulfur (ppm)**	**HC**	**CO**	**NOx**	**PM**	**BSFC (lbs/hp-hr)**
1998 Standard	< 500	1.3	15.5	4.0	0.10	NS
2D	450	0.15	1.13	4.05	0.075	0.398
CARB ULSD	50	0.08	0.96	3.72	0.063	0.392
CARB ULSD + FBC	50	0.10	0.85	3.78	0.053	0.391
Jet A + Additives + FBC	<300	0.13	0.84	3.66	0.050	0.397

[0044] These results are surprising, from the standpoint that the CARB USLD fuel has been the subject of considerable investigation and development, yet does not provide improved results as compared to the invention with FBC catalyst containing low levels of platinum and cerium. Thus, the invention provides a very practical approach to reducing a

range of polluting emissions without creating a need for difficult and expensive processing to achieve the ultra low sulfur contents now thought to be essential to particulate control.

Example 2

[0045] This example presents results for a platinum and cerium bimetallic FBC used in commercial ultra low sulfur diesel at a total of 4 ppm metal versus normal sulfur fuel and a reference ULSD and tested on a 1998 DDC Series 60 Engine. The results are summarized in the table below:

[0046] **Emissions Results From a 1998 DDC Series 60 Engine on Various Fuels (Replicate Hot FTP Tests)**

	gr/bhp-hr				lb/hp-hr
	HC	CO	NOx	PM	BSFC
1998 Standard	1.3	15.5	4.0	0.10	NS
Base No. 2D	0.13	1.0	4.0	0.08	.413
ULSD + Bimetallic FBC @ 0.25 Pt/3.75 Ce	0.16	0.9	3.7	0.06	.410
Reference ULSD	0.35	0.9	3.9	0.08	.416

[0047] The above table shows improvements for the FBC treated fuel in HC (54%), NOx (5%), PM (25%) and fuel economy (1.4%) for a treated ultra low sulfur diesel (ULSD) fuel against a reference ULSD without the additive.

Example 3

[0048] Testing was conducted on a 1990 DTA-466 International 7.6 liter engine over three twenty minute hot transient test cycles. Average emissions for NO_x, NO and NO_2 and particulates were measured in grams/hp-hr are presented in the table below.

[0049] Baseline emissions on commercial No. 2D (>300ppm Sulfur) and ULSD (<15ppm Sulfur) showed similar NO_2 emissions as a percentage of total NOx species at 17 and 18% of total nitrogen species. Particulates were slightly lower for the ULSD at 0.244 gram/hp-hr.

[0050] Installation in the exhaust of a heavily catalyzed diesel oxidation catalyst (HCDOC) with 75 g/cu ft loading of PGM and a lightly catalyzed wire mesh filter (LCWMF) with 14 g/cu ft loading of platinum group metal (PGM) used with a bimetallic platinum/cerium FBC at 0.5/7.5 ppm in ULSD fuel produced reduction in particulates of

59%, but increased NO_2 emissions to 58% of total nitrogen oxide species. The cerium additive was cerium hydroxy propionate oleate and the platinum additive was platinum COD.

[0051] When the DOC was removed, particulate reduction efficiency decreased slightly to 57% but NO_2 was only 25% of total nitrogen oxide species. After a further 25 hours of operation on treated fuel both particulates and NO_2 were further unexpectedly reduced.

[0052] One unexpected positive result observed in the testing was the reduction in both particulate emissions and percentage NO_2 when the FBC was added to either baseline No. 2D or ULSD without the installation of any after treatment devices. For No. 2D, the particulates were reduced by 15% from 0.253 to 0.215 on treated fuel (Pt/Ce at 0.15/7.5 ppm) and NO_2 decreased from 17% to 13%. For the ULSD, the particulates decreased from 0.244 to 0.207 with the addition of FBC (Pt/Ce at 0.5/7.5 ppm) to the fuel while NO_2 decreased by 15% from 18% to 12%. Thus there are benefits to the use of the FBC alone or with catalyzed after treatment devices to reduce particulates and other emissions. Highly catalyzed DOCs, advocated by the prior art as important aids in particulate reduction due to their generation of NO_2, are shown here to be no more effective than the right FBC for particulate reduction and can adversely affect NO_2 emission. This has not been disclosed in the prior art.

[0053] **Comparison of Emissions from 1990 International 7.6 Liter DTA-466 Engine**

(Average of Triplicate Hot-Start Tests)

Pollutant Amounts (gr/hr-hr)

	Pollutant Amounts (gr/hr-hr)						
Fuel and Aftertreatment	**NOx**	**NO**	**NO_2**	**% NO_2**	**Particulates**	**HC**	**CO**
No. 2D	6.1	5.0	1.1	17	0.253	0.3	1.4
No. 2D + FBC (Pt/Ce @ 0.15/7.5 ppm)	6.0	5.3	0.7	13	0.215	0.3	1.3
ULSD	5.6	4.6	1.0	18	0.244	0.3	1.1
ULSD + FBC	5.7	5.0	0.7	12	0.207	0.2	1.0
ULSD + FBC + HCDOC + LCWMF	5.5	2.3	2.2	58	0.104	0.0	0.0
ULSD + FBC + LCWMF	5.5	4.1	1.4	25	0.108	0.0	0.2
ULSD + FBC + CWMF (25 hrs)	5.5	4.4	1.1	21	0.094	0.0	0.2

Notes: DOC = 75 gr/cu ft PGM loading
CWMF = 14 gr/cu ft PGM loading
FBC = 0.5 ppm Pt/7.5 ppm Ce, unless noted

Example 4

[0054] Engine Dynamometer testing was conducted on a Cummins 275hp 8.3 liter diesel engine certified to meet 1991 California and US Environmental Protection Agency Federal Emission standards. The test cycle was the EPA transient test protocol under the US Federal Test Procedure (FTP).

[0055] This transient cycle is described by means of percent of maximum torque and percent of rated speed for each one-second interval over a test cycle of 1199 second duration. The first five minutes of the cycle is designated as the New York Non-Freeway (NYNF) portion of the test and represents city operation with extensive idle time. The second five minutes is called the Los Angeles Non Freeway (LANF) portion. This part of the test also represents city operation, but without extensive idle time. The third five minute section of the test is called the Los Angeles Freeway (LAF) portion. This is representative of high speed freeway operation. The final five minutes is a repeat of the NYNF portion.

[0056] These four parts give the 20 minute EPA transient cycle. Results represent the mean of triplicate "hot-start" repeat tests for each fuel.

[0057] Results are presented graphically for reduction in emissions of hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and particulates (PM) for each fuel tested relative to emissions from a standard No. 2 on-highway reference fuel containing 386ppm sulfur.

[0058] Addition of a bimetallic platinum/cerium fuel borne catalyst (FBC) at a concentration of 0.15ppm platinum and 7.5ppm cerium metal in fuel produced particulate reductions of 11 % (No.2D + FBC) in Graph 1. For comparison a commercial ultra low sulfur diesel fuel with 9ppm sulfur was run with no FBC and produced particulate reduction of 6% versus baseline No. 2D as shown in the Graph (ULSD). This same ULSD treated with a fuel borne catalyst at 0.5ppm Pt and 7.5 Ce then produced PM reduction of 13% along with the highest reductions in HC, CO and NO_x emissions versus the baseline No. 2D or the untreated ULSD. These data confirm the engine out pollutant reduction

benefits, including particulate reduction, of the FBC in standard or ultra low sulfur fuels. The results are summarized in **Fig. 1**.

Example 5

[0059] In another test on a 1990 model year Cummins 8.3 liter engine manufactured to 1991 Federal Emission Standards, with a different baseline than in Example 4, the engine was operated on baseline No. 2D fuel over triplicate "hot start" 20 minute transient cycles. Emissions were reported as the average in grams/hp-hr in the Table below. Particulate emissions were measured at 0.189 gr/hp-hr. Operation on ultra low sulfur diesel fuel (ULSD) produced a minor reduction in particulate emissions to 0.182 μg/hp-hr. NO_2 emissions remained at 15 – 16% of total nitrogen oxide emissions for either baseline fuel.

[0060] Treatment of the No. 2D with a bimetallic FBC at 0.15 ppm platinum and 7.5 ppm cerium produced a particulate reduction of 13% to 0.164 gr/hp-hr with a reduction in NO_2 from 0.8 gr/hp-hr to 0.6 gr/hp-hr. This is in contrast to traditional approaches for particulate reduction which use heavily catalyzed devices to convert NO to NO_2 and can also convert sulfur to sulfate particulate emissions on No. 2 fuel. A 13% PM reduction is surprising for a low level FBC and significant given the minor PM reduction achieved from ULSD alone.

[0061] Further testing showed the benefits of a bimetallic FBC at a ratio of 0.5 ppm Pt and 7.5 ppm Ce were maintained in a ULSD fuel. PM reductions of 12% were achieved versus baseline ULSD while maintaining lower NO_2 emissions.

[0062] **Engine Out Data for a Bimetallic FBC on a 1991 Certified Emissions Cummins 8.3 Liter**
(Average of Triplicate Hot Tests)

Fuel	HC	CO	NOx	NO	NO_2	% NO_2	PM
Baseline No. 2D	0.4	1.1	4.9	4.1	0.8	16%	0.189
Baseline ULSD	0.4	1.1	4.7	4.0	0.7	15%	0.182
Baseline No.2D + 0.15/7.5	0.3	1.0	5.0	4.4	0.6	12%	0.164
ULSD + 0.5/7.5	0.3	1.0	4.8	4.2	0.6	13%	0.160

Example 6

[0063] Similar replicate testing conducted on a 1998 Detroit Diesel 12.7 liter engine is Presented in Graph 2 and showed an 11% reduction in particulates for the FBC in the No. 2D fuel at a 0.5ppm Pt/7.5ppm Ce treat rate and a 15% reduction for an untreated ULSD fuel. When added to the ULSD fuel, the FBC increased particulate reduction to 28% versus the baseline on untreated No.2D fuel.

[0064] These results again confirm the ability of the FBC to reduce engine out emissions, including PM, when added to No.2D or ULSD fuels. The results are summarized in **Fig.2**.

Example 7

[0065] Testing on a 1990 International Harvister 7.6 liter engine showed reductions in PM of 15% for a No. 20 fuel treated with the FBC at a O.15/7.5ppm treat rate. For comparison, a commercial ULSD with no FBC provided 3% PM reduction. With the addition of the FBC to ULSD at 0.15/7.5ppm dose rate, the particulates were reduced by 18%; used with a low aromatic ULSD, the FBC produced reduction in particulates of 29%. The results are summarized in **Fig. 3**.

Example 8

[0066] A series of tests were conducted on a 1995 Navistar 7.6 liter engine installed on a transient engine dynamometer. Triplicate hot test cycles were run for a baseline on No.2D fuel (> 300 ppm S) and then for each of three different FBC additives used in ULSD (< 15 ppm S).

[0067] Additive A delivered 0.15/4/4 ppm Pt/Ce/Fe; Additive B delivered 0.15 ppm/7.5 ppm Pt/Ce; and Additive C delivered 0.15/5.6/2.4 ppm Pt/Ce/Fe. All additives contained the same commercial detergent package to assist with stability of the catalyst. Results show similar reductions for all three additives in HC, CO, NOx and NO_2. Particulate reductions for bimetallic Additive B appear slightly better at 32% versus baseline No. 2D while Additives A and C both delivered PM reduction of 25%. In all cases the blend of additive with the ULSD provided unexpectedly good reduction in NOx and NO_2.

[0068] In certain applications the use of a trimetallic may present cost advantages versus a bimetallic or may be preferred for use in regeneration of exhaust aftertreatment devices such as DOCs, DPFs, wire mesh filters or combined systems.

[0069] **Engine Out Data for Bimetallic and Trimetallic Additives on a 1995 Navistar DT466 7.6 liter Engine**
(Average of Triplicate Hot Test Results in gr/hp-hrs)

Fuel/Additive	HC	CO	NOx	NO	NO_2	% NO_2	PM
Baseline No. 2D	0.2	1.2	4.7	3.3	1.4	30%	0.106
ULSD + Additive A	0.1	1.0	4.1	3.7	0.4	10%	0.079
ULSD + Additive B	0.1	1.0	4.2	3.6	0.6	14%	0.072
ULSD + Additive C	0.1	1.0	4.2	3.7	0.6	14%	0.078

Notes: A = 0.15/4/4 Pt/Ce
B = 0.15/7.5 Pt/Ce
C = 0.15/5.6/2.4 Pt/Ce

[0070] The above description is intended to enable the person skilled in the art to practice the invention. It is not intended to detail all of the possible modifications and variations which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such modifications and variations be included within the scope of the invention which is seen in the above description and otherwise defined by the following claims. The claims are meant to cover the indicated elements and steps in any arrangement or sequence which is effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

CLAIMS

1. A diesel fuel for powering a diesel engine with reduced emission of particulates without the need for an after treatment device, comprising:

a base fuel comprising distillate,

and a fuel borne catalyst comprising platinum and cerium and/or iron, wherein the platinum is employed at a level of from 0.05 to 0.5 ppm and the levels of cerium and/or iron being from 0.5 to 10 ppm.

2. A diesel fuel according to claim 1, wherein the diesel fuel contains less than 15ppm sulfur.

3. A diesel fuel according to claim 1, wherein the cerium and/or iron are present at total concentrations of from 3 to 8 ppm.

4. A diesel fuel according to claim 1, which comprises a base fuel selected from the group consisting of ultra low sulfur diesel fuel, No. 1 diesel fuel, No. 2 diesel fuel, jet fuel, biologically-derived fuels, comprising fatty acid esters derived from triglycerides and mixtures of two or more of these.

5. A method for reducing the emissions of particulates, hydrocarbons and carbon monoxide from a diesel engine directly out of the engine prior to contact with an oxidizer or particulate trap comprising:

adding a fuel-soluble platinum group metal composition and at least one other catalytic compound comprising fuel-soluble compounds of cerium to a diesel fuel to lower the emissions of particulates, unburned hydrocarbons and carbon monoxide, wherein the platinum is employed at a level of from 0.05 to 0.5 ppm and the levels of cerium and/or iron being from 3 to 10 ppm; and

operating a diesel engine with the fuel.

6. The method according to claim 5, wherein the diesel fuel contains less than 15ppm sulfur.

7. The method according to claim 5 wherein, wherein the cerium and/or iron are present at total concentrations of from 0.5 to less than 8 ppm.

8. The method according to claim 5, wherein the diesel comprises a base fuel selected from the group consisting of ultra low sulfur diesel fuel, No. 1 diesel fuel, No. 2 diesel fuel, jet fuel, biologically-derived fuels, comprising fatty acid esters derived from triglycerides and mixtures of two or more of these.

9. The method according to claim 5, wherein exhaust from operating the diesel engine is passed through a diesel particulate filter.

10. The method according to claim 5, wherein exhaust from the diesel engine is passed through a diesel oxidation catalyst.

11. A process for improving combustion of pilot fuel in a dual-fuel diesel engine, which operates principally on natural gas, comprising: adding to a pilot fuel, a multi catalyst composition comprising platinum at concentrations of from only 0.0005 to less than 0.15 ppm and cerium and/or iron at total concentrations of from only 0.5 to less than 8 ppm.

12. A process for combusting a carbonaceous fuel comprising: mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels reduced to as low as 0.0005 ppm for platinum and levels as low as 0.5 ppm for the cerium and iron; and combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements.

13. A process for combusting a carbonaceous fuel comprising: mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels of from about 0.0005 to 2 ppm for platinum and levels of from about 1 to 25 ppm for the cerium and iron; combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements; then, for at least a period of time changing the amount of catalyst utilized by mixing with fuel or combustion air a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels reduced to as low as 0.0005 ppm for platinum and levels as low as 0.5 ppm for the cerium and iron;

and combusting fuel with air in the presence of the catalyst in a regimen of treatment that will utilize effective catalyst levels for a time and under conditions, which will achieve one or more of the noted improvements.

14. A process for combusting a carbonaceous fuel comprising: for at least a part of a treatment regimen utilizing higher catalyst concentrations, mixing with fuel a multi-component combustion catalyst comprising a platinum composition and cerium and/or iron compositions at levels of 0.0005 to less than 0.15 ppm for platinum and levels of 0.05 to less than 1.0 ppm for the cerium and iron; and combusting the fuel with air in a regimen of treatment that will achieve one or more of the noted improvements.