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Description

[0001] This invention relates to a fuel composition, in particular a gasoline composition for use in motor vehicles.

[0002] For many years manufacturers of spark ignition combustion engines have been striving for higher efficiency to make optimum use of the hydrocarbon fuels. But such engines require gasolines of higher octane number, which has been achieved in particular by addition of organo lead additives, and latterly with the advent of unleaded gasolines, by addition of MTBE. But combustion of any gasoline gives rise to emissions in the exhaust gases, e.g. of carbon dioxide, carbon monoxide, nitrogen oxides (NOx) and toxic hydrocarbons and such emissions are undesirable.

[0003] US4059646 relates to a method for the production of triptane and states that "Because of the superiority of triptane as a blending agent for high-grade gasoline, a process for producing triptane, as well as other hydrocarbons, from methanol or dimethyl ether could have great economic importance." It also states "The triptane product may be separated from the other reaction products before use, or the reaction products mixture may be used directly as a fuel blending agent".

[0004] GB2106933 relates to additives for improving the octane rating of liquid motor fuels which is said may comprise an aniline base having added thereto toluene in a proportion of between 1 and 25 percent by weight and triptane, xylene or mixtures thereof in a proportion of between 1 and 25 percent by weight.

[0005] Motor gasolines have been discovered having high Octane Number but producing low emissions on combustion.

[0006] The present invention provides an unleaded blend composition having a Motor Octane Number (MON) of at least 80 comprising component (a) at least 5% or preferably at least 8 or 10% (by volume of the total composition) of at least one hydrocarbon having the following formula I

$$R\text{-}CH_2\text{-}CH(CH_3)\text{-}C(CH_3)_2\text{-}CH_3 \qquad I$$

wherein R is hydrogen or methyl

and component (b) at least one saturated liquid aliphatic hydrocarbon having 4 to 12, 4-10 such as 5-10 e.g. 5 - 8 carbon atoms. In another embodiment component (b) is contained in at least one of isomerate, alkylate, straight run gasoline, light reformate, light hydrocrackate and aviation alkylate. Preferably the composition comprises at least one of an olefin (e.g. in amount of 1-30%) and/or at least one aromatic hydrocarbon (e.g. in amount of 1-50%, especially 3-28%) and/or less than 5% of benzene. The composition may preferably comprise 10-40% triptane, less than 5% benzene and have a Reid Vapour Pressure at 37.8°C measured according to ASTMD323 of 30-120kPa. The composition is usually an unleaded motor gasoline base blend composition.

[0007] The present invention also provides an unleaded formulated motor gasoline which comprises said base composition and at least one motor gasoline additive.

[0008] If R is hydrogen the hydrocarbon is triptane. If R is methyl the hydrocarbon is 2,2,3 trimethylpentane. Especially preferred is triptane. Triptane and 2,2,3 trimethylpentane may be used individually or in combination with each other, for example, in a weight ratio of 10:90 - 90:10, preferably, 30:70 - 70:30.

[0009] The hydrocarbon of formula I, preferably triptane may be present in amount of 5-95% or 8-90% such as 10-90%, or 15-65% e.g. 10-40% such as 20-35% by volume or 40-90% such as 40-55% or 55-80% or 8-35% such as 8-20% by volume. Unless otherwise stated all percentages in this specification are by volume, and disclosures of a number of ranges of amounts in the composition or gasoline for 2 or more ingredients includes disclosures of all sub-combinations of all the ranges with all the ingredients.

[0010] Triptane or 2,2,3 trimethylpentane may be used in a purity of at least 95% but is preferably used as part of a hydrocarbon mixture e.g. with at least 50% of the compound of formula I. This mixture may be obtained for example by alkylation of an iso alkane e.g. reaction of propene and iso butane or obtained via distillation of the product of a catalytic cracking reaction to give a C_4 fraction containing olefin and hydrocarbon, alkylation to produce a C_{4-9} especially a C_{6-9} fraction which is distilled to give a predominantly C_8 fraction, which usually contains trimethyl pentanes including 2,2,3 trimethyl pentane and/or 2,3,3 trimethyl pentane. To produce triptane this fraction can be demethylated to give a crude product comprising at least 5% of triptane, which can be distilled to increase the triptane content in the mixture; such a distillate may comprise at least 10% or 20% of triptane and 2,2,3 trimethylpentane but especially at least 50% e.g. 50-90% the rest being predominantly of other aliphatic C7 and C8 hydrocarbons e.g. in amount 10-50% by volume. Triptane may be prepared generally as described in Rec. Trav. Chim. 1939, Vol.58 pp 347-348 by J.P.Wibaut et al, which involves reaction of pinacolone with methyl magnesium iodide followed by dehydration (e.g. with sulphuric acid) to form triptene, which is hydrogenated e.g. by catalytic hydrogenation to triptane. Alternatively triptane and 2,2,3 trimethylpentane may be used in any commercially available form.

[0011] The invention will be further described with triptane exemplifying the compound of formula I but 2,2,3 trimethylpentane may be used instead or as well.

[0012] The gasoline composition also contains as component (b) at least one liquid saturated hydrocarbon of 5-10 carbons especially predominantly branched chain C_7 or C_8 compounds e.g. iso C_7 or iso C_8. This hydrocarbon may be

substantially pure e.g. n-heptane, isooctane or isopentane or a mixture e.g. a distillation product or a reaction product from a refinery reaction e.g. alkylate. The hydrocarbon may have a Motor Octane Number (MON) of 0-60 but preferably has a MON value of 60-96 such as isomerate (bp 25-80°C). Research Octane Number RON may be 80-105 e.g. 95-105, while the ROAD value (average of MON and RON) may be 60-100.

[0013] Component (b) may comprise a hydrocarbon component having boiling point (preferably a final boiling point) higher than, preferably one boiling at least 20°C more than, the compound of formula I e.g. triptane such as 20-60°C more than triptane but less than 225°C e.g. less than 170°C and usually is of Motor Octane Number of at least 92 e.g. 92-100; such components are usually alkanes of 7-10 carbons especially 7 or 8 carbons, and in particular have at least one branch in their alkyl chain, in particular 1-3 branches, and preferably on an internal carbon atom and especially contain at least one $-C(CH_3)_2-$ group.

[0014] The volume amount of the component (b) in total (or the volume amount of mixtures comprising component (b), such as the total of each of the following (if present) (i)-(iv)) (i) catalytic reformate, (ii) heavy catalytic cracked spirit, (iii) light catalytic cracked spirit and (iv) straight run gasoline in the composition is usually 10-80% e.g. 25-70%, 40-65% or 20-40%, the higher percentages being usually used with lower percentages of component (a).

[0015] Component (b) may be a mixture of the liquid saturated hydrocarbons e.g. a distillation product e.g. naphtha or straight run gasoline or a reaction product from a refinery reaction e.g. alkylate including aviation alkylate (bp 30-190°C) isomerate (bp 25-80°C), light reformate (bp 20-79°C) or light hydrocrackate. The mixture may contain at least 60% or at least 70% w/w e.g. 60-95 or 70-90% w/w liquid saturated aliphatic hydrocarbon.

Volume amounts in the composition of the invention of the component (b) mixtures (primarily saturated liquid aliphatic hydrocarbon fractions e.g. the total of isomerate, alkylate, naphtha and straight run gasoline (in each case (if any) present in the composition) may be 4-60%, such as 4-25% or preferably 10-55% such as 25-45%. Alkylate or straight run gasoline are preferably present, optionally together but preferably in the absence of the other, in particular in amount of 2-50% such as 10-45 e.g. 10-25%, 25-45% or 25-40%. The compositions of the invention may also comprise naphtha e.g. in volume amount of 0-25% such as 2-25%,10-25% or 2-10%.

[0016] The compositions may comprise a hydrocarbon component which is a saturated aliphatic hydrocarbon of 4-6 carbons and which is more volatile and has a lower boiling point (preferably a lower final boiling point) than the compound of Formula I in particular one boiling at least 30°C such as 30-60°C below that of triptane at atmospheric pressure, and especially is itself of Motor Octane Number greater than 88 in particular at least 90 e.g. 88-93 or 90-92. Examples of the hydrocarbon component include alkanes of 4 or 5 carbons in particular iso-pentane, which may be substantially pure or crude hydrocarbon fraction from alkylate or isomerate containing at least 30% e.g. 30-80% such as 50-70%, the main contaminant being up to 40% mono methyl pentanes and up to 50% dimethyl butanes. The hydrocarbon component may be an alkane of boiling point (at atmospheric pressure) 60-100°C less than that of triptane e.g. n and/or iso butane optionally in blends with the C_5 alkane of 99.5:0.5 to 0.5:99.5, e.g. 88:12 to 75:25. n Butane alone or mixed with isopentane is preferred, especially in the above proportions, and in particular with a volume amount of butane in the composition of up to 20% such as 1-15% e.g. 1-8, 3-8 or 8-15%.

[0017] Cycloaliphatic hydrocarbons e.g. of 5-7 carbons such as cyclopentane or cyclohexane may be present but usually in amounts of less than 15% of the total e.g. 1-10%.

[0018] Volume amounts in the composition of the total of isomerate, alkylate, naphtha, straight run gasoline, 4-6 carbon liquid aliphatic hydrocarbon (as defined above) and cycloaliphatic hydrocarbon (in each case if present) may be 5-60%, such as 8-25%, 15-55% such as 30-50%.

[0019] The gasoline compositions of the invention also preferably contain at least one olefin, (in particular with one double bond per molecule) which is a liquid alkene of 5-10 e.g. 6-8 carbons, such as a linear or branched alkene e.g. pentene, isopentene hexene, isohexene or heptene or 2 methyl 2 pentene, or a mixture comprising alkenes which may be made by cracking e.g. catalytically or thermally cracking a residue from crude oil, e.g. atmospheric or vacuum residue; the mixture may be heavy or light catalytically cracked spirit (or a mixture there of). The cracking may be steam assisted. Other examples of olefin containing mixtures are "C6 bisomer", catalytic polymerate, and dimate. The olefinic mixtures usually contain at least 10% w/w olefins, such as at least 40% such as 40-80% w/w. Preferred mixtures are (xi) steam cracked spirit (xii) catalytically cracked spirit (xiii) C6 bisomer and (xiv) catalytic polymerate, though the optionally cracked catalytically spirits are most advantageous. Amounts in the total composition of the olefinic mixtures especially the sum of (xi) - (xiv) (if any present) maybe 0-55, e.g. 10-55 or 18-37 such as 23-35 or 20-55 such as 40-55% Amounts of (xi) and (xii) (if present) in total in the composition are preferably 18-55, such as 18-35, 18-30 or 35-55% (by volume).

[0020] The olefin or mixture of olefins usually has an MON value of 70-90, usually a RON value of 85-95 and a ROAD value of 80-92.

[0021] The volume amount of olefin(s) in total in the gasoline composition of the invention may be 0% or 0-30%, e.g. 0.1-30% such as 1-30% in particular 2-25, 5-30; (especially 3-10), 5-18.5, 5-18 or 10-20%. Preferably the composition contains at least 1% olefin and a maximum of 18% or especially a maximum of 14%, but may be substantially free of olefin.

[0022] The compositions may also contain at least one aromatic compound, preferably an alkyl aromatic compound such as toluene or o, m, or p xylene or a mixture thereof or a trimethyl benzene. The aromatics may have been added

as single compounds e.g. toluene, or may be added as an aromatics mixture containing at least 30% w/w aromatic compounds such as 30-100% especially 50-90%. Such mixtures may be made from catalytically reformed or cracked gasoline obtained from heavy naphtha. Example of such mixtures are (xxi) catalytic reformate and (xxii) heavy reformate. Amounts of the single compounds e.g. toluene in the composition may be 0-35%, such as 2-33% e.g. 10-33%, while amounts of the aromatics mixtures especially the total of the reformates (xxi) & (xxii) (if any) in the composition may be 0-50%, such as 1-33% e.g. 2-15% or 2-10% or 15-32% v/v, and total amount of reformates (xxi), (xxii) and added single compounds (e.g. toluene) may be 0-50% e.g. 0.5-20% or 5-40, such as 15-35 or 5-25% v/v.

[0023] The aromatics usually have a MON value of 90-110 e.g. 100-110 and a RON value of 100-120 such as 110-120 and a ROAD value of 95-110. The volume amount of aromatic compounds in the composition is usually 0% or 0-50% such as less than 40% or less than 28% or less than 20% such as 1-50%, 2-40%, 3-28%, 4-25%, 5-20% (especially 10-20%), 4-10% or 20-35% especially of toluene. The gasoline composition may also be substantially free of aromatic compound. Amounts of aromatic compounds of less than 42%, e.g. less than 35% or especially less than 30% are preferred. Preferably the amount of benzene is less than 5% preferably less than 1.5% or 1% e.g. 0.1-1% of the total volume or less than 0.1% of the total weight of the composition.

[0024] The compositions may also contain at least one oxygenate octane booster, usually an ether, usually of Motor Octane Number of at least 96-105 e.g. 98-103. The ether octane booster is usually a dialkyl ether, in particular an asymmetric one, preferably wherein each alkyl has 1-6 carbons, in particular one alkyl being a branched chain alkyl of 3-6 carbons in particular a tertiary alkyl especially of 4-6 carbons such as tert-butyl or tert-amyl, and with the other alkyl being of 1-6 e.g. 1-3 carbons, especially linear, such as methyl or ethyl. Examples of such oxygenates include methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether and methyl tertiary amyl ether. The oxygenate may also be an alcohol of 1-6 carbons e.g. ethanol.

[0025] The volume amount of the oxygenate may be 0 or 0-25% such as 1-25%, 2-20%, 2-10% or 5-20% especially 5-15%, but advantageously less than 3% such as 1-3% (especially of MTBE and/or ethanol). The oxygenate may also be substantially absent from the composition or gasoline of the invention.

[0026] Aromatic amines e.g. liquid ones such as aniline may be present if at all in amount of less than 5% by volume, and are preferably substantially absent e.g. less than 100ppm. The relative volume ratio of the amine to triptane is usually less than 3:1 e.g. less than 1:2.

[0027] The composition of the invention contains components (a) and (b), and the formulated unleaded gasoline also contains at least one motor gasoline additive, for example as listed in ASTM D-4814 the contents of which is herein incorporated by reference or specified by a regulatory body, e.g. US California Air Resources Board (CARB) or Environmental Protection Agency (EPA). These additives are distinct from the liquid fuel ingredients, such as MTBE. Such additives may be the lead free ones described in Gasoline and Diesel Fuel Additives, K Owen, Publ. By J.Wiley, Chichester, UK, 1989, Chapters 1 and 2, USP 3955938, EP 0233250 or EP 288296, the contents of which are herein incorporated by reference. The additives maybe pre-combustion or combustion additives. Examples of additives are antioxidants, such as one of the amino or phenolic type, corrosion inhibitors, anti-icing additives e.g. glycol ethers or alcohols, engine detergent additives such as ones of the succinic acid imide, polyalkylene amine or polyether amine type and anti-static additives such as ampholytic surface active agents, metal deactivators, such as one of thioamide type, surface ignition inhibitors such as organic phosphorus compounds, combustion improvers such as alkali metal salts and alkaline earth metal salts of organic acids or sulphuric acid monoesters of higher alcohols, anti valve seat recession and additives such as alkali metal compounds, e.g. sodium or potassium salts such as borates or carboxylates, and colouring agents, such as azodyes. One or more additives (e.g. 2-4) of the same or different types may be used, especially combinations of at least one antioxidant and at least one detergent additive. Antioxidants such as one or more hindered phenols e.g. ones with a tertiary butyl group in one or both ortho positions to the phenolic hydroxyl group are preferred in particular as described in Ex.1 hereafter. In particular the additives may be present in the composition in amounts of 0.1-100ppm e.g. 1-20ppm of each, usually of an antioxidant especially one or more hindered phenols. Total amounts of additive are usually not more than 1000ppm e.g. 1-1000ppm.

[0028] The compositions and gasolines are free of organolead compounds, and usually of manganese additives such as manganese carbonyls.

[0029] The compositions and gasolines may contain up to 0.1 % sulphur, e.g. 0.000-0.02% such as 0.002-0.01 %w/w.

[0030] The gasoline compositions of the invention have a MON value of 80 to less than 98, such as 80-95, 83-93 or 93-98. The RON value is usually 90-120 e.g. 102-120 or preferably 90-102 preferably 90-100 e.g. 90-99, such as 90-93 e.g. 91, or 93-98 e.g. 94.5-97.5, or 97-101 while the ROAD value is usually 85-115 e.g. 98-115 or preferably 85-98 such as 85-95 e.g. 85-90, or 90-95 or 95-98. Preferred gasoline compositions have MON 80-83, RON 90-93, and ROAD 85-90, or MON 83-93, RON 93-98 and ROAD 85-95 or MON 83-93, RON 97-101 and ROAD 90-95. The Net calorific value of the gasoline (also called the Specific Energy) is usually at least 18000 Btu/lb e.g. at least 18500, 18700 or 18,900 such as 18500-19500, such as 18700-19300 or 18900-19200; the calorific value may be at least 42MJ/kg e.g. at least 43.5 MJ/kg such as 42-45 or 43-45 such as 43.5-44.5MJ/kg. The gasoline usually has a boiling range (ASTM D86) of 20-225°C, in particular with at least 2% e.g. 2-15% boiling in the range 171-225°C. The gasoline is usually such

that at 70°C at least 10% is evaporated while 50% is evaporated on reaching a temperature in the range 77-120°C preferably 77-116°C and by 185°C, a minimum of 90% is evaporated. The gasoline is also usually that 10-50% may be evaporated at 70°C, 40-74% at 100°C, 70-97% at 150°C and 90-99% may be evaporated at 180°C. The Reid Vapour Pressure of the gasoline at 37.8°C measured according to ASTM D323 is usually 30-120, e.g. 40-100 such as 61-80 or preferably 50-80, 40-65, e.g. 40-60 or 40-50Kpa.

[0031] The gasoline compositions, when free of any oxygenates usually have a H:C atom ratio of at least 1.8:1 e.g. at least 2.0:1 or at least 2.1 or 2.2:1, such as 1.8-2.3:1 or 2.0-2.2:1. Advantageously the gasoline composition meets the following criteria.

$$\text{Atom H:C} \times [1 + \text{oxy}] \times \left[\text{Net } \frac{\text{Heat of}}{200} \text{ Combustion} + \text{ROAD}\right] \geq y,$$

wherein Atom H:C is the fraction of hydrogen to carbon in the hydrocarbons in the composition, oxy means the molar fraction of oxygenate, if any in the composition, Net Heat of Combustion is the energy derived from burning 11b (454g) weight of fuel (in gaseous form) in oxygen to give gaseous water and carbon dioxide expressed in Btu/lb units [MJ/kg times 430.35], and y is at least 350, 380, 410 or 430, in particular 350-440 e.g. 380-420 especially 400-420.

[0032] Preferably the motor gasoline of this invention comprises 10-90% of triptane, 10-80% of component (b), 0-25% naphtha, 0-15% of butane, 5-20% of olefin, 3-28% aromatics and 0-25% oxygenate, in particular with 5-20% aromatics and 5-15% olefins.

[0033] In a preferred embodiment of this invention the motor gasoline of this invention contains 8-65% of triptane (especially 15-35%), 0.1-30% such as 2-25% olefins, especially 3-14% and 0-35% aromatics such as 0-30% e.g. 5-35, 5-20 (especially 5-15%) or 20-30%, and 5-50% component (b) mixtures e.g. 10-45% such as 20-40%. Such gasolines may also contain oxygenates, such as MTBE especially in amount of less than 3% e.g. 0.1-3% and especially contain less than 1.5% benzene e.g. 0.1-1%. Such gasolines preferably have RON of 97-99, MON 87-90 and ROAD values of 92-94.5.

[0034] The motor gasolines of the invention are ones with 5-25% triptane, 5-15% olefins, 15-35% aromatics and 40-65% component (b), in particular 15-25% triptane, 7-15%, olefins 15-25% aromatics and 45-52% component (b) mixture of RON value 96.5-97.5, or 5-15% triptane, 7-15% olefins, 15-25% aromatics and 55-65% compound (b) of RON value 94.5-95.5.

[0035] Examples of motor gasolines of the invention are ones having 1-15% e.g. 3-12% butane, 0-20% e.g. 5-15% ether e.g. MTBE, 20-80 e.g. 25-70% of refinery mixed liquid (usually C_6-C_9)streams (apart from naphtha) (such as mixtures of (i)-(iv) above), 0-25% e.g. 2-25% naphtha, 5-70% e.g. 15-65% triptane, with RON 93-100 e.g. 94-98, MON 80-98 e.g. 83-93 or 93-98, and RVP 40-80 such as 40-65Kpa: Such gasolines usually contain 1-30% e.g. 2-25% olefins and 2-30% e.g. 4-25% aromatics. Amounts of olefins of 15-25% are preferred for RON values of 94-98 e.g. 94-96 and 2-15% e.g. 2-7% for RON values of 96-100 such as 96-98.

[0036] Particularly preferred examples of fuel composition comprise 15-35% e.g. 20-35% triptane, 0-18.5% e.g. 2-18.5% olefin, 5-40% e.g. 5-35% aromatics 25-65% saturates and less than 1% benzene, and 18-65% e.g 40-65% triptane, 0-18-5% e.g. 5-18.5% olefins, 5-42% e.g. 5-28% aromatics, 35-55% saturates and less than 1% benzene.

[0037] Another fuel composition may comprise 25-40% e.g. 30-40% such as 35% of alkylate, 10-25% e.g. 15-25% such as 20% of isomerate, 10-25% e.g. 15-25% such as 20% of light hydrocrackate and 20-35% e.g. 20-30% such as 25% of triptane and optionally 0-5% butane. Such a composition is preferably substantially paraffinic and is substantially free of olefins and aromatics.

[0038] Other fuel compositions of the invention may have different ranges of the Antiknock Index (also known as The ROAD Index), which is the average of MON and RON.

[0039] For ROAD Indexes of 85.5-88.5, the compositions may comprise 8-30% triptane e.g. 15-30%, and 10-50% e.g. 20-40% total component (b) mixture, 5-30%, e.g. 5-20% total olefins and 10-40 e.g. 15-35% total aromatics, or 8-30% triptane, 10-50% total component (b) mixture, 5-40% total aromatic mixtures e.g. 20-30% and 10-60% e.g. 30-55% total olefinic mixtures.

[0040] For ROAD Indexes of 88.5-91.0 the compositions may comprise 5-25% (or 5-15%) triptane, 20-45% total component (b) mixture, 0-25% e.g. 1-10 or 10-25% total olefins, and 10-35% e.g. 10-20% or 20-35% total aromatics or 5-25% (5-15%) triptane, 20-45% total component (b) mixture, 0-35% total aromatic mixtures e.g. 1-15 or 15-35%, and 5-65% e.g. 5-30 or 30-65% total olefinic mixtures.

[0041] For ROAD Indexes of 91.0-94.0 the fuel compositions of the invention may comprise 5-65% e.g. 5-20, 20-30, 30-65 or 40-65% triptane and 5-40% (5-35%) e.g. 5-12 or 12-40% (12-30%) total component (b) mixture 1-30% e.g. 1-10 or 10-25% total olefins and 5-55% e.g. 5-15 or 15-35 or 35-55% total aromatics, or the above amounts of triptane with 0-55 e.g. 0.5-25% e.g. 10-25% or 25-55% of aromatic fractions and 0 or 10-60% e.g. 10-30% or 35-60% total olefin fractions.

[0042] For ROAD values of 94-97.9, the fuel compositions may comprise 20-65% triptane e.g. 40-65% triptane, 0-15% e.g. 5-15% total olefins, 0-20% e.g. 5-20% total aromatics and 5-50 e.g. 30-50% total component (b) mixture, or the above amounts of triptane and total component (b) mixture with 0-30% e.g. 10-30% aromatic fractions and 0-30 e.g. 5-30% olefinic fraction, or the above amounts of triptane e.g. 20-40% triptane, total component b mixture, total olefins and total aromatics, with 2-15% aromatic fractions and 18-35% olefinic fractions.

[0043] The invention can provide motor gasolines, in particular of 91, 95, 97, 98 and 110 RON values, with desired high Octane Levels but low emission values on combustion in particular of at least one of total hydrocarbons, total air toxics, NOx, carbon monoxide, and carbon dioxide, especially of both total hydrocarbons and NOx. Thus the invention also provides the use of a compound of formula I, in particular triptane, in unleaded motor gasoline of MON at least 80 e.g. 80 to less than 98, e.g. as an additive to or component therein, to reduce the emission levels on combustion, especially of at least one of total hydrocarbons, total air toxics NOx, carbon monoxide and carbon dioxide especially both of total hydrocarbons and NOx. The invention also provides a method of reducing emissions of exhaust gases in the combustion of unleaded motor gasoline fuels of MON of at least 80 which comprises having a compound of formula I present in the fuel which is a gasoline of the invention. The invention also provides use of an unleaded gasoline of the invention in a spark ignition combustion engine to reduce emissions of exhaust gases. While the compositions of the invention may be used in supercharged or turbocharged engines, they are preferably not so used, but are used in normally aspirated ones. The compound of formula I e.g. triptane can reduce one or more of the above emission levels better than amounts of alkylate or a mixture of aromatics and oxygenate at similar Octane Number and usually decrease the fuel consumption as well.

[0044] The present invention is illustrated in the following Examples.

Examples 1-6

[0045] In these Examples 2,2,3 trimethylbutane (triptane) 99% purity was mixed with various refinery fractions and butane, and optionally methyl tertiary butyl ether, to produce a series of gasoline blends, for making unleaded motor gasolines.

[0046] Formulated gasolines were made by mixing each blend with a phenolic antioxidant 55% minimum 2,4 dimethyl-6-tertiary butyl phenol 15% minimum 4 methyl-2, 6-ditertiary-butyl phenol with the remainder as a mixture of monomethyl and dimethyl-tertiary butyl phenols.

[0047] In each case the gasolines were tested for MON and RON, and their Reid Vapour Pressure at 37.8°C and their calorific value, and their distillation properties. The results are shown in table 1.

Table 1

Example	1	2 *	3 *	4	5	6 *
Composition % v/v						
Triptane	10.0	50.0	50.0	25.0	25.0	60.0
Butane	10.0	5.0	5.0	5.0	5.0	5.0
Mixed Fractions (apart from	60.0	30.0	30.0	65.0	50.0	35.0
Naphtha) of which						
Catalytic reformate	5.0	0	0	18.1	0	1.3
HCC	6.48	18.62	17.68	0	9.31	22.73
LCC	48.52	0	19.05	46.90	36.41	0.00
SRG	0	11.38	3.27	0	4.28	10.85
Isopentane	0	0	0	0	0	0.12
Naphtha	20.0	5.0	5.0	5.0	20.0	0.00
MTBE	0	10.0	0	0	0	0
Analysis, %v/v						
Aromatics	14.1	6.3	8.5	19.1	10.0	7.9

(continued)

Analysis, %v/v						
Olefins	23.5	3.2	11.7	21.4	18.5	3.8
Antioxidant mg/l	15	15	15	15	15	15
Distillation °C						
T 10%	43.6	58.0	58.4	51.2	54.0	60.0
T 50%	89.1	93.2	97.1	85.5	91.9	99.2
T 90%	154.0	177.8	176.9	140.4	159.0	185.0
Reid Vapour Pressure kPa	78.1	46.9	47.4	63.9	57.3	42.9
RON	95.0	97.3	97.0	97.0	95.0	99.4
MON	85.9	97.2	95.4	90.0	89.0	87.3
ROAD	90.45	97.25	96.2	93.5	92.0	93.35
* Not according to the present invention.						

In the above table mixed fractions means a blend of refinery fractions in which HCC is heavy catalytically cracked spirit, LCC is light catalytically cracked spirit and SRG is straight run gasoline.

Example 7

[0048] The combustion characteristics of the gasolines of Ex. 1-6 were tested against standard unleaded gasolines. Combustion of the gasolines of Ex.1-6gave less carbon dioxide emissions than from equal volumes of the standard gasolines of similar ROAD Octane Number.

Example 8 and Comparative Ex A-C

[0049] The emission characteristics on combustion of a series of gasoline fuels with 25% of different components were compared, the components being heavy reformate (comp A), triptane (Ex8), alkylate (comp B) and a mix of 10% heavy reformate and 15% MTBE (comp C). The gasoline fuels and their properties were as follows. Formulated gasolines were made by addition of the phenolic antioxidant in amount and nature as in Ex 1-7.

Example	**A**	**8**	**B**	**C**
Composition				
Butane	3	3	3	3
Reformate	22	22	22	22
Alkylate	40	40	65	40
Bisomer (’CCS’)	10	10	10	10
Heavy Reformate	25			10
Triptane		25		
MTBE				15
Density kg/l	0.7623	0.7163	0.7191	0.7424
RON	101.2	100.2	98.5	101.1
MON	89.4	93.2	88.3	90.2
ROAD	95.3	96.7	93.4	95.65
%Aromatics	38.9	13.9	13.9	23.9
% Olefins	10.2	10.2	10.2	10.2
% Saturates	50.9	75.9	75.9	65.9
% Benzene	0.9	0.9	0.9	0.9

[0050] The fuels were tested in a single cylinder research engine at a number of different engine settings. The speed/load was 20/7.2 rps/Nm/, or 50/14.3 rps/Nm the LAMBDA setting was 1.01 or 0.95, and the ignition setting was set or optimized. The emissions of CO, CO_2, total hydrocarbons, NOx, and total air toxics (benzene, butadiene, formaldehyde and acetaldehyde) were measured from the exhaust gases. The results from the different engine settings were averaged and showed that, compared to the base blend (Comp. Ex. A) the emissions with the compositions containing heavy reformate and MTBE (Comp. C), 25% alkylate (Comp. B) and 25% triptane (Ex8) were reduced, the degrees of change being as follows.

Table 2

Example	% CO	%CO_2	%THC	%NOx	%TAT	%FC
Comp C (MTBE	-4.9	-2.3	-6.2	-6.5	-9.2	+1.4
Comp B (alkylate)	-7.9	-4.5	-4.0	-8.0	-13.1	-2.9
8 /triptane	-9.6	-5.6	-6.6	-10.1	-18.7	-4.1

Where THC is total hydrocarbons, TAT is total air toxics. The Fuel Consumption (FC) was also measured in g/kWhr and the change relative to the base blend are also shown in Table 2.

Example 9-22

[0051] Gasolines were made up as in Ex 1-6 from components as shown in the table below, and had the properties shown. They gave low carbon dioxide emissions.

Example	**9 ***	**10 ***	**11 ***	**12**	**13**	**14**	**15 ***
Composition % v/v							
Triptane	10.0	25.0	60	10	18.0	10.0	24.0
Butane	4.7	4.7	4.71	0	0	0	0
Mixed Fractions (apart from	85.3	70.3	35.29	76.21	73.6	90.0	45.4
Naphtha) of which							
Catalytic reformate	10.0	10.0	0	21.28	10.0	15.3	25.2
CCS	0	0	0	10	0	0	0
Steam cracked spirit	0	0	0	9.7	41.1	48.7	10.0
SRG	35.3	35.3	35.29	15.72	22.5	26.0	0
Isopentane	0	0	0	0	0	0	0
Naphtha	0	0	0	13.79	8.4	0	30.6
Ethanol	0	0	0	5	0	0	0
Heavy reformate	10	10	0	9.51	0	0	0
Toluene	30	15	0	0	0	0	0
Cyclohexane	0	0	0	5	0	0	0
Light hydrocrackate	0	0	0	0	0	0	0
C6 Bisomer	0	0	0	0	0	0	10.2
Analysis, %v/v							
Aromatics	48.0	33.0	1	31	23.6	29.2	2.2
Olefins	0.1	0.1	0.1	6.1	8.8	10.4	12.5
Sulphur % w/w	0.000	0.000			0.002	0.001	0.004
Benzene	0.7	0.7			0.6	0.9	1.0

(continued)

Example	9 *	10 *	11 *	12	13	14	15 *
Antioxidant mg/l	15	15	15	15	15	15	15
Distillation °C							
T 10%	58.0	55.9			53.6	51.5	61.0
T 50%	95.9	89.9			77.0	77.0	89.6
T 90%	156.6	157.0			136.9	142.6	140.4
Reid Vapour Pressure kPa	51.6	54.0			56.9	60.0	50.0
RON	97.3	96.1	101.4	96.0	91.0	92.0	91.0
MON	88.1	87.8	88.8	83.8	81.6	81.8	82.0
ROAD	92.7	91.9	95.1	89.9	86.3	86.9	86.5
* not according to the present invention							

Example	16	17	18	19	20 ***	21	22	23
Composition % v/v								
Triptane	10	25	60	10	25.0	25.0	25.0	25.0**
Butane	2.96	2.96	2.96	0	3.32	1.07		3
Mixed Fractions (apart from Naphtha)	87.04	72.04	37.04	76.21	54.95	65.42	75.0	
Catalytic reformate *	19.78	4.78		21.28	23.42	8.21	7.53	40
CCS	5	5	5	10				
Steam cracked spirit *	47.42	47.42	18.0	9.7		30.01	30.00	
SRG				15.72				
Alkylate					31.53	27.20	37.47	22
Naphtha				13.79	16.73	8.51		
Ethanol				5				
Heavy reformate				9.51				
Cyclohexane	5	5	5	5				
Light hydrocrackate	7.93	7.93	7.93	0				
C6 Bisomer	1.91	1.91	1.91	0				10
Analysis, %v/v								
Aromatics	32.1	23	8	31	16.4	16.8	15.6	25.5
Olefins	14	13.9	7.3	6.1	0.2	7.8	7.8	10.2
Benzene					1.0	0.5	0.5 ..	1.71
Sulphur % w/w					0.0002	0.0004	0.0004	0.0001
Antioxidant mg/l	10	10	10	10	10	10	10	10
Distillation % 70°C					22.7	31.2	30.5	18.5
% 100°C					53.3	60.0	59.2	42.5

(continued)

Example	16	17	18	19	20 ***	21	22	23
% 150°C					95.8	94.9	95.1	97.2
% 180°C					98.7	98.1	98.1	100
Reid Vap. Press. kPa					60.0	55.0	52.7	62.2
RON	97.3	98.9	104.0	96.0	98.6	100.9	102.9	102.7
MON	85.5	87.2	93.4	83.8	87.5	87.5	89.5	90.5
ROAD	91.4	93.05	96.7	89.8	93.05	94.2	96.2	96.6

* In Ex.20-22 different fractions were used, e.g. different reformates.
** In Ex.23, the triptane was replaced by 2,2,3-trimethyl pentane.
*** Not according to the present invention

Examples 24-8 and Comparative Example D

[0052] Emission characteristics were obtained as in Ex.8 (apart from Lamba settings of 1.00 and 0.95 set for the base fuel (Comp.D) on combustion of a series of gasoline fuels with different components namely reformate, (high aromatics), (Comp.D), triptane, Ex.24-27 and triptane/ethanol Ex.28. Fuel consumption was also measured in g/kWhr. Formulated gasolines were made by addition of the phenolic antioxidant in amount and nature as in Ex.1-7. The compositions were as shown in Table 3. The results were expressed in Table 4 as the percentage change in emissions or in fuel consumption compared to Ex.D.

Table 3

Example	24 **	25	26	27 **	28	D
Composition % v/v						
Triptane	40	10	25	60	10	
Butane	2.96	2.96	2.96	2.96		2.96
Mixed Fractions (apart from		87.04	72.04	37.04		
Naphtha) of which						
Catalytic reformate *		19.78	4.78		21.28	25.25
CCS	5	5	5	5	10	5
Steam cracked spirit *	37.2	47.42	47.42	1.7.2	9.7	47.42
SRG					15.72	
Toluene						4.53
Naphtha					13.79	
Ethanol					5	
Heavy reformate					9.51	
Cyclohexane	5	5	5	5	5	5
Light hydrocrackate *	7.93	7.93	7.93	7.93		7.93
C6 Bisomer *	1.91	1.91	1.91	1.91		1.91
Analysis, %v/v						
Aromatics	15.0	31.2	21.7	7.8	31.1	39.2
Olefms	13.4	16.2	16.1	8.3	6.5	16.2
Sulphur % w/w	0.007	0.007	0.007	0.007	0.012	0.007

(continued)

Example	24 **	25	26	27 **	28	D
Antioxidant mg/l	10	10	10	10	10	10
Distillation °C %						
T 10%						
T 50%						
T 90%						
Reid Vapour Pressure kPa						
RON	98.7	96.8	97.5	101.0	93.2	96.6
MON	86.1	82.8	83.7	89.6	82.4	82.5
ROAD	92.4	89.8	90.6	95.3	88.1	89.55
* Denotes that a different fraction was used, compared to the Examples in other Tables e.g. different raffinate. ** not according to the present invention						

Table 4

Example	% CO	% CO2	% THC	% NOx	% TAT	% Fuel Composition
25	-3.3	-2.1	-4.7	-4.0	-5.0	-1.4
26	-8.6	-3.8	-8.7	-7.0	-19.1	-2.5
27	-17.4	-6.8	-10.5	-18.0	-35.3	-4.5
24	-14.9	-5.0	-7.9	-12.2	-28.7	-3.4
28	-11.7	-2.2	-3.2	-10.3	-10.1	+0.1

Table 5

Example	F.G	29
Composition % v/v		
Triptane		25
Butane	0.75	0
Mixed Fractions (apart from Naphtha) of which		
Catalytic reformate *	11.0	7.5
Steam cracked spirit *	31.5	30.0
Alkylate	40.9	37.5
Toluene	15.8	0
Analysis, %v/v		
Aromatics	34.2	15.6
Olefins	8.2	7.8
Saturates	57.6	76.6
Sulphur ppm	7.3	10
Benzene %w/w	0.75	0.64
Antioxidant mg/l	10	10

(continued)

Example	F.G	29
Distillation % Evap. 70°C	18.8	21.6
E % 100°C	44.4	64.5
E % 150°C	92.8	93.3
E % 180°C	96.4	98
Reid Vapour Pressure kPa	56.8	52.2
RON	99.5	99.7
MON	87.6	89.3
ROAD	93.05	94.5

Examples 29 and Comparative Ex. F, G

[0053] 3 gasoline fuels (Ex.29, F and G) were compared for production of emissions on combustion in cars. The gasoline fuels had the compositions and properties as shown in Table 5 and the formulated gasolines included antioxidant as in Ex.1. The fuels met the requirements of 2005 Clean Fuel specification according to Directive 98/70 EC Annexe 3. The cars were regular production models, namely 1998 Ford Focus (1800cc), 1996-7 VW Golf (1600cc), 1998 Vauxhall Corsa (1000cc), 1994-5 Peugeot 106 (1400cc) and 1998 Mitsubishi GDI (1800cc) each fitted with a catalytic converter. The Corsa had 3 cylinders, the rest 4 cylinders, while the 106 had single point injection; the Mitsubishi had direct injection and the rest multipoint injection for their combustion.

[0054] 2 separate base fuel experiments (comp F & G) were done. The emissions were tested in triplicate in a dynamometer on the European Drive Cycle test as described in the MVEG test cycle (EC.15.04+EUDC) modified to start sampling on cranking and 11 sec. Idle as given in Directive 98/69 EC (the disclosure of which is hereby incorporated by reference). The EDC test over 11km comprises the ECE cycle (City driving test) repeated 4 times followed by the Extended Urban Drive Cycle test (incorporating some driving at up to 120km/hr). The emissions were measured out of the engine (i.e. upstream of the catalytic converter) and also as tailpipe emissions (i.e. downstream of the converter) and were sampled every second (except for the Focus) and cumulated over the test, the results being expressed as g emission per km travelled. The emissions of the first ECE cycle with the Focus were not measured. The emissions tested were for the total hydrocarbons, CO_2, CO and NO_x and the fuel consumption was determined on a gravimetric basis. The geometric means of the emission and consumption results across the 5 cars were obtained. The values for the Comparative fuels were averaged.

[0055] In the following tests, the CO_2 emissions averaged over the 5 cars were lower with the triptane fuel (Ex.29) compared to the averaged base fuel results (Comp.F, G), namely Total tailpipe emissions in EDC tests, EUDC test and ECE test, the reductions being respectively 2.8%, 2.7% and 2.8%. The Fuel Consumptions averaged over the 5 cars were lower with the triptane fuel (Ex.29) compared to the averaged base results (Comp.F, G) in those same tests, the reductions being respectively, 0.6%, 0.6% and 0.5%. The tailpipe emissions results for THC, CO and NO_x in at least some parts of the total EDC cycle showed trends towards triptane giving lower emissions than the base fuel, but the differences may or may not be confirmed in view of the limited number of vehicles tested.

[0056] The ECE tests simulates city driving and has 4 identical repeats of a specified speed profile, which profile has 3 progressively higher speed sections interspersed by zero speed sections (the average speed being 19km/hr). The first profile corresponds to driving from a cold start. In a cold engine, the effects of friction, lubricants and the nature of the fuel among others, differ from those with a hot engine in an unpredictable way, and it is with cold engines that most tailpipe emissions are produced, because the catalytic converter becomes increasingly effective at reducing emissions when it becomes hot. In addition a Lambda sensor upstream of the converter controls the fuel/air ratio entering the engine, but this is not effective with a cold engine (resulting in an unregulated fuel/air ratio); after cold start the sensor quickly becomes effective, (resulting in a regulated fuel/air ratio), even when the catalyst is not yet hot enough to be effective. Thus cold start operations are different from hot running operations and yet contribute to a large amount of tailpipe emissions.

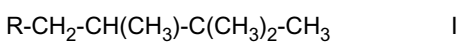
[0057] The out of engine results from the first profile ECE tests (simulating cold start) with the above fuels (Ex.29 and Comp.F, G) were the same as the tailpipe emissions as the catalyst was not effective then. The results in these cold start tests for CO_2, HC, CO and NO_x averaged over the Golf, Corsa, Peugeot and Mitsubishi, and also averaged over the Golf, Corsa and Peugeot showed trends toward triptane giving lower emissions than the base fuel, but the differences may or may not be confirmed in view of the limited number of vehicles tested.

[0058] This period of cold start simulated as above may correspond in real life to a period of time or distance, which may vary, depending on how the car is driven and/or ambient conditions e.g. up to 1 km or 4 or 2 min, or a temperature of the engine coolant (e.g. radiator water temperature) of up to 50°C. The car engine may also be deemed cold if it has not been operated for the previous 4hr before start, usually at least 6hr before start.

[0059] Thus the present invention also provides of method of reducing emissions of exhaust gases in the combustion of unleaded gasoline fuels of MON of at least 80 e.g. 80 to less than 98 from cold start of a spark ignition combustion engine, which comprises having a compound of formula I present in the fuel which is a gasoline of the invention.

Claims

1. An unleaded formulated motor gasoline having a MON of 80 to less than 98 comprising a base blend composition having a Motor Octane Number (MON) of at least 80 comprising component (a) at least 5% (by volume of the total composition) of at least one hydrocarbon having the following formula I



wherein R is hydrogen or methyl
and component (b) at least one saturated liquid aliphatic hydrocarbon having 4 to 12 carbon atoms, and at least one motor gasoline additive selected from anti-oxidants, corrosion inhibitors, anti-icing additives, engine detergent additives and anti-static additives, wherein the gasoline comprises (by volume) 5-25% of triptane, 5-15% olefins, 15-35% aromatics and 40-65% component (b).

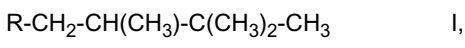
2. A gasoline as claimed in claim 1 which contains 15-25 % by volume triptane, 7-15 % by volume olefins, 15-25% by volume aromatics and 45-52% by volume component (b) mixture of RON value 96.5-97.5.

3. A gasoline as claimed in claim 1 which contains 5-15 % by volume triptane, 7-15 % by volume olefins, 15-25% by volume aromatics and 55-65% by volume compound (b) of RON value 94.5-95.5.

4. A gasoline according to any one of the preceding claims wherein the additive is an antioxidant.

Patentansprüche

1. Unverbleiter formulierter Ottomotorenkraftstoff mit einem MON von 80 bis weniger als 98, umfassend eine Grundgemischzusammensetzung mit einer Motor-Octan-Zahl (MON) von mindestens 80, umfassend Komponente (a) mindestens 5 % (auf das Volumen der Gesamtzusammensetzung) von mindestens einem Kohlenwasserstoff der nachstehenden Formel I



worin R Wasserstoff oder Methyl darstellt,
und Komponente (b) mindestens einen gesättigten flüssigen aliphatischen Kohlenwasserstoff mit 4 bis 12 Kohlenstoffatomen und mindestens einen Ottomotorenkraftstoffzusatz, ausgewählt aus Antioxidanzien, Korrosionsinhibitoren, Anti-Icing-Zusätzen, Motorenreinigungszusätzen und antistatischen Zusätzen, wobei der Ottokraftstoff (auf das Volumen) 5 - 25 % Triptan, 5 - 15 % Olefine, 15 - 35 % Aromaten und 40 - 65 % Komponente (b) umfasst.

2. Ottokraftstoff nach Anspruch 1, enthaltend 15 - 25 Volumenprozent Triptan, 7 - 15 Volumenprozent Olefine, 15 - 25 Volumenprozent Aromaten und 45 - 52 Volumenprozent Komponente (b)-Gemisch vom RON-Wert 96,5 - 97,5.

3. Ottokraftstoff nach Anspruch 1, enthaltend 5 - 15 Volumenprozent Triptan, 7 - 15 Volumenprozent Olefine, 15 - 25 Volumenprozent Aromaten und 55 - 65 Volumenprozent Verbindung (b) vom RON-Wert 94,5 - 95,5.

4. Ottokraftstoff nach einem der vorangehenden Ansprüche, worin der Zusatz ein Antioxidanz ist.

Revendications

1. Essence automobile formulée sans plomb ayant un indice d'octane moteur (IOM) allant de 80 jusqu'à moins de 98 comprenant une composition de mélange de base ayant un IOM d'au moins 80 comprenant un composant (a) ayant au moins 5% (du volume de la composition totale) d'au moins un hydrocarbure répondant à la formule I suivante

$$R\text{-}CH_2\text{-}CH(CH_3)\text{-}C(CH_3)_2\text{-}CH_3 \qquad I$$

dans laquelle R représente de l'hydrogène ou un groupe méthyle,
et un composant (b) ayant au moins un hydrocarbure aliphatique liquide saturé ayant de 4 à 12 atomes de carbone, et au moins un additif pour essence automobile choisi parmi des antioxydants, des inhibiteurs de corrosion, des additifs anti-givrage, des additifs détersifs du moteur et des additifs antistatiques, l'essence comprenant (en volume) de 5 à 25% de triptane, de 5 à 15% d'oléfines, de 15 à 35% de composés aromatiques et de 40 à 65% de composant (b).

2. Essence selon la revendication 1 qui contient de 15 à 25% en volume de triptane, de 7 à 15% en volume d'oléfines, de 15 à 25% en volume de composés aromatiques et de 45 à 52% en volume d'un mélange de composants (b) de valeur d'indice d'octane recherche (IOR) allant de 96,5 à 97,5.

3. Essence selon la revendication 1 qui contient de 5 à 15% en volume de triptane, de 7 à 15% en volume d'oléfines, de 15 à 25% en volume de composés aromatiques et de 55 à 65% en volume de composant (b) de valeur d'indice d'octane recherche (IOR) allant de 94,5 à 95,5.

4. Essence selon l'une quelconque des revendications précédentes dans laquelle l'additif est un antioxydant.