(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 641 960 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.09.2013 Bulletin 2013/39

(51) Int Cl.:
C10L 1/06 *(2006.01)* ***C10L 1/16*** *(2006.01)*
C10L 10/10 *(2006.01)*

(21) Application number: **13160463.9**

(22) Date of filing: **21.03.2013**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **21.03.2012 US 201261613517 P**

(71) Applicant: **Shell Internationale Research Maatschappij B.V.**
2596 HR The Hague (NL)

(72) Inventor: **Shea, Timothy**
The Woodlands, TX 77380 (US)

(74) Representative: **Matthezing, Robert Maarten et al**
Shell International B.V.
LSI
PO Box 384
2501 CJ The Hague (NL)

(54) Fuel composition and its use

(57) A fuel composition is provided that contains a major amount of a mixture of hydrocarbons in the gasoline boiling range and a minor amount of and (b) a minor amount of alpha-terpinene.

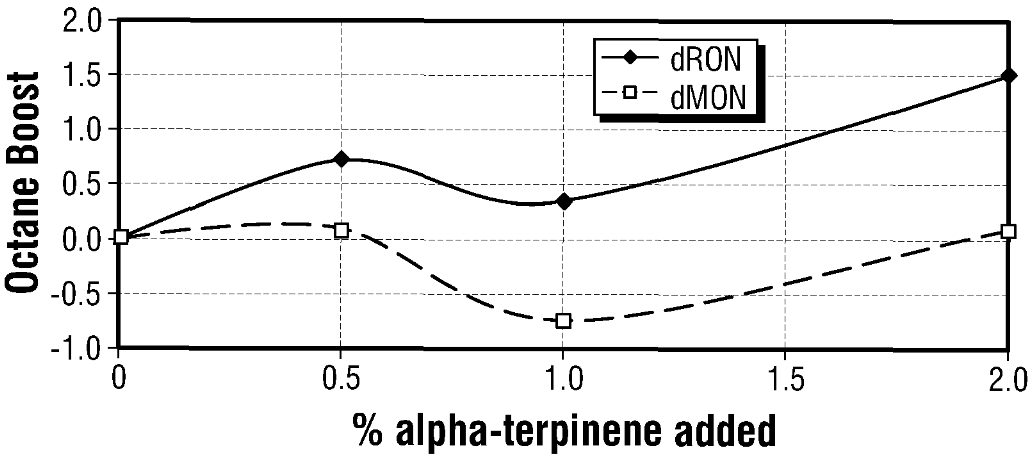

FIG. 1

EP 2 641 960 A1

Description

Cross Reference to Related Application

[0001] The present application claims the benefit of priority from U.S. Provisional Patent Application Ser. No. 61/613,517 filed March 21, 2012.

Field of the Invention

[0002] Embodiments of the present invention relate to a gasoline composition and its use, particularly, in combustion engines.

Background of the Invention

[0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present invention. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present invention. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of any prior art.

[0004] Spark initiated internal combustion gasoline engines require fuel of a minimum octane level which depends upon the design of the engine. Petroleum refineries are constantly faced with the challenge of continually improving their products to meet increasingly severe governmental efficiency and emission requirements, and consumers' desires for enhanced performance. For example, in producing a fuel suitable for use in an internal combustion engine, petroleum producers blend a plurality of hydrocarbon containing streams to produce a product that will meet governmental combustion emission regulations and the engine manufacturers performance fuel criteria, such as research octane number (RON), motor octane number (MON), and/or the road index (or octane rating) which is the average of RON and MON.

[0005] A commonly used measure of a gasoline's ability to burn without knocking is its octane number. Octane numbers compare a gasoline's tendency to knock against the tendency of a blend of heptane and isooctane to knock. Gasolines that match a blend of 87% isooctane and 13% heptane are given an octane number of 87. There are three ways of reporting octane numbers. Measurements made at high speed and high temperatures with variable ignition timing to stress the fuel's knock resistance are reported as motor octane numbers. Measurements taken under relatively mild engine conditions with variable compression ratio are known as research octane numbers. The road-index octane numbers reported on gasoline pumps are an average of these two.

[0006] Similarly, engine manufacturers conventionally design spark ignition type internal combustion engines around the properties of the fuel. For example, engine manufacturers endeavor to inhibit to the maximum extent possible the phenomenon of auto- ignition which typically results in knocking and, potentially engine damage, when a fuel with insufficient knock- resistance is combusted in the engine.

[0007] Under typical driving situations, engines operate under a wide range of conditions depending on many factors including ambient conditions (air temperature, humidity, etc.), vehicle load, speed, rate of acceleration, and the like. Fuel blenders have to design products which perform well under such diverse conditions. This naturally requires compromise, as oftentimes fuel properties or engine parameters that are desirable under certain speed/load conditions prove detrimental to overall performance at other speed/load conditions. It is desirable to that will perform well in modern gasoline engines.

[0008] Higher octane ratings correlate to higher activation energies (the amount of applied energy required to initiate combustion). Since higher octane fuels have higher activation energy requirements, it is less likely that a given compression will cause uncontrolled ignition (autoignition or detonation). A fuel with a higher octane rating can be burnt in an engine with a high compression ratio without causing detonation. Compression is directly related to power and to thermodynamic efficiency so engines that require a higher octane fuel usually develop more motive power and therefore do more work in relation to the calorific value of the fuel (BTU) being used. Power output is a function of the properties of the fuel used, as well as the design of the engine itself, and is related to octane rating of the fuel. Power is limited by the maximum amount of fuel-air mixture that can be brought into the combustion chamber. When the throttle is partly open, only a small fraction of the total available power is produced because the manifold is operating at pressures far below that of the external atmosphere (depression). In this case, the octane requirement is far lower than when the throttle is opened fully and the manifold pressure increases to almost that of the external atmosphere, or higher in the case of forced induction engines (See supercharged or turbocharged engines).

[0009] Many high-performance engines are designed to operate with a high maximum compression, and thus demand fuels of higher octane. A common misconception is that power output or fuel efficiency can be improved by burning fuel of higher octane than that specified by the engine manufacturer. The power output of an engine depends in part on the energy density of the fuel being burnt. Fuels of different octane ratings may have similar densities, but because switching to a higher octane fuel does not add more hydrocarbon content or oxygen, the engine cannot develop more power.

[0010] However, burning fuel with a lower octane rating than that for which the engine is designed often results in a reduction of power output and efficiency. Many modern engines are equipped with a knock sensor which sends a signal to the engine control unit, which in turn retards the ignition timing when detonation is detected. Retarding the ignition timing reduces the tendency of the fuel- air mixture to detonate, but also reduces power output and fuel efficiency. Because of this, under conditions of high load and high temperature, a given engine may have a more consistent power output with a higher octane fuel, as such fuels are less prone to detonation.

[0011] Another method of defining the octane quality of fuels is by the Octane Index (OI) as defined according to equation 1.

$$OI = (1\text{-}K)RON + KMON = RON - KS \qquad \text{(equation 1)}$$

where S = RON - MON

[0012] S is also known as the sensitivity of the fuel. K is a constant for a given engine, based on its operating conditions as described in Kalghatgi, G.T., "Fuel anti- knock quality- Part I. Engine Studies", SAE Paper # 2001- 01- 3584, SAE Trans., Journal of Fuels and Lubricants, Vol. 110, 2001; and Kalghatgi, G.T., "Fuel anti- knock quality- Part II. Vehicle Studies- how relevant is Motor Octane Number (MON) in modern engines?", SAE Paper # 2001- 01- 3585, SAE Trans., Journal of Fuels and Lubricants, Vol. 110, 2001.

[0013] Modern engines tend to operate with K values that are negative, which results in a decreased dependence on MON. Kalghatgi articles explain that fuels with high sensitivity actually possess a greater OI, and therefore increased knock resistance. The increased octane index in turn, provides greater power and acceleration.

Summary of Embodiments of the Invention

[0014] Accordingly, it is desirable to have a fuel composition with a high sensitivity with the same or significantly similar octane number. Embodiments of the present invention provide such a fuel composition.

[0015] In accordance with certain of its aspects, one embodiment of the present invention provides a gasoline composition comprising (a) a major amount of a mixture of hydrocarbons in the gasoline boiling range and (b) a minor amount of alpha-terpinene.

[0016] According to certain other aspects of the invention, there is provided a method for operating a spark ignition engine comprising: (a) providing to the engine a gasoline composition containing (i) a major amount of a mixture of hydrocarbons in the gasoline boiling range and (ii) a minor amount of alpha-terpinene, and (b) burning the gasoline composition in the engine.

[0017] In one embodiment, the alpha-terpinene is present in an amount from 0.01% by weight to 10% by weight base on the total weight of the gasoline composition. In another embodiment, the alpha-terpinene is present in an amount from 0.5% by weight to 5% by weight base on the total weight of the gasoline composition. In yet another embodiment, the alpha-terpinene is present in an amount from 0.5% by weight to 3% by weight base on the total weight of the gasoline composition.

[0018] In one embodiment, the gasoline composition has an Octane Index defined as (RON + MON)/2 of at least 80. In another embodiment, the gasoline composition further comprises at least one gasoline additive. In one embodiment, the gasoline additive comprises a detergent additive. In one embodiment, the detergent additive has a treat rate in a range of from 0.007 weight percent to 0.76 weight percent based on the final fuel composition.

[0019] In one embodiment, the mixture of hydrocarbons in the gasoline boiling range comprises a saturated hydrocarbon content ranging from 40% to 80% by volume, an olefinic hydrocarbon content from 0% to 30% by volume and an aromatic hydrocarbon content from 10% to 60% by volume. In another embodiment, the mixture of hydrocarbons in the gasoline boiling range is present in an amount of at least 50% v/v.

[0020] Other features of embodiments of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

Brief Description of the Drawings

[0021] Embodiments of the invention may be better understood by reference to the drawing in combination with the detailed description of specific embodiments presented herein, which are exemplary and not intended to be limiting.

FIG. 1 demonstrates the effect of alpha-terpinene to 83 octane fuel from Examples 2 - Example 4 according to certain aspects of the invention.

FIG. 2 represents the effect of alpha-terpinene on fuel sensitivity from Examples 2 - Example 4 according to certain aspects of the invention

Detailed Description of Preferred Embodiments of the Invention

[0022] Embodiments of a blended fuel composition according to aspects of the invention increase the sensitivity of the fuel without significantly altering the octane number. Fuel sensitivity is increased by increasing the delta between RON and MON. It has been found that fuels with high sensitivity perform better in modem gasoline engines.

[0023] Modern engines have been found to exhibit performance benefits when operated using high sensitivity fuels up to the octane requirement of the given engine. This is due to the value of K becoming increasingly more negative. Future engine developments such as downsizing and turbocharging are expected to make K increasingly more negative as well. This would result in the need for fuels with greater sensitivity, while retaining the same average octane value (R+M/2) to allow the engine to operate at optimum performance.

[0024] Although increasing the octane index of a fuel cannot improve an engine's performance when the octane requirement of the engine is satisfied, there are typically many conditions where the fuel does not meet the octane requirement of the engine, such as under strong acceleration. At these times, a knock sensor normally retards the ignition timing to prevent knocking from occurring. During these periods, the engine is not operating at optimum conditions. Therefore, by increasing the sensitivity, these periods of non-optimum performance may be reduced.

[0025] In one embodiment, the gasoline composition is lead- free and comprises alpha- terpinene. The terpinenes are a group of isomeric hydrocarbons that are classified as terpenes. They each have the same molecular formula and carbon framework, but they differ in the position of carbon- carbon double bonds. For use in a gasoline composition according to aspects of the invention, alpha- terpinene can be obtained by any suitable method. It may be synthetic or naturally occurring. In one embodiment, the alpha- terpinene or α- Terpinene also known as 1- methyl- 4- isopropyl- 1, 3- cyclohexadiene) is available from TCI America, and MP Biomedicals. By way of example, in one embodiment, α- Terpinene is a natural product that has been isolated from cardamom and marjoram oils, and from other natural sources. In another embodiment, biosynthesis of α- terpinene may occur via the mevalonate pathway because its starting reactant, dimethylallyl pyrophosphate (DMAPP), is derived from mevalonic acid. Geranyl pyrophosphate (GPP) is produced from the reaction of a resonance- stable allylic cation, formed from the loss of the diphosphate group from DMAPP, and isopentenyl pyrophosphate (IPP), and a subsequent loss of proton. GPP then loses the diphosphate group to form geranyl cation. The reintroduction of the diphosphate group to the cation produces linalyl pyrophosphate (LPP) . LPP then forms a cation by losing its diphosphate group. Cyclization is then completed yielding the menthyl/ α- terpinyl cation. A 1, 2- hydride shift via a Wagner- Meerwein rearrangement produces the terpinen- 4- yl cation. Loss of a hydrogen from this cation provides α- terpinene.

[0026] In a preferred embodiment, the gasoline composition comprises a major amount of a mixture of hydrocarbons in the gasoline boiling range and a minor amount of α-terpinene As used herein for α-terpinene component, the term "minor amount" means less than 10% by weight of the total gasoline composition, preferably less than 5% by weight of the total fuel composition and more preferably less than 3% by weight of the total fuel composition, such as 1% by weight, 1.5% by weight, 2% by weight, or 2.5% by weight. Further, the term "minor amount" also refers to at least some amount, preferably at least 0.001%, more preferably at least 0.5% by weight of the total gasoline composition.

[0027] In one embodiment, a mixture of hydrocarbons in the gasoline boiling range comprises a liquid hydrocarbon distillate fuel component, or mixture of such components, containing hydrocarbons which boil in the range from 0 °C to 250°C (ASTM D86 or EN ISO 3405) or from 20 °C or 25 °C to 200 °C or 230°C. The optimal boiling ranges and distillation curves for such base fuels will typically vary according to the conditions of their intended use, for example the climate, the season and any applicable local regulatory standards or consumer preferences.

[0028] The hydrocarbon fuel component(s) may be obtained from any suitable source. They may for example be derived from petroleum, coal tar, natural gas or wood, in particular petroleum. Alternatively, they may be synthetic products such as from a Fischer-Tropsch synthesis. Conveniently, they may be derived in any known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons, hydrocracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

[0029] In a preferred embodiment, the hydrocarbon fuel component(s) comprise components selected from one or more of the following groups: saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and oxygenated hydrocarbons. In a particular embodiment, a mixture of hydrocarbons in the gasoline boiling range comprises a mixture of saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and, optionally, oxygenated hydrocarbons. In a preferred embodiment, a mixture of hydrocarbons in the gasoline boiling range gasoline mixtures comprises a saturated hydrocarbon content ranging from 40% to 80% by volume, an olefinic hydrocarbon content from 0% to 30% by volume and an aromatic hydrocarbon content from 10% to 60% by volume. In one embodiment, the base fuel is derived from straight run gasoline, polymer gasoline, natural gasoline, dimer and trimerized olefins, synthetically produced aromatic hydrocarbon mixtures, or from catalytically cracked or thermally cracked petroleum stocks, and mixtures of these. The hydrocarbon composition and octane level of the base fuel are not critical. In a specific embodiment, the octane level, (RON + MON)/2, will generally be above 80. Any conventional motor fuel base can be employed in embodiments of the present invention. For example, in certain embodiments, hydrocarbons in the gasoline can be replaced by up to a substantial amount of conventional alcohols or ethers, conventionally known for use in fuels. In one embodiment, the base fuels are desirably substantially free of water since water could impede a smooth combustion.

[0030] The gasoline base fuel, or a mixture of hydrocarbons in the gasoline boiling range, represents the major proportion of a fuel composition of embodiments of the invention. The term "major amount" is used herein because the amount of hydrocarbons in the gasoline boiling range is often 50 weight or volume percent or more. For instance, in one embodiment, the concentration of the gasoline base fuel is 50% v/v or greater. In one embodiment, the concentration of the base fuel is up to 99.5% v/v, preferably up to 99.9, and more preferably up to 99.95% v/v or 99.5% v/v. In another embodiment, the concentration is up to 60% v/v, 65% v/v, 70% v/v, 80% v/v, or 90% v/v. In yet another embodiment, the concentration is up to 95% v/v, 98% v/v, or 99% v/v.

[0031] In a preferred embodiment, the fuel composition is not an emulsion. In such an embodiment, the gasoline base fuel and the alpha-terpinene are miscible and do not separate into layers overtime.

[0032] The hydrocarbon fuel mixture of an embodiment is substantially lead- free, but may contain minor amounts of blending agents such as methanol, ethanol, ethyl tertiary butyl ether, methyl tertiary butyl ether, tert- amyl methyl ether and the like, at from 0.1% by volume to 15% by volume of the base fuel, although larger amounts may be utilized. In one embodiment, the fuel can also contain one or more conventional additives including antioxidants such as phenolics, e.g., 2, 6- di- tertbutylphenol or phenylenediamines, e.g., N, N'- di- sec- butyl- p- phenylenediamine, dyes, metal deactivators, dehazers such as polyester- type ethoxylated alkylphenol- formaldehyde resins. Corrosion inhibitors, such as a polyhydric alcohol ester of a succinic acid derivative having on at least one of its alpha- carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 50 carbon atoms, for example, pentaerythritol diester of polyisobutylene- substituted succinic acid, the polyisobutylene group having an average molecular weight of 950, in an amount from 1 ppm (parts per million) by weight to 1000 ppm by weight, may also be present.

[0033] In one embodiment, an effective amount of alpha-terpinene is introduced into the combustion zone of the engine in a variety of ways to improve fuel sensitivity. As mentioned, a preferred method is to add a minor amount of alpha-terpinene to the fuel.

[0034] The fuel compositions of embodiments of the present invention may also contain one or more additional additive components. When detergents are utilized, the fuel composition will comprise a mixture of a major amount of hydrocarbons in the gasoline boiling range as described hereinbefore, a minor amount of alpha-terpinene as described hereinbefore and a minor amount of one or more detergents. As noted above, a carrier as described hereinbefore may also be included. As used herein, for the additive components, the term "minor amount" means less than 10% by weight of the total fuel composition, preferably less than 1% by weight of the total fuel composition and more preferably less than 0.1% by weight of the total fuel composition. However, the term "minor amount" will contain at least some amount, preferably at least 0.001%, more preferably at least 0.01% by weight of the total fuel composition.

[0035] In a preferred embodiment, if present, the one or more detergents are added directly to the hydrocarbons, blended with one or more carriers, blended with alpha-terpinene, or blended with one or more carriers before being added to the hydrocarbon. In certain embodiments, alpha-terpinene can be added at the refinery, at a terminal, at retail, or by the consumer.

[0036] In one embodiment, the treat rate of the fuel additive detergent packages that contain one or more detergents in the final fuel composition is generally in the range of from 0.007 weight percent to 0.76 weight percent based on the final fuel composition. The fuel additive detergent package may contain one or more detergents, dehazer, corrosion inhibitor and solvent. In addition a carrier fluidizer may sometimes be added to help in preventing intake valve sticking at low temperature.

[0037] In one embodiment, a spark ignition engine can be operated with greater octane index by (a) providing a gasoline composition containing (i) a major amount of a mixture of hydrocarbons in the gasoline boiling range and (ii) a minor amount of alpha-terpinene to said engine, and (b) burning in said engine such gasoline composition as described above.

[0038] While embodiments of the invention are susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of examples herein described in detail. It should be understood, that the detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims. Aspects present invention will be illustrated by the following illustrative embodiments, which are provided for illustration only and are not to be construed as limiting the claimed invention in any way.

Examples

Octane Test Methods

[0039] In the following examples, the Research Octane Number (RON) (ASTM D2699) and Motor Octane Number (MON) (ASTM D2700) will be the techniques used in determining the (RON + MON)/2 octane improvement of the fuel. The RON and MON of a spark-ignition engine fuel is determined using a standard test engine and operating conditions to compare its knock characteristic with those of primary reference fuel blends of known octane number. Compression ratio and fuel-air ratio are adjusted to produce standard knock intensity for the sample fuel, as measured by a specific electronic detonation meter instrument system. A standard knock intensity guide table relates engine compression ratio to octane number level for this specific method. The specific procedure for the RON can be found in ASTM D-2699 and the MON can be found in ASTM D-2700.

[0040] Table I contains the engine conditions necessary in determine the RON and MON of a fuel.

Table I

RON and MON Test Conditions		
Test Engine Conditions	Research Octane Number	Motor Octane Number
Test Method	ASTM D-2699-92	ASTM D-2700-92
Engine	Cooperative Fuels Research (CFR) Engine	Cooperative Fuels Research (CFR) Engine
Engine RPM	600 RPM	900 RPM
Intake Air Temperature	Varies with Barometric Pressure (eq 88Kpa=19.4°C, 101.6kPa = 52.2°C)	38°C
Intake Air Humidity	3.56-7.12 g H2O/kg dry air	3.56-7.12 g H2O/kg dry air
Intake mixture temperature	not specified	149°C
Coolant Temperature	100°C	100°C
Oil Temperature	57°C	57°C
Ignition Advance-fixed	13 degrees BTDC	Varies with compression ratio (eq 14-26 degrees BTDC)
Carburetor Venture	Set according to engine altitude (eq 0-500 m=14.3, 500-1000 m=15.1 mm)	14.3 mm

Base Fuel I

[0041] The base fuel used in the test for Example 1 and Comparative Examples 1 and 2 was an 87 (RON + MON)/2 regular base fuel. The base fuel physical properties can be found in Table II.

Table II

87 Octane Base Fuel Physical Properties	
API Gravity	61.9
RVP	13.45
Distillation, (°F)	
IBP	87.1
10%	107.3
20%	123.2
30%	141.0
40%	161.5

(continued)

87 Octane Base Fuel Physical Properties	
50%	185.9
60%	218.1
70%	260.2
80%	308.6
90%	349.0
95%	379.3
End Pt.	434.7
% Recovered	97.2
% Residue	1.1
% Loss	1.7
FIA (vol%)	
Aromatic	28
Olefins	12.7
Saturates	59.3
Gum (mg/100ml)	
Unwashed	3
MON	81.9
RON	92
(RON+MON)/2	87
Oxygenates	None

Base Fuel II

[0042] The base fuel used in the test for Examples 2-5 was an 83 (RON + MON)/2 regular base fuel. The base fuel physical properties can be found in Table III.

Table III

83 Octane Base Fuel Physical Properties		
	Method	Results
Sulfur, ppm	D-5453	61
API Gravity		58.6
RVP		9.26
Distillation (°F)	D86	
IBP		99
10%		129.7
20%		149.9
30%		169.8
40%		189.1
50%		209.3
60%		233.6

(continued)

83 Octane Base Fuel Physical Properties		
	Method	Results
70%		262.2
80%		296.7
90%		336.3
95%		361.5
End Pt.		414.2
% Recovered		97.2
% Residue		1.1
% Loss		1.7
Aromatics (vol%)		27.5
Olefins (vol%)		7.8
Saturates (vol%)		64.6
Gum (mg/100 ml)	(ASTM D-384)	
Unwashed		3.5
Washed		<0.5
MON	(ASTM D-2700-4)	79.7
RON	(ASTM D-2699-04)	87.4
(RON+MON)/2		83.5
Oxygenate (vol%)		None

Examples 1 and Comparative Examples 1-2

[0043] The alpha terpinene and as comparative examples gamma-terpinene or 1,4-cyclohexadiene were added to a gallon of 87 Octane base fuel at a treat rate of 0.4 moles per liter of fuel according to Table IV. The individual additives were submitted for RON and MON testing in triplicate.

Table IV

Example #	Additive	***Additive Amount*** (moles/L of fuel)
Comparative 1	Gamma-terpinene	0.4
Comparative 2	1,4-cyclohexadiene	0.4
1	Alpha-terpinene	0.4

[0044] The change in RON, change in MON and the sensitivity change (RON-MON) from the base fuel were as follows:

Table V

	ΔRON	ΔMON	Sensitivity Δ (RON-MON)	OI
alpha-terpinene	1.1	-1.3	2.4	86.5
Gamma-terpinene	0	-3.5	3.5	85.0
1,4-cyclohexadiene	0.6	-0.9	1.5	86.5

Where ΔRON is defined as the difference in RON values obtained for the basefuel and the basefuel + additive. The value of ΔMON is defined similarly. The Octane Index (OI) value is defined as (RON+MON)/2

[0045] As can be seen from Table IV, the alpha and gamma isomers yield different results. The sensitivity of the fuel containing alpha-terpinene has increased without significant change to the octane rating (octane index); whereas the gamma-terpinene containing fuel has increased sensitivity, but at the cost of lower octane index. The resulting decrease in octane index will reduce the performance of the engine, as the fuel will exhibit reduced resistance to engine knock.

[0046] 1, 4- cyclohexadiene is an example of the "root" chemical class that also produced a different result, it does not appreciably reduce the overall octane number of the fuel, but it does exhibit a much smaller sensitivity change. The alpha- terpinene raises the RON as much as it lowers the MON, thus creating greater fuel sensitivity without altering the octane index number.

Examples 2-5

[0047] The alpha terpinene was added to a gallon of 83 Octane base fuel at a treat rate according to Table VI. The individual additives were submitted for RON and MON testing in triplicate.

Table VI

Example #	Additive	Additive Amount (wt%)
2	Alpha-terpinene	0.0
3	Alpha-terpinene	0.5
4	Alpha-terpinene	1.0
5	Alpha-terpinene	2.0

[0048] FIGS. 1 and 2 show graphs of the change in Octane Boost (Octane Index) and the sensitivity change (RON-MON) from the base fuel (denoted as dRON-dMON). In particular, the graph in FIG. 1 details effect of the alpha-terpinene addition to octane boost of the fuel. The graph in FIG. 2 details the sensitivity effect of the alpha-terpinene addition to fuel.

[0049] The results in FIG. 1 show that the ability of alpha-terpinene to increase the sensitivity of a fuel increases with concentration. This effect is not unexpected, as increasing the amount of additive should result in an increased effect. It is unexpected, however, to observe the negative impact on MON at a 1% treat rate. In certain embodiments, this concentration is ideal for use of alpha-terpinene as a sensitivity enhancer, because the RON increase is cancelled by the MON decrease, resulting in an overall effect on (RON + MON)/2 of zero. Similarly, the data in FIG. 1 shows that alpha-terpinene may be added at varying concentrations to alter the overall effect on the basefuel. At 0.5%, a small effect on sensitivity can be found, with a small increase in octane. At 1.0%, a large effect on sensitivity can be found, with no impact on octane, and at 2.0%, a large effect is observed, along with a positive increase on fuel octane.

[0050] FIG. 2 examines only the effect on fuel sensitivity when alpha-terpinene is added. As shown, with 0.5% alpha-terpinene added, the fuel sensitivity increases by about 0.6. With 1.0% alpha-terpinene added, the fuel sensitivity increases by about 1.1. With 2.0% alpha-terpinene added, the fuel sensitivity increases by about 1.4. FIG. 2 shows that after 1.0% alpha-terpinene is added, the benefit begins to reduce. However, even after 2.0% of alpha-terpinene is added, there continues to be an observed benefit. Therefore, in certain embodiments, it is important to note the change in responsiveness when alpha-terpinene is added at concentrations below 1.0% compared to concentrations above 1.0%.

[0051] Further modifications and alternative embodiments of various aspects of the invention will be apparent to those skilled in the art in view of this description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements described herein without departing from the spirit and scope of the invention as described in the following claims.

Claims

1. A gasoline composition comprising (a) a major amount of a mixture of hydrocarbons in the gasoline boiling range and (b) a minor amount of alpha-terpinene.

2. The gasoline composition according to claim 1 wherein the alpha-terpinene is present in an amount from 0.01% by weight to 10% by weight base on the total weight of the gasoline composition.

3. The gasoline composition according to any preceding claim having an Octane Index defined as (RON + MON)/2 of at least 80.

4. The gasoline composition according to any preceding claim further comprising at least one gasoline additive.

5. The gasoline composition according to claim 4 wherein the at least one gasoline additive comprises a detergent additive.

6. The gasoline composition according to claim 5 wherein the detergent additive has a treat rate in a range of from 0.007 weight percent to 0.76 weight percent based on the final fuel composition.

7. The gasoline composition according to any preceding claim wherein the mixture of hydrocarbons in the gasoline boiling range comprises a saturated hydrocarbon content ranging from 40% to 80% by volume, an olefinic hydrocarbon content from 0% to 30% by volume and an aromatic hydrocarbon content from 10% to 60% by volume.

8. A method for operating a spark ignition engine comprising: (a) providing to said engine a gasoline composition containing (i) a major amount of a mixture of hydrocarbons in the gasoline boiling range and (ii) a minor amount of alpha-terpinene, and (b) burning said gasoline composition in said engine.

9. The method according to claim 8 wherein the alpha-terpinene is present in the gasoline composition an amount from 0.01% by weight to 10% by weight base on the total weight of the gasoline composition.

10. The method according to claim 8 or 9 wherein the gasoline composition has an average octane number (RON + MON)/2 of at least 80.

11. The method according to any of claims 8 - 10 wherein the gasoline composition further comprises at least one gasoline additive.

12. The method according to claim 11 wherein the at least one gasoline additive comprises a detergent additive.

13. The method according to claim 12 wherein the detergent additive has a treat rate in a range of from 0.007 weight percent to 0.76 weight percent based on the final fuel composition.

14. The method according to any of claims 8 - 13 wherein the mixture of hydrocarbons in the gasoline boiling range comprises a saturated hydrocarbon content ranging from 40% to 80% by volume, an olefinic hydrocarbon content from 0% to 30% by volume and an aromatic hydrocarbon content from 10% to 60% by volume.

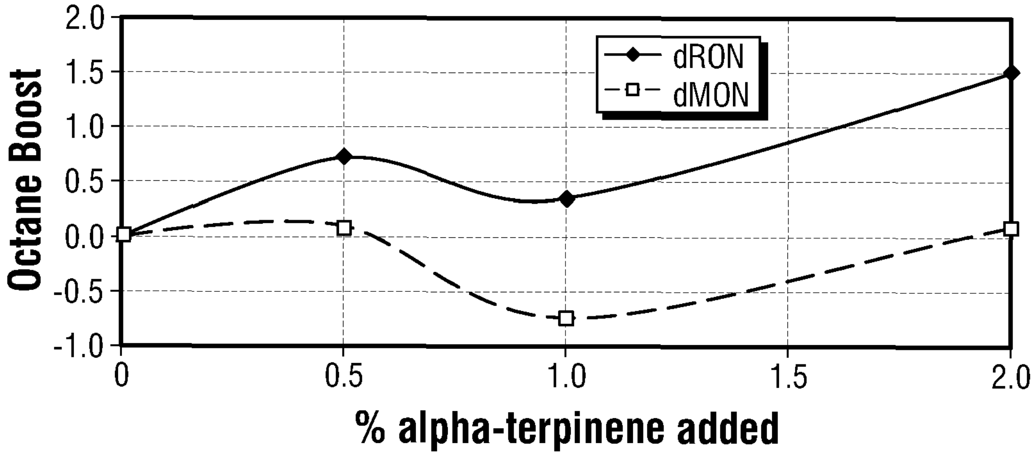
Octane Boost
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
0
0.5
1.0
1.5
2.0
% alpha-terpinene added
dRON
dMON

FIG. 1

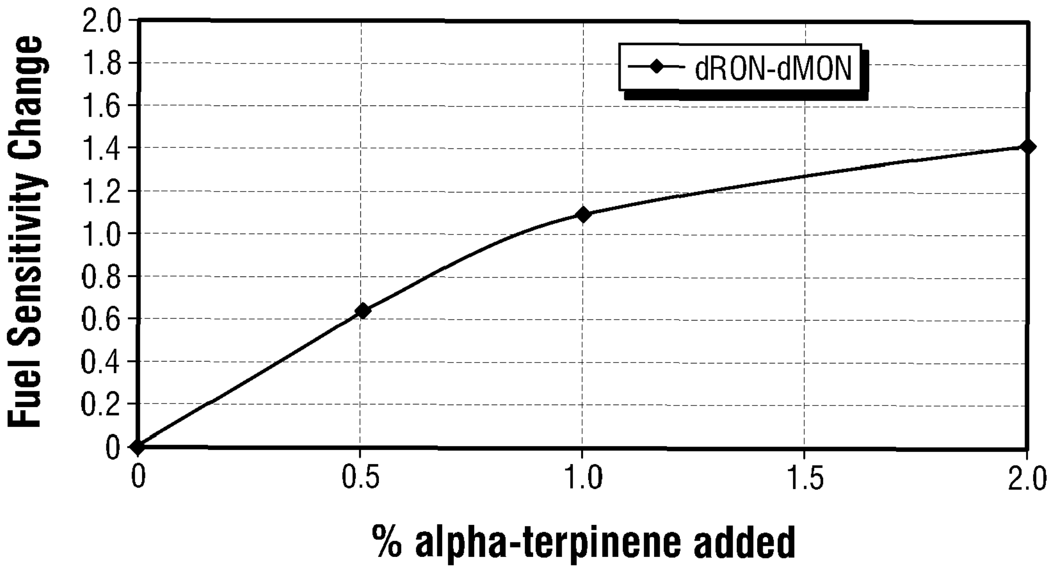
Fuel Sensitivity Change
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
0.5
1.0
1.5
2.0
% alpha-terpinene added
dRON-dMON

FIG. 2

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 13 16 0463

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 10 05 785 B (BATAAFSCHE PETROLEUM) 4 April 1957 (1957-04-04) * example 7 *	1-4,8-11	INV. C10L1/06 C10L1/16 C10L10/10
A	WO 2010/136436 A1 (SHELL INT RESEARCH [NL]; FELIX-MOORE ALLISON [GB]; LANGE JEAN-PAUL [NL) 2 December 2010 (2010-12-02) * page 13, line 14 - line 27 * * claim 1 *	1-14	
A	US 2011/308140 A1 (CRACKNELL ROGER FRANCIS [GB] ET AL) 22 December 2011 (2011-12-22) * paragraph [0031]; claims 1,3 *	1-14	
A	WO 2008/071628 A1 (SHELL INT RESEARCH [NL]; CRACKNELL ROGER FRANCIS [GB]) 19 June 2008 (2008-06-19) * claim 1 *	1-14	

TECHNICAL FIELDS SEARCHED (IPC)

C10L

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	28 May 2013	Klaes, Daphne

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 13 16 0463

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-05-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1005785 B	04-04-1957	BE 513666 A	28-05-2013
		DE 1005785 B	04-04-1957
WO 2010136436 A1	02-12-2010	CA 2762420 A1	02-12-2010
		EP 2435541 A1	04-04-2012
		JP 2012528218 A	12-11-2012
		US 2011041792 A1	24-02-2011
		WO 2010136436 A1	02-12-2010
US 2011308140 A1	22-12-2011	AU 2011271224 A1	10-01-2013
		CN 103025853 A	03-04-2013
		EP 2582777 A1	24-04-2013
		US 2011308140 A1	22-12-2011
		WO 2011163122 A1	29-12-2011
WO 2008071628 A1	19-06-2008	EP 2126011 A1	02-12-2009
		WO 2008071628 A1	19-06-2008

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 61613517 A **[0001]**

Non-patent literature cited in the description

- **KALGHATGI, G.T.** Fuel anti-knock quality - Part I. Engine Studies. *SAE Paper # 2001-01-3584, SAE Trans., Journal of Fuels and Lubricants,* 2001, vol. 110 **[0012]**
- **KALGHATGI, G.T.** Fuel anti-knock quality - Part II. Vehicle Studies - how relevant is Motor Octane Number (MON) in modern engines?. *SAE Paper # 2001-01-3585, SAE Trans., Journal of Fuels and Lubricants,* 2001, vol. 110 **[0012]**