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(54) **METHOD OF REDUCING THE VAPOUR PRESSURE OF ETHANOL-CONTAINING MOTOR FUELS FOR SPARK IGNITION COMBUSTION ENGINES**

VERFAHREN ZUR VERRINGERUNG DES DAMPFDRUCKES VON ETHANOLHALTIGEN
MOTORTREIBSTOFFEN FÜR FUNKENGEZÜNDETE VERBRENNUNGSMOTOREN

PROCEDE PERMETTANT DE REDUIRE LA PRESSION DE LA VAPEUR DES CARBURANTS A
BASE D'ETHANOL DANS DES MOTEURS A COMBUSTION A ALLUMAGE COMMANDE

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Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

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Description

[0001] This invention relates to motor fuel for spark ignition internal combustion engines. More particularly the invention relates to a method for lowering the dry vapour pressure equivalent (DVPE) of a fuel composition including a hydrocarbon liquid and ethanol by using an oxygen-containing additive. The ethanol and DVPE adjusting components used to obtain the fuel composition are preferably derived from renewable raw materials. By means of the method of the invention motor fuels containing up to 20 % by volume of ethanol meeting standard requirements for spark ignition internal combustion engines operating with gasoline are obtainable.

Background of the invention

[0002] Gasoline is the major fuel for spark ignition internal combustion engines. The extensive use of gasoline results in the pollution of the environment. The combustion of gasoline derived from crude oil or mineral gas disturbs the carbon dioxide balance in the atmosphere, and causes the greenhouse effect. Crude oil reserves are decreasing steadily with some countries already facing crude oil shortages.

[0003] The growing concern for the protection of the environment, tighter requirements governing the content of harmful components in exhaust emissions, and crude oil shortages, force industry to develop urgently alternative fuels which burn more cleanly.

[0004] The existing global inventory of vehicles and machinery operating with spark ignition internal combustion engines does not allow currently the complete elimination of gasoline as a motor fuel.

[0005] The task of creating alternative fuels for internal combustion engines has existed for a long time and a large number of attempts have been made to use renewable resources for yielding motor fuel components.

[0006] U.S. Patent No. 2,365,009, issued in 1944 describes the combination of C_{1-5} , alcohols and C_{3-5} hydrocarbons for use as a fuel. In U.S. Patent No. 4,818,250 issued in 1989 it is proposed to use limonene obtained from citrus and other plants as a motor fuel, or as a component in blends with gasoline. In U.S. Patent No. 5,607,486 issued in 1997, there are disclosed novel engine fuel additives comprising terpenes, aliphatic hydrocarbons and lower alcohols.

[0007] Zudkevitch D. et al., in "Thermodynamics of reformulated automotive fuels" Hydrocarbon processing, vol 74, No. 6, 1995 disclose in table 5 thereof two fuel compositions comprising base gasoline, ethanol (5% and 3.2%, respectively) and 12% of ETBE. Using the vapour pressure data given in table 5 it can be calculated that the two fuel compositions exhibit a remaining ethanol induced vapour pressure increase of 32.1 and 30.3%, respectively.

[0008] Currently tert-butyl ethers are widely used as components of gasolines. Motor fuels comprising tert-butyl ethers are described in U.S. Patent No. 4,468,233 issued in 1984. The major portion of these ethers is obtained from petroleum refining, but can equally be produced from renewable resources.

[0009] Ethanol is a most promising product for use as a motor fuel component in mixtures with gasoline. Ethanol is obtained from the processing of renewable raw material, known generically as biomass, which, in turn, is derived from carbon dioxide under the influence of solar energy.

[0010] The combustion of ethanol produces significantly less harmful substances in comparison to the combustion of gasoline. However, the use of a motor fuel principally containing ethanol requires specially designed engines. At the same time spark ignition internal combustion engines normally operating on gasoline can be operated with a motor fuel comprising a mixture of gasoline and not more than about 10 % by volume of ethanol. Such a mixture of gasoline and ethanol is presently sold in the United States as gasohol. Current European regulations concerning gasolines allow the addition to gasoline of up to 5 % by volume of ethanol.

[0011] The major disadvantage of mixtures of ethanol and gasoline is that for mixtures containing up to about 20 % by volume of ethanol there is an increase in the dry vapour pressure equivalent as compared to that of the original gasoline.

[0012] Figure 1 shows the behaviour of the dry vapour pressure equivalent (DVPE) as a function of the ethanol content of mixtures of ethanol and gasoline A92 summer, and gasoline A95 summer and winter at 37.8°C. The gasolines known as A92 and A95 are standard gasolines purchased at gas stations in the United States and Sweden. Gasoline A92 originated in the United States and gasoline A95, in Sweden. The ethanol employed was fuel grade ethanol produced by Williams, USA. The DVPE of the mixtures was determined according to the standard ASTM D5191 method at the SGS laboratory in Stockholm, Sweden.

[0013] For the range of concentrations by volume of ethanol between 5 and 10% which is of particular interest for use as a motor fuel for standard spark ignition engines, the data in Fig. 1 show that the DVPE of mixtures of gasoline and ethanol can exceed the DVPE of source gasoline by more than 10%. Since the commercial petroleum companies normally supply the market with gasoline already at the maximum allowed DVPE, which is strictly limited by current regulations, the addition of ethanol to such presently commercially available gasolines is not possible.

[0014] It is known that the DVPE of mixtures of gasoline and ethanol can be adjusted. U.S. Patent No. 5,015,356 granted on May 14, 1991 proposes reformulating gasoline by removing both the volatile and non-volatile components

from C₄ - C₁₂ gasoline to yield either C₆ - C₉ or C₆ - C₁₀ intermediate gasoline. Such fuels are said to better facilitate the addition of alcohol over current gasoline because of their lower dry vapour pressure equivalent (DVPE). A disadvantage of this method of adjusting the DVPE of mixtures of gasoline and ethanol is that in order to obtain such a mixture it is necessary to produce a special reformulated gasoline, which adversely affects the supply chain and results in increased prices for the motor fuel. Also, such gasolines and their mixtures with ethanol have a higher flash point, which impairs their performance properties.

[0015] It is known that some chemical components decrease DVPE when added to gasoline or to a mixture thereof with ethanol. For example, U.S. Patent No. 5,433,756 granted on July 18, 1995 discloses chemical clean-combustion-promoter compounds comprising, in addition to gasoline, ketones, nitro-paraffin and also alcohols other than ethanol. It is noted that the composition of the catalytic clean-combustion-promoter disclosed in the patent reduces the DVPE of gasoline fuel.

[0016] Nothing is mentioned in this patent about the impact of the clean-combustion-promoter composition on the DVPE of mixtures of gasoline and ethanol.

[0017] U.S. Patent No. 5,688,295 granted on November 18, 1997 provides a chemical compound as an additive to gasoline or as a fuel for standard gasoline engines. In accordance with the invention, an alcohol-based fuel additive is proposed. The fuel additive comprises from 20 - 70% alcohol, from 2.5 - 20% ketone and ether, from 0.03 - 20% aliphatic and silicon compounds, from 5 - 20% toluene and from 4 - 45% mineral spirits. The alcohol is methanol or ethanol. It is noted in the patent that the additive improves gasoline quality and specifically decreases DVPE. The disadvantages of this method of motor fuel DVPE adjustment are that there is a need for large quantities of the additive, namely, not less than 15 % by volume of the mixture; and the use of silicon compounds, which form silicon oxide upon combustion, results in increased engine wear.

[0018] In WO9743356 a method for lowering the vapour pressure of a hydrocarbon-alcohol blend by adding a co-solvent for the hydrocarbon and alcohol to the blend, is described. A spark ignition motor fuel composition is also disclosed, including a hydrocarbon component of C₅ - C₈ straight-chained or branched alkanes, essentially free of olefins, aromatics, benzene and sulphur, in which the hydrocarbon component has a minimum anti-knock index of 65, according to ASTM D2699 and D2700 and a maximum DVPE of 15 psi, according to ASTM D5191; a fuel grade alcohol; and a co-solvent for the hydrocarbon component and alcohol in which the components of the fuel composition are present in amounts selected to provide a motor fuel with a minimum anti-knock index of 87 and a maximum DVPE of 15 psi. The co-solvent used is biomass-derived 2-methyltetrahydrofuran (MTHF) and other heterocyclical ethers such as pyrans and oxepans, MTHF being preferred.

[0019] The disadvantages of this method for adjusting the dry vapour pressure equivalent of mixtures of hydrocarbon liquid and ethanol are the following:

(1) It is necessary to use only hydrocarbon components C₅ - C₈ which are straight-chained or branched alkanes (i) free of such unsaturated compounds as olefins, benzene and other aromatics, (ii) free of sulphur and, as follows from the description of the invention, (iii) the hydrocarbon component is a coal gas condensate or natural gas condensate;

(2) It is necessary to use as a co-solvent for the hydrocarbon component and ethanol only one particular class of chemical compounds containing oxygen; namely, ethers, including short-chained and heterocyclic ethers;

(3) It is necessary to use a large quantity of ethanol in the fuel, not less than 25%;

(4) It is necessary to use a large quantity of co-solvent, not less than 20%, of 2-methyltetrahydrofuran; and

(5) It is required to modify the spark ignition internal combustion engine when operating with such fuel composition and, specifically, one must change the software of the on-board computer or replace the on-board computer itself.

[0020] Accordingly, it is an object of the present invention to provide a method by which the above-mentioned drawbacks of the prior art can be overcome. It is a primary object of the invention to provide a method of reducing the vapour pressure of a C₃ to C₁₂ hydrocarbon based fuel mixture containing up to 20% by volume of ethanol for conventional gasoline engines to not more than the vapour pressure of the C₃ to C₁₂ hydrocarbon itself.

SUMMARY OF THE INVENTION

[0021] The above-mentioned object of the present invention has been accomplished by means of the method of claim 1.

[0022] The present inventors have found that specific types of compounds exhibiting an oxygen-containing group

surprisingly lower the vapour pressure of a gasoline-ethanol mixture.

[0023] This effect can unexpectedly be further enhanced by means of specific $C_6 - C_{12}$ hydrocarbon compounds.

[0024] They have also found that the octane number of the resulting hydrocarbon based fuel mixture surprisingly can be maintained or even increased by using the oxygen-component of the present invention.

[0025] According to the present method up to about 20 % by volume of fuel grade ethanol (b) can be used in the whole fuel compositions. The oxygen-containing additives (c) used can be obtained from renewable raw materials, and the hydrocarbon component (a) used can for example be any standard gasoline (which does not have to be reformulated) and can optionally contain aromatic fractions and sulphur, and also hydrocarbons obtained from renewable raw materials.

[0026] By means of the method of the invention fuels for standard spark ignition internal combustion engines can be prepared, which fuels allow such engines to have the same maximum performance as when operated on standard gasoline currently on the market. A decrease in the level of toxic emissions in the exhaust and a decrease in the fuel consumption can also be obtained by using the method of the invention.

[0027] According to one aspect of the invention, in addition to the dry vapour pressure equivalent (DVPE), the anti-knock index (octane number) can also be desirably controlled.

[0028] It is yet another object to provide an additive mixture of fuel grade ethanol (b) and oxygen-containing additive (c), and the further component (d), being individual hydrocarbons of the $C_6 - C_{12}$ fraction or their mixtures, which additive mixture subsequently can be used in the inventive method, i.e., added to the hydrocarbon component (a). The mixture of (b), (c), and (d), can also be used per se as a fuel for modified engines, i.e., not standard-type gasoline engines. The additive mixture can also be used for adjusting the octane number and/or for lowering the vapour pressure of a high vapour pressure hydrocarbon component.

[0029] Further objects and advantages of the present invention will be evident from the following detailed description, examples and dependent claims.

Brief description of the drawings

[0030] In Figure 1, the behaviour of the dry vapour pressure equivalent (DVPE) as a function of the ethanol content of prior art mixtures of ethanol and gasoline is shown.

[0031] In Figure 2, the behaviour of the dry vapour pressure equivalent (DVPE) of different fuels of the present invention as a function of the ethanol content thereof is shown.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0032] The present method enables the use of $C_3 - C_{12}$ hydrocarbon fractions as hydrocarbon component (a), including narrower ranges within this broader range, without restriction on the presence of saturated and unsaturated hydrocarbons, aromatics and sulphur. In particular, the hydrocarbon component can be a standard gasoline currently on the market, as well as other mixtures of hydrocarbons obtained in the refining of petroleum, off-gas of chemical-recovery coal carbonisation, natural gas and synthesis gas. Hydrocarbons obtained from renewable raw materials can also be included. The $C_3 - C_{12}$ fractions are usually prepared by fractional distillation or by blending various hydrocarbons.

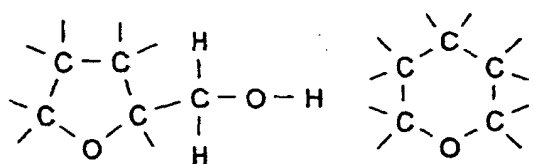
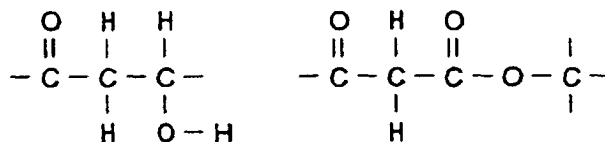
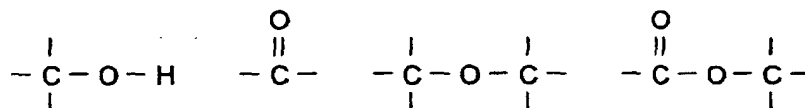
[0033] Importantly, and as previously mentioned, the component (a) can contain aromatics and sulphur, which are either co-produced or naturally found in the hydrocarbon component.

[0034] According to the method of the present invention the DVPE can be reduced for fuel mixtures containing up to 20% volume of ethanol, calculated as pure ethanol. According to the claimed method the vapour pressure of the hydrocarbon based ethanol-containing fuel mixture is reduced by 80% of the ethanol-induced vapour pressure increase, and more preferably the vapour pressure of the hydrocarbon based ethanol-containing fuel mixture is reduced to a vapour pressure corresponding to that of the hydrocarbon component alone.

[0035] As will be evident from the examples, the DVPE can be reduced if desired to a level even lower than that of the hydrocarbon component used.

[0036] According to a most preferred embodiment the other properties of the fuel, such as for example the octane number, are kept within the required standard limits.

[0037] This is accomplished by adding to the motor fuel composition at least one oxygen-containing organic compound (c) other than ethanol, and component (d). The oxygen-containing organic compound enables adjustment of (i) the dry vapour pressure equivalent, (ii) the anti-knock index and other performance parameters of the motor fuel composition as well as (iii) the reduction of the fuel consumption and the reduction of toxic substances in the engine exhaust emissions. The oxygen-containing compound (c) has oxygen bound in at least any one of the following functional groups:

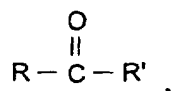


[0038] Such functional groups are present, for example, in the following classes of organic compounds and which can be used in the present invention: alcohols, ketones, ethers, esters, hydroxy-ketones, ketone esters, and heterocyclics with oxygen-containing rings.

[0039] The fuel additive can be derived from fossil-based sources or preferably from renewable sources such as biomass.

[0040] The oxygen-containing fuel additive (c) can typically be an alcohol, other than ethanol. In general, aliphatic or alicyclic alcohols, both saturated and unsaturated, preferably alkanols, are employed. More preferably, alkanols of the general formula: R-OH where R is alkyl with 3 to 10 carbon atoms, most preferably 3 to 8 carbon atoms, such as propanol, isopropanol, n-butanol, isobutanol, tert-butanol, n-pentanol, isopentanol, tert-pentanol, 4-methyl-2-pentanol, diethylcarbinol, diisopropylcarbinol, 2-ethylhexanol, 2,4,4-trimethylpentanol, 2,6-dimethyl-4-heptanol, linalool, 3,6-dimethyl-3-octanol, phenol, phenylmethanol, methylphenol, methylcyclohexanol or similar alcohols, are employed, as well as their mixtures.

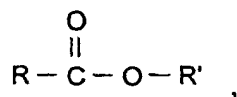
[0041] The component (c) can also be an aliphatic or alicyclic ketone, both saturated and unsaturated, of the general formula



where R and R' are the same or different and are each C₁-C₆ hydrocarbons, which also can be cyclic, and are preferably C₁-C₄ hydrocarbons. Preferred ketones have a total (R+R') of 4 to 9 carbon atoms and include methylethyl ketone, methylpropyl ketone, diethylketone, methylisobutyl ketone, 3-heptanone, 2-octanone, diisobutyl ketone, cyclohexanone, acetophenone, trimethylcyclohexanone, or similar ketones, and mixtures thereof.

[0042] The component (c) can also be an aliphatic or alicyclic ether, including both saturated and unsaturated ethers, of the general formula R-O-R', wherein R and R' are the same or different and are each a C₁-C₁₀ hydrocarbon group. In general, lower (C₁-C₆) dialkyl ethers are preferred. The total number of carbon atoms in the ether is preferably from 6 to 10. Typical ethers include methyltertamyl ether, methylisoamyl ether, ethylisobutyl ether, ethyltertbutyl ether, dibutyl ether, diisobutyl ether, diisoamyl ether, anisole, methylanisole, phenetole or similar ethers and mixtures thereof.

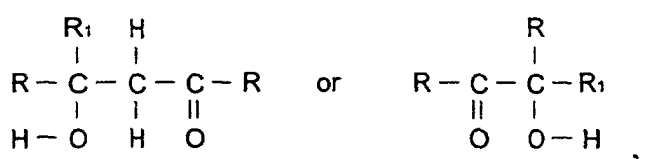
[0043] The component (c) may further be an aliphatic or alicyclic ester, including saturated and unsaturated esters, of the general formula



where R and R' are the same or different. R and R' are preferably hydrocarbon groups, more preferably alkyl groups and most preferably alkyl and phenyl having 1 to 6 carbon atoms. Especially preferred is an ester where R is C₁-C₄ and R' is C₄-C₆. Typical esters are alkyl esters of alkanolic acids, including n-butylacetate, isobutylacetate, tert-butylacetate, isobutylpropionate, isobutylisobutyrate, n-amylacetate, isoamylacetate, isoamylpropionate, methylbenzoate, phenylacetate, cyclohexylacetate, or similar esters and mixtures thereof. In general, it is preferred to employ an ester having from 5 to 8 carbon atoms.

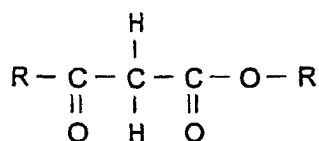
[0044] The additive (c) can simultaneously contain two oxygen-containing groups connected in the same molecule with different carbon atoms.

[0045] The additive (c) can be a hydroxyketone. A preferred hydroxyketone has the general formula:



where R is hydrocarbyl, and R₁ is hydrogen or hydrocarbyl, preferably lower alkyl, i.e. (C₁-C₄). In general, it is preferred to employ a ketol having 4 to 6 carbon atoms. Typical hydroxy-ketones include 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 4-hydroxy-4-methyl-2-pentanone, or similar ketols or mixture thereof.

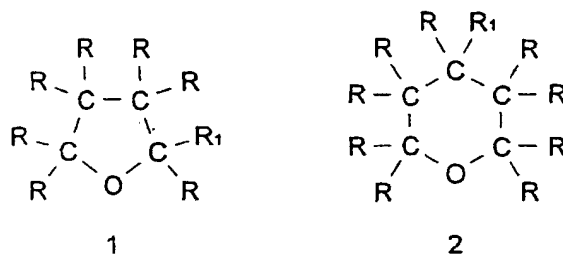
[0046] In yet another embodiment the fuel additive (c) is a ketone ester, preferably of the general formula:



where R is hydrocarbyl, preferably lower alkyl, i.e. (C₁-C₄).

[0047] Typical ketone esters include methylacetoacetate, ethyl acetoacetate and tert-butyl acetoacetate. Preferably, such ketone esters have 6 to 8 carbon atoms.

[0048] The additive (c) can also be a ring-oxygen-containing heterocyclic compound and, preferably, the oxygen-containing heterocycle has a C₄ - C₅ ring. More preferably, the heterocycle additive has a total of 5 to 8 carbon atoms. The additive can preferably have the formula (1) or (2) as follows:



where R is hydrogen or hydrocarbyl, preferably -CH₃, and R₁ is -CH₃, or -OH, or -CH₂OH, or CH₃CO₂CH₂-.

[0049] A typical heterocyclic additive (c) is tetrahydrofurfuryl alcohol, tetrahydrofurfurylacetate, dimethyltetrahydrofuran, tetramethyltetrahydrofuran, methyltetrahydropyran, 4-methyl-4-oxytetrahydropyran or similar heterocyclic additives, or mixtures thereof.

[0050] Component (c) can also be a mixture of any of the compounds set out above from one or more of the above-mentioned different compound classes.

[0051] Suitable fuel grade ethanol (b) to be used according to the present invention can readily be identified by the person skilled in the art. A suitable example of the ethanol component is ethanol containing 99.5% of the main substance. Any impurities included in the ethanol in an amount of at least 0.5 % by volume thereof and falling within the above-mentioned definition of component (c) should be taken into account when determining the amount used of component (c). That is, such impurities must be included in an amount of at least 0.5% in the ethanol in order to be taken into account as a part of component (c). Any water, if present in the ethanol, should preferably amount to no more than about 0.25 % by volume of the total fuel mixture, in order to meet the current standard requirements on fuels for gasoline engines.

[0052] Thus, a denatured ethanol mixture as supplied to the market, containing about 92% of ethanol, hydrocarbons and by-products, can also be used as the ethanol component in the fuel composition according to the invention.

[0053] Unless otherwise indicated all amounts are in % by volume based on the total volume of the motor fuel composition.

[0054] Generally, the ethanol (b) is employed in amounts from 0.1% to 20%, typically from about 1% to 20 % by volume, preferably 3% to 15 % by volume and more preferably from about 5 to 10 % by volume. The oxygen-containing additive (c) is generally employed in amounts from 0.05% to about 15 % by volume, more generally from 0.1 to about 15 % by volume, preferably from about 3 - 10 % by volume and most preferably from about 5 to 10 % by volume.

[0055] In general, the total volume of ethanol (b) and oxygen-containing additive (c) employed is from 0.15 to 25 % by volume, normally from about 0.5 to 25 % by volume, preferably from about 1 to 20 % by volume, more preferably from 3 to 15 % by volume, and most preferably from 5 to 15 % by volume.

[0056] The ratio of ethanol (b) to oxygen-containing additive (c) in the motor fuel composition is thus generally from 1:150 to 400:1, and is more preferably from 1:10 to 10:1.

[0057] The total oxygen content of motor fuel composition based on the ethanol and the oxygen additive, expressed in terms of weight % oxygen based on total weight of motor fuel composition, is preferably no greater than about 7 wt. %, more preferably no greater than about 5 wt. %.

[0058] According to a preferred embodiment of the invention to obtain a motor fuel suitable for the operation of a standard spark ignition internal combustion engine the aforesaid hydrocarbon component, ethanol, and additional oxygen-containing component are admixed to obtain the following properties of the resulting motor fuel composition:

- density at 15°C and at normal atmospheric pressure of not less than 690 kg/m³;
- oxygen content, based on the amount of oxygen-containing components, of not more than 7% w/w of the motor fuel composition;
- anti-knock index (octane number) of not lower than the anti-knock index (octane number) of the source hydrocarbon component and preferably for 0.5(RO_N+MO_N) of not less than 80;
- dry vapour pressure equivalent (DVPE) essentially the same as the DVPE of the source hydrocarbon component and preferably from 20 kPa to 120 kPa;
- acid content of not more than 0.1% by weight HAC;
- pH from 5 to 9;
- aromatic hydrocarbons content of not more than 40 % by volume, including benzene, and for benzene alone, not more than 1 % by volume;
- limits of evaporation of the liquid at normal atmospheric pressure in % of source volume of the motor fuel composition:

initial boiling point, min	20°C;
volume (at 70°C, min) of the liquid evaporated	25% by volume;
volume (at 100°C, min) of the liquid evaporated	50% by volume;
volume (at 150°C, min) of the liquid	75% by

(continued)

evaporated volume (at 190°C, min) of the liquid evaporated residue of distillation, max. final boiling point, max.	volume; 95% by volume; 2% by volume; 205°C;
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- sulfur content of not more than 50mg/kg;
- resins content of not more than 2mg/ 100ml.

[0059] According to a preferred embodiment of the method of the invention the hydrocarbon component and ethanol should be added together, followed by the addition of the additional oxygen-containing compound or compounds to the mix. Afterwards, the resulting motor fuel composition should preferably be maintained at a temperature not lower than -35°C, for at least about one hour. It is a feature of this invention that the components of the motor fuel composition can be merely added to each other to form the desired composition. It is generally not required to agitate or otherwise provide any significant mixing to form the composition.

[0060] According to a preferred embodiment of the invention to obtain a motor fuel composition suitable for operating a standard spark ignition internal combustion engine and with a minimal harmful impact on the environment, it is preferable to use oxygen-containing component(s) originating from renewable raw material(s).

[0061] Component (d) is used for further lowering the vapour pressure of the fuel mixture of components (a), (b) and (c). An individual hydrocarbon selected from a C₆ - C₁₂ fraction of aliphatic or alicyclic saturated and unsaturated hydrocarbons can be used as component (d). Preferably the hydrocarbon component (d) is selected from a C₈-C₁₁ fraction. Suitable examples of (d) are benzene, toluene, xylene, ethylbenzene, isopropylbenzene, isopropyltoluene, diethylbenzene, isopropylxylene, tert-butylbenzene, tert-butyltoluene, tert-butylxylene, cyclooctadiene, cyclooctotetraene, limonene, isooctane, isononane, isodecane, isooctene, myrcene, allocymene, tert-butylcyclohexane or similar hydrocarbons and mixtures hereof.

[0062] Hydrocarbon component (d) can also be a fraction boiling at 100-200°C, obtained in the distillation of oil, bituminous coal resin, or synthesis gas processing products.

[0063] As already mentioned the invention further relates to an additive mixture consisting of components (b) and (c) and, optionally also component (d), which subsequently can be added to the hydrocarbon component (a) and is also possible to use as such as a fuel for a modified spark ignition combustion engine.

[0064] The additive mixture preferably has a ratio of ethanol (b) to additive (c) of 1: 150 to 200:1 by volume. According to a preferred embodiment of the additive mixture, said mixture comprises the oxygen-containing component (c) in an amount from 0.5 up to 99.5 % by volume, and ethanol (b) in an amount from 0.5 up to 99.5 % by volume, and component (d) comprising at least one C₆ - C₁₂ hydrocarbon, more preferably C₈-C₁₁ hydrocarbon, in an amount from 0 up to 99 % by volume, preferably from 0% up to 90%, more preferably from 0 up to 79,5%, and most preferably from 5 up to 77% of the additive mixture. The additive mixture has a ratio of ethanol (b) to the sum of the other additive components (c)+(d) from 1:200 to 200:1 by volume, more preferable a ratio of ethanol (b) to the sum of the components (c) + (d) is from 1:10 to 10:1 by volume.

[0065] The octane number of the additive mixture can be established, and the mixture be used to adjust the octane number of the component (a) to a desired level by admixing a corresponding portion of the mixture (b), (c), (d) to component (a).

[0066] As examples demonstrating the efficiency of the present invention the following motor fuel compositions are presented which are not to be construed as limiting the scope of the invention, but as merely providing illustrations of some of the presently preferred embodiments of this invention.

[0067] As will be obvious to the person skilled in the art, all the fuel compositions of the following Examples can of course also be obtained by first preparing an additive mixture of components (b), (c), and (d), which mixture thereafter can be added to the component (a), or vice versa. In this case a certain amount of mixing may be required.

EXAMPLES

[0068] To prepare the blended motor fuel the following was used as the components (b), (c), and (d):

- fuel grade ethanol purchased in Sweden at Sekab and in the USA from ADM Corp. and Williams;
- oxygen-containing compounds, individual unsubstituted hydrocarbons and mixtures hereof purchased in Germany from Merck and in Russia from Lukoil.

- Naphtha, which is an oil straight run gasoline containing aliphatic and alicyclic saturated and unsaturated hydrocarbons. Alkylate, which is a hydrocarbon fraction consisting almost completely of isoparaffine hydrocarbons obtained in alkylation of isobutene by butanol. Alkylbenzene, which is a mixture of aromatic hydrocarbons obtained in benzene alkylation. Mostly, technical grade alkylbenzene comprises ethylbenzene, propylbenzene, isopropylbenzene, butylbenzene and others.

[0069] All the testing of source gasolines and ethanol-containing motor fuels, including those comprising the components of this invention was performed employing the standard ASTM methods at the laboratory of SGS in Sweden and at Auto Research Laboratories, Inc., USA.

[0070] The drivability testing was performed on a 1987 VOLVO 240 DL according to the standard test method EU2000 NEDC EC 98/69.

[0071] The European 2000 (EU 2000) New European Driving Cycle (NEDC) standard test descriptions are identical to the standard EU/ECE Test Description and Driving Cycle (91/441 EEC resp. ECE-R 83/01 and 93/116 EEC). These standardised EU tests include city driving cycles and extra urban driving cycles and require that specific emission regulations be met. Exhaust emission analysis is conducted with a constant volume sampling procedure and utilises a flame ionisation detector for hydrocarbon determination. Exhaust Emission Directive 91/441 EEC (Phase I) provides specific CO, (HC + NO) and (PM) standards, while EU Fuel Consumption Directive 93/116 EEC (1996) implements consumption standards.

[0072] The testing was performed on a 1987 Volvo 240 DL with a B230F, 4-cylinder, 2.32 litre engine (No. LG4F20-87) developing 83 kW at 90 revolutions/second and a torque of 185 Nm at 46 revolutions/ second.

EXAMPLE 1

[0073] Example 1 demonstrates the possibility of reducing the dry vapour pressure equivalent of the ethanol-containing motor fuel for the cases when gasolines with dry vapour pressure equivalent according to ASTM D-5191 at a level of 90 kPa (about 13 psi) are used as a hydrocarbon base.

[0074] To prepare the mixtures of this composition winter gasolines A92, A95, and A98, presently sold on the market and purchased in Sweden from Shell, Statoil, Q80K and Preem, were used.

[0075] Fig. 1 demonstrates the behaviour of the DVPE of the ethanol-containing motor fuel based on winter A95 gasoline. The ethanol-containing motor fuels based on winter A92 and A98 used in this example also demonstrate a similar behaviour.

[0076] The source gasoline comprised aliphatic and alicyclic C₄-C₁₂ hydrocarbons, including both saturated and unsaturated ones.

[0077] The winter A92 gasoline used had the following specification:

DVPE = 89,0 kPa

Anti-knock index 0.5(ROK + MON)=87.7

[0078] The fuel 1-1 (not according to the invention) contained A92 winter gasoline and ethanol and had the following properties for different ethanol contents:

A92 : Ethanol = 95 : 5 % by volume

DVPE = 94.4 kPa

0.5(ROK + MON) = 89.1

A92 : Ethanol = 90 : 10 % by volume

DVPE = 94.0 kPa

0.5(ROK + MON) = 90.2

[0079] The following different embodiments of the fuels 1-3 demonstrate the possibility of adjusting the dry vapor pressure equivalent (DVPE) of the ethanol-containing motor fuel based on winter A92 gasoline.

[0080] The inventive fuel 1-3 contained A92 winter gasoline (a), ethanol (b), oxygen-containing additives (c) and hydrocarbons C₆-C₁₂ (d), and had the following properties for the various compositions:

A92 : Ethanol : Isoamyl alcohol : Alkylate = 79 : 9 : 2 : 10 % by volume

The boiling temperature of the alkylate is 100-130°C

DVPE = 88.5 kPa

0.5(ROK + MON) = 90.25

A92 : Ethanol : Isobutyl acetate : Naphtha = 80 : 5 : 5 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 88.7 kPa

0.5(ROK + MON) = 88.6

A92 : Ethanol : Tert-butanol : Naphtha = 81 : 5 : 5 : 9 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 87.5 kPa

$0.5(\text{RON} + \text{MON}) = 89.6$

[0081] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel induced by the presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the winter gasoline is 90 kPa.

A92 : Ethanol : Isoamyl alcohol : Benzene : Ethylbenzene : Diethyl benzene = 82.5 : 9.5 : 0.5 : 0.5 : 3 : 4 % by volume

DVPE = 90 kPa

$0.5(\text{RON} + \text{MON}) = 91.0$

A92 : Ethanol : Isobutyl acetate : Toluene = 82.5 : 9.5 : 0.5 : 7.5 % by volume DVPE = 90 kPa

$0.5(\text{RON} + \text{MON}) = 90.8$

A92 : Ethanol : Isobutanol : Isoamyl alcohol : m-Xylene = 82.5 : 9.2 : 0.2 : 0.6 : 7.5 % by volume

DVPE = 90 kPa

$0.5(\text{RON} + \text{MON}) = 90.9$

[0082] The following compositions 1-6 demonstrate the possibility of adjusting the dry vapor pressure equivalent (DVPE) of the ethanol-containing motor fuel based on winter A98 gasoline.

[0083] The winter A98 gasoline had the following specification:

DVPE = 89,5 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 92.35$

[0084] The comparative fuel 1-4 contained A98 winter gasoline and ethanol and had the following properties for the various compositions:

A98 : Ethanol = 95 : 5 % by volume

DVPE = 95.0 kPa

$0.5(\text{RON} + \text{MON}) = 92.85$

A98 : Ethanol = 90 : 10 % by volume

DVPE = 94.5 kPa

$0.5(\text{RON} + \text{MON}) = 93.1$

[0085] The fuel 1-6 contained A98 winter gasoline (a), ethanol (b), oxygen-containing additives (c), and $\text{C}_6\text{-C}_{12}$ hydrocarbons (d) and had the following properties for the various compositions:

A98 : Ethanol : Isoamyl alcohol : Isooctane = 80 : 5 : 5 : 10 % by volume

DVPE = 82.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.2$

A98 : Ethanol : Isoamyl alcohol : m-Isopropyl toluene = 78.2 : 6.1 : 6.1 : 9.6 % by volume

DVPE = 81.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.8$

A98 : Ethanol : Isobutanol : Naphtha = 80 : 5 : 5 : 10 % by volume

The boiling point of the naphtha is 100-200°C.

DVPE = 82.5 kPa

$0.5(\text{RON} + \text{MON}) = 92.35$

A98 : Ethanol : Isobutanol : Naphtha : m-Isopropyl toluene = 80 : 5 : 5 : 5 : 5 % by volume

The boiling point of the naphtha is 100-200°C.

DVPE = 82.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.25$

A98 : Ethanol : Tert-butyl acetate : Naphtha = 83 : 5 : 5 : 7 % by volume

The boiling temperature of the naphtha is 100-200°C

DVPE = 82.1 kPa

$0.5(\text{RON} + \text{MON}) = 92.5$

[0086] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the winter gasoline is 90 kPa.

A98 : Ethanol : Isoamyl alcohol : Isooctane = 85 : 5 : 5 : 5 % by volume

DVPE = 90.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.3$

A98 : Ethanol : Isobutanol : Naphtha = 85 : 5 : 5 : 5 % by volume

The boiling temperature of the naphtha is 100-200°C

DVPE = 90.0 kPa

$$0.5(\text{RON} + \text{MON}) = 93.0$$

A98 : Ethanol : Isobutanol : Isopropyl xylene = 85 : 9.5 : 0.5 : 5 % by volume

DVPE = 90 kPa

$$0.5(\text{RON} + \text{MON}) = 93.1$$

[0087] The motor fuel compositions below demonstrate that it might be necessary to reduce the excess DVPE of the motor fuel caused by presence of ethanol below the level of DVPE of the source gasoline. Normally, this is required when DVPE of the source gasoline is higher than the limits of the regulations in force for the corresponding spending gasoline. In this way, for example, it is possible to transform the winter grade gasoline into the summer grade gasoline. The DVPE level for the summer gasoline is 70 kPa.

A98 : Ethanol : Isobutanol : Isooctane : Naphtha = 60 : 9.5 : 0.5 : 15 : 15 % by volume

The boiling point of the naphtha is 100-200°C.

DVPE = 70 kPa

$$0.5(\text{RON} + \text{MON}) = 92.85$$

A98 : Ethanol : Isobutanol : Alkylate : Naphtha = 60 : 9.5 : 0.5 : 15 : 15 % by volume

The boiling point of the naphtha is 100-200°C.

The boiling point of the alkylate is 100-130°C.

DVPE = 70 kPa

$$0.5(\text{RON} + \text{MON}) = 92.6$$

A98 : Ethanol : Tert-butyl acetate : Naphtha = 60 : 9 : 3 : 28 % by volume

The boiling point of the naphtha is 100-200°C.

DVPE = 70 kPa

$$0.5(\text{RON} + \text{MON}) = 91.4$$

[0088] The following fuels 1-9 and 1-10 demonstrate the possibility of adjusting the dry vapor pressure equivalent (DVPE) of the ethanol-containing motor fuel based on winter A95 gasoline.

[0089] The winter A95 gasoline had the following specification:

DVPE = 89.5 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 90.1$

[0090] Testing in accordance with the standard test method EU 2000 NEDC EC 98/69 as described above demonstrated the following results:

CO (carbon monoxide)	2.13g/km;
HC (hydrocarbons)	0.280g/km;
NO _x (nitrogen oxides)	0.265g/km;
CO ₂ (carbon dioxide)	227.0g/km;
NMHC*	0.276g/km;
Fuel consumption, F _c 1/100km	9.84

* Non-methane hydrocarbons.

[0091] The comparative fuel 1-7 contained A95 winter gasoline and ethanol, and had the following properties for the various compositions:

A95 : Ethanol = 95 : 5 % by volume

DVPE = 94.9 kPa

$$0.5(\text{RON} + \text{MON}) = 91.6$$

A95 : Ethanol = 90 : 10 % by volume (referred to as RFM 1 below)

DVPE = 94.5 kPa

$$0.5(\text{RON} + \text{MON}) = 92.4$$

[0092] The testing of the reference fuel mixture (RFM 1) demonstrated the following results, as compared to the winter A95 gasoline:

CO	-15.0%;
HC	-7.3%;
NO _x	+ 15.5%;
CO ₂	+2.4%;
NMHC*	-0.5%;

(continued)

Fuel consumption, F_c , 1/100km	+4.7%
"-" represents a reduction in emission, while "+" represents an increase in emission.	

[0093] The fuel 1-9 contained A95 winter gasoline (a), ethanol (b), the oxygen-containing additives (c), and C_6-C_{12} hydrocarbons (d) and had the following properties for the various compositions:

A95 : Ethanol: Isoamyl alcohol : Alkylate = 83.7 : 5 : 2 : 9.3 % by volume

The boiling temperature of the alkylate is 100-130°C

DVPE = 88.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 91.65$

A95 : Ethanol: Isoamyl alcohol: Naphtha = 83.7 : 5 : 2 : 9.3% by vol.

The boiling temperature of the naphtha is 100-200°C

DVPE = 88.5 kPa

$0.5(RO\text{N} + MO\text{N}) = 90.8$

A95 : Ethanol : Isobutyl acetate : Alkylate = 81:5:5:9% by volume

The boiling temperature of the alkylate is 100-130°C

DVPE = 87.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 92.0$

A95 : Ethanol: Isobutyl acetate : Naphtha = 81 : 5 : 5 : 9 % by volume

The boiling temperature of the naphtha is 100-200°C

DVPE = 87.5 kPa

$0.5(RO\text{N} + MO\text{N}) = 91.1$

[0094] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the winter gasoline is 90 kPa.

A95 : Ethanol: Isoamyl alcohol: Xylene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 90.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 92.1$

A95 : Ethanol : Isobutanol : Isoamyl alcohol : Naphtha = 80 : 9.2 : 0.2 : 0.6 : 10% by volume

The boiling temperature of the naphtha is 100-200°C

DVPE = 90.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 91.0$

A95 : Ethanol : Isobutanol : Isoamyl alcohol: Naphtha : Alkylate = 80 : 9.2 : 0.2 : 0.6 : 5 : 5 % by volume

The boiling temperature of the naphtha is 100-200°C.

The boiling point of the alkylate is 100-130°C.

DVPE = 90.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 91.6$

[0095] The motor fuel compositions below demonstrate that it might be necessary to reduce the excess DVPE of the motor fuel caused by presence of ethanol below the level of DVPE of the source gasoline. Normally, this is required when DVPE of the source gasoline is higher than the limits of the regulations in force for the corresponding gasoline. In this way, for example, it is possible to transform the winter grade gasoline into the summer grade gasoline. The DVPE level for the summer gasoline is 70 kPa.

A95 : Ethanol : Isobutanol : Isoamyl alcohol : Naphtha : Isooctane = 60 : 9.2 : 0.2 : 0.6 : 15 : 15 % by volume

The boiling temperature of the naphtha is 100-200°C.

DVPE = 70.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 91.8$

A95 : Ethanol: Tert-butyl acetate : Naphtha = 60 : 9 : 1 : 30 % by volume

The boiling temperature of the naphtha is 100-200°C.

DVPE = 70.0 kPa

$0.5(RO\text{N} + MO\text{N}) = 90.4$

[0096] The fuel 1-10 contains 75 % by volume A95 winter gasoline, 9.6 % by volume ethanol, 0.4 % by volume isobutyl alcohol, 4.5 % by volume m-isopropyl toluene and 10.5 % by volume naphtha with boiling temperature of 100-200°C. This fuel formulation demonstrates the possibility of decreasing the DVPE, increasing the octane number, decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the reference mixture of gasoline and ethanol (RFM 1). The motor fuel composition has the following properties:

density at 15°C, according to ASTM D 4052	749.2 kg /m ³ ;
initial boiling point, according to ASTM D 86	29°C;
vaporizable portion - 70°C	47.6 % by volume;
vaporizable portion - 100°C	55.6 % by volume;
vaporizable portion - 150°C	84.2 % by volume;
vaporizable portion - 180°C	97.5 % by volume;
final boiling point	194.9°C;
evaporation residue	1.3 % by volume;
loss by evaporation	1.6 % by volume;
oxygen content, according to ASTM D4815 acidity, according to ASTM D 1613	3.7%w/w;
weight% HAc	0.004;
pH, according to ASTM D1287	6.6;
sulfur content, according to ASTM D 5453	18mg/kg;
gum content, according to ASTM D381	1 mg/100ml;
water content, according to ASTM D6304 aromatics, according to SS 155120,	0.03% w/w;
including benzene	30.2 % by volume;
benzene alone, according to EN 238	0.7 % by volume;
DVPE, according to ASTM D 5191	89.0kPa;
anti-knock index 0.5(RON+MON), according to ASTM D 2699-86 and ASTM D 2700-86	92.6

[0097] The motor fuel formulation 1-10 was tested in accordance with the standard test method EU 2000 NEDC EC 98/69 and the following results, as compared to winter A95 gasoline, were obtained:

CO	-21%;
HC	-9%;
NO _x	+ 12.8%;
CO ₂	+2.38%;
NMHC	-6.4%;
Fuel consumption, Fc 1/100km	+3.2%

[0098] The fuel formulations 1-1 to 1-10 showed reduced DVPE over the tested ethanol-containing motor fuels based on summer grade gasoline. Similar results are obtained when other oxygen-containing compounds of this invention are substituted for the additives of the examples 1-1 to 1-10.

[0099] To prepare the above fuel formulations 1-1 to 1-10 of this motor fuel composition, initially gasoline was mixed with ethanol and the corresponding oxygen-containing additive was added to the fuel mixture. The motor fuel composition obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the above formulations were prepared without the use of any mixing devices.

[0100] The effect of the reduction of the vapour pressure of the ethanol-containing gasolines while increasing the ethanol content in the resulting composition from 0 to 11 % by volume was also observed when part of the oxygen-containing additive was replaced by C₆-C₁₂ hydrocarbons (component (d)). The compositions below demonstrate the effect achieved by means of the invention.

[0101] An additive mixture comprising 40 % by volume of ethanol, 10 % by volume of isobutanol and 50 % by volume of isopropyltoluene was mixed with winter gasoline with DVPE not higher than 90 kPa. The various compositions obtained had the following properties:

A92 : Ethanol: Isobutanol : Isopropyltoluene = 85 : 6 : 1.5 : 7.5 % by volume

DVPE = 84.9 kPa

0.5(RON + MON) = 93.9

A95 : Ethanol: Isobutanol : Isopropyltoluene = 80 : 8 : 2 : 10 % by volume

DVPE = 84.0 kPa

0.5(RON + MON) = 94.1

A98 : Ethanol: Isobutanol : Isopropyltoluene = 86 : 5.6 : 1.4 : 7 % by volume

DVPE = 85.5 kPa

0.5(RON + MON) = 93.8

[0102] Similar results were obtained when other oxygen-containing compounds and also C₆-C₁₂ hydrocarbons of

the present invention were used in the ratio of the invention to prepare the additive mixture, which was then used for preparation of the ethanol-containing gasolines. These gasolines entirely meet the requirements for the motor fuels used in the standard spark ignition engines.

EXAMPLE 2

[0103] Example 2 demonstrates the possibility of reducing the dry vapour pressure equivalent of the ethanol-containing motor fuel for the cases when gasolines with a dry vapour pressure equivalent according to ASTM D-5191 at a level of 70 kPa (about 10 psi) are used as a hydrocarbon base.

[0104] To prepare the mixtures of this composition summer gasolines A92, A95 and A98 presently sold on the market and purchased in Sweden from Shell, Statoil, Q8OK, and Preem, were used.

[0105] The source gasoline comprised aliphatic and alicyclic C₄-C₁₂ hydrocarbons, including saturated and unsaturated ones.

[0106] Figure 1 shows the behaviour of the DVPE of the ethanol-containing motor fuel based on summer A95 gasoline. The ethanol-containing motor fuels based on winter A 92 and A98 gasolines, respectively, demonstrated similar behaviour.

[0107] The following fuels 2-3 demonstrate the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing motor fuel based on summer A92 gasoline.

[0108] The summer A92 gasoline had the following properties:

DVPE = 70,0 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 87.5$

[0109] The comparative fuel 2-1 contained A92 summer gasoline and ethanol, and had the following properties for the various compositions:

A92 : Ethanol = 95 : 5 % by volume

DVPE = 77.0 kPa

$0.5(\text{RON} + \text{MON}) = 89.3$

A92 : Ethanol = 90 : 10 % by volume

DVPE = 76.5 kPa

$0.5(\text{RON} + \text{MON}) = 90.5$

[0110] The fuel 2-3 contained A92 summer gasoline (a), ethanol (b), the oxygen-containing additives (c), and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A92 : Ethanol : Methyl ethyl ketone : Isooctane = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 69.0 kPa

$0.5(\text{RON} + \text{MON}) = 91.0$

A92 : Ethanol : Isobutanol : Isooctane = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 69.0 kPa

$0.5(\text{RON} + \text{MON}) = 91.1$

A92 : Ethanol : Isobutanol : Isononane = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 68.8 kPa

$0.5(\text{RON} + \text{MON}) = 91.0$

A92 : Ethanol : Isobutanol : Isodecane = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 68.5 kPa

$0.5(\text{RON} + \text{MON}) = 90.8$

A92 : Ethanol : Isobutanol : Isooctene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 68.9 kPa

$0.5(\text{RON} + \text{MON}) = 91.2$

A92 : Ethanol : Isobutanol : Toluene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 68.5 kPa

$0.5(\text{RON} + \text{MON}) = 91.4$

A92 : Ethanol : Isobutanol : Naphtha = 80 : 9.5 : 0.5 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 67.5 kPa

$0.5(\text{RON} + \text{MON}) = 90.4$

A92 : Ethanol : Isobutanol : Naphtha : Toluene = 80 : 9.5 : 0.5 : 5 : 5 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 67.5 kPa

$0.5(\text{RON} + \text{MON}) = 90.9$

A92 : Ethanol : Isobutanol : Naphtha : Isopropyltoluene = 80 : 9.5 : 0.5 : 5 : 5 % by volume

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The boiling temperature for the naphtha is 100-200°C

DVPE = 67.5 kPa

$0.5(\text{RON} + \text{MON}) = 91.2$

[0111] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the summer gasoline is 70 kPa.

A92 : Ethanol : Isobutanol : Isodecane = 82.5 : 9.5 : 0.5 : 7.5 % by volume

DVPE = 70.0 kPa

$0.5(\text{RON} + \text{MON}) = 90.85$

A92 : Ethanol : Isobutanol : Tert-butylbenzene = 82.5 : 9.5 : 0.5 : 7.5 % by volume

DVPE = 70.0 kPa

$0.5(\text{RON} + \text{MON}) = 91.5$

A92 : Ethanol : Isobutanol : Isoamyl alcohol : Naphtha : Tert-butyltoluene = 82.5 : 9.2 : 0.2 : 0.6 : 5 : 2.5 % by volume

DVPE = 70.0 kPa

$0.5(\text{RON} + \text{MON}) = 91.1$

[0112] The following fuels 2-6 demonstrate the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing motor fuel based on summer A98 gasoline.

[0113] The summer A98 gasoline had the following specification:

DVPE = 69,5 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 92.5$

[0114] The comparative fuel 2-4 contained A98 summer gasoline and ethanol, and had the following properties for the various compositions:

A98 : Ethanol = 95 : 5 % by volume

DVPE = 76.5 kPa

$0.5(\text{RON} + \text{MON}) = 93.3$

A98 : Ethanol = 90 : 10 % by volume

DVPE = 76.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.7$

[0115] The fuel 2-6 contained A98 summer gasoline (a), ethanol (b), the oxygen-containing additives (c), and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A98: Ethanol : Isobutanol : Isooctane = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 69.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.7$

A98 : Ethanol : Isopropanol : Alkylbenzene = 80 : 5 : 5 : 10 % by volume

DVPE = 68.5 kPa

$0.5(\text{RON} + \text{MON}) = 94.0$

[0116] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by the presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the summer gasoline is 70 kPa.

A98 : Ethanol : Isobutanol : Isooctane = 81.5 : 9.5 : 0.5 : 8.5 % by volume

DVPE = 70.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.5$

A98 : Ethanol : Tert-butanol : Limonene = 86 : 7 : 4 : 4 % by volume

DVPE = 70.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.6$

[0117] The following fuels 2-9 to 2-10 demonstrate the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing motor fuel based on summer A95 gasoline.

[0118] The summer A95 gasoline had the following specification:

DVPE = 68,5 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 89.8$

[0119] The testing performed as above demonstrated for the summer A95 gasoline the following results:

CO (carbon monoxide)	2.198g/km;
HC (hydrocarbons)	0.245g/km;

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(continued)

NO _x (nitrogen oxides)	0.252g/km;
CO ₂ (carbon dioxide)	230.0g/km;
NMHC*	0.238g/km;
Fuel consumption, F _c 1/100km	9.95

* Non-methane hydrocarbons.

[0120] The comparative fuel 2-7 contained A95 summer gasoline and ethanol, and had the following properties for the various compositions:

A95 : Ethanol = 95% : 5 % by volume

DVPE = 75.5 kPa

0.5(ROn + MON) = 90.9

A95 : Ethanol = 90% : 10 % by volume (also referred to as RFM2 below)

DVPE = 75.0 kPa

0.5(ROn + MON) = 92.25

[0121] The testing of the reference fuel mixture (RFM 2) demonstrated the following results, as compared to summer A95 gasoline:

CO	-9.1%;
HC	-4.5%;
NO _x	+7.3%;
CO ₂	+4.0%;
NMHC*	-4.4%;
Fuel consumption, F, 1/100km	+3.6%
"-" represents a reduction in emission, while "+" represents an increase in emission	

[0122] The fuel 2-9 contained A95 summer gasoline (a), ethanol (b), the oxygen-containing additives (c), and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A95 : Ethanol : Tert-pentanol: Alkylbenzene = 80 : 7 : 4 : 9 % by volume

DVPE = 67.5 kPa

0.5(ROn + MON) = 93.6

A95 : Ethanol: Tert-butanol: Alkylbenzene = 80 : 7 : 4 : 9 % by volume

DVPE = 68.0 kPa

0.5(ROn + MON) = 93.8

A95 : Ethanol: Propanol: Xylene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 68.0 kPa

0.5(ROn + MON) = 93.1

A95 : Ethanol: Diethylketone : Xylene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 68.0 kPa

0.5(ROn + MON) = 93.2

A95 : Ethanol : Isobutanol : Naphtha : Isopropyltoluene = 80 : 9.5 : 0.5 : 5 : 5 % by volume

The boiling temperature for the naphtha is 100-170°C

DVPE = 68.0 kPa

0.5(ROn + MON) = 92.4

A95 : Ethanol : Isobutanol : Naphtha : Alkylate = 80 : 9.5 : 0.5 : 5 : 5 % by volume

The boiling temperature for the naphtha is 100-170°C

The boiling temperature for the alkylate is 100-130°C

DVPE = 68.5 kPa

0.5(ROn + MON) = 92.2

[0123] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by the presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the summer gasoline is 70 kPa.

A95 : Ethanol : Isobutanol : Isoamyl alcohol : Xylene = 82.5 : 9.2 : 0.2 : 0.6 : 7.5 % by volume

DVPE = 70.0 kPa

0.5(RON + MON) = 93.0

A95 : Ethanol : Isobutanol : Isoamyl alcohol : Cyclooctadiene = 82.5 : 9.2 : 0.2 : 0.6 : 7.5 % by volume

DVPE = 70.0 kPa

0.5(RON + MON) = 92.1

[0124] The fuel formulation 2-10 contained 81.5% by volume of A95 summer gasoline, 8.5% by volume of m-isopropyltoluene, 9.2% by volume of ethanol, and 0.8% by volume of isoamyl alcohol. Formulation 2-10 was tested to demonstrate how the inventive composition maintained the dry vapour pressure equivalent at a same level as the source gasoline while increasing the octane number, while decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the mixture RFM 2 of gasoline and ethanol. Formulation 2-10 had the following specific properties:

density at 15°C, according to ASTM D4052	754.1kg/m ³ ;
initial boiling point, according to ASTM D 86	26.6°C;
vaporisable portion - 70°C	45.2 % by volume;
vaporisable portion - 100°C	56.4 % by volume;
vaporisable portion - 150°C	88.8 % by volume;
vaporisable portion - 180°C	97.6 % by volume;
final boiling point	186.3°C;
evaporation residue	1.6 % by volume;
loss by evaporation	0.1 % by volume;
oxygen content, according to ASTM D4815	3.56% w/w;
acidity, according to ASTM D1613 weight% HAc	0.007;
pH, according to ASTM D 1287	8.9;
sulfur content, according to ASTM D 5453	16mg/kg;
gum content, according to ASTM D381	<1mg/100ml;
water content, according to ASTM D6304	0.12% w/w;
aromatics, according to SS 155120, including benzene	30.3 % by volume;
benzene alone, according to EN 238	0.8 % by volume;
DVPE, according to ASTM D 5191	68.5kPa;
anti-knock index 0.5(RON+MON), according to ASTM D 2699-86 and ASTM D 2700-86	92.7

[0125] The motor fuel Formulation 2-10 was tested in accordance with test method EU 2000 NEDC EC 98/69 as above and gave the following results in comparison (+) or (-)% with the results for the source A95 summer gasoline:

CO	-0.18%
HC	-8.5%;
NOx	+5.3%;
CO ₂	+2.8%;
NMHC	-9%;
Fuel consumption, Fc, 1/100km	+3.1%

[0126] The fuel formulations 2-1 to 2-10 showed reduced DVPE over the tested ethanol-containing motor fuels based on summer grade gasoline. Similar results are obtained when other oxygen-containing additives of the invention are substituted for the additives of the examples 2-1 to 2-10.

[0127] To prepare all the above fuel formulations 2-1 to 2-10 of this motor fuel composition, initially gasoline was mixed with ethanol, to which mixture was then added the corresponding oxygen-containing additive. The motor fuel composition obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the above formulations were prepared without the use of any mixing devices.

[0128] The use of an additive mixture comprising ethanol and oxygen-containing compounds other than ethanol for preparation of the ethanol-containing gasolines was accomplished with summer grade gasolines. The fuel compositions below demonstrate the possibility of obtaining the ethanol-containing gasolines to meet standard requirements for summer grade gasolines, including vapour pressure of not higher than 70 kPa.

[0129] Figure 2 shows the behaviour of the dry vapour pressure equivalent (DVPE) as a function of the ethanol content when mixing summer A95 gasoline with the additive mixture 3 comprising 35 % by volume of ethanol , 5 % by

volume of isoamyl alcohol, and 60 % by volume of naphtha boiling at temperatures between 100-170°C.

[0130] Figure 2 demonstrates that varying the ethanol content in gasoline within the range from 0 to 20% does not induce an increase of the vapour pressure for these compositions higher than the requirements of the standards for DVPE of the summer grade gasolines, which is 70 kPa.

[0131] Similar DVPE behaviour was observed for A92 and A98 summer gasoline mixed with an additive mixture comprising 35 % by volume of ethanol, 5 % by volume of isoamyl alcohol, and 60 % by volume of naphtha boiling at 100-170°C.

[0132] The ratio between ethanol and the oxygen-containing compound other than ethanol in the additive mixture, which is used for preparation of the ethanol-containing gasolines, is of substantial importance. The ratio between the components of the additive established by the present invention enables to adjust the vapour pressure of the ethanol-containing gasolines over a wide range.

[0133] Similar results were obtained when other oxygen-containing compounds (c) and also C₆-C₁₂ hydrocarbons (d) of this invention were used in the ratio established by this invention to prepare the additive mixture, which was then used for preparation of the ethanol-containing gasolines. These gasolines entirely meet the requirements for the motor fuels used in the standard spark ignition engines.

[0134] Moreover, the additive mixture comprising ethanol and the oxygen-containing compound of this invention other than ethanol with the ratio of the present invention can be used as an independent motor fuel for the engines adapted for operation on ethanol.

EXAMPLE 3

[0135] Example 3 demonstrates the possibility of reducing the dry vapour pressure equivalent of the ethanol-containing motor fuel for the cases when gasolines with dry vapour pressure equivalent according to ASTM D-5191 at a level of 48 kPa (about 7 pSi) are used as the hydrocarbon base.

[0136] To prepare the mixtures of this composition lead-free summer gasolines A92, A95, and A98 meeting US standards and purchased in the USA under the trademarks Phillips J Base Fuel, Union Clear Base and Indolene, were used.

[0137] The source gasolines comprised aliphatic and alicyclic C₅-C₁₂ hydrocarbons, including both saturated and unsaturated ones.

[0138] Fig. 1 shows the behaviour of the DVPE of the ethanol-containing motor fuel based on US summer grade A92 gasoline. The ethanol-containing motor fuels based on US summer A95 and A98 gasolines, respectively, demonstrated similar behaviour. The US summer A92 gasoline had the following specification:

DVPE = 47,8 kPa

Anti-knock index 0.5(ROK + MON)=87.7

[0139] The fuel 3-1 contained US A92 summer gasoline and ethanol and had the following properties for the various compositions:

A92 : Ethanol = 95 : 5 % by volume

DVPE = 55.9 kPa

0.5(ROK + MON) = 89.0

A92 : Ethanol = 90 : 10 % by volume

DVPE = 55.4 kPa

0.5(ROK + MON) = 90.1

[0140] The fuel 3-3 contained US A92 summer gasoline (a), ethanol (b), the oxygen-containing additives (c), and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A92 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 47.8 kPa

0.5(ROK + MON) = 89.5

A92 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : m-Isopropyltoluene = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

DVPE = 47.0 kPa

0.5(ROK + MON) = 90.5

A92 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Isooctane = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

DVPE = 47.8 kPa

0.5(ROK + MON) = 90.3

[0141] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by the presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the US summer grade gasoline is 7 psi, which corresponds to 48.28 kPa.

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A92 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 76 : 9.2 : 0.3 : 0.1 : 14.4 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 89.6$

A92 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha : Isooctane = 76 : 9.2 : 0.3 : 0.1 : 10.4 : 4 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 89.8$

A92 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha : m-Isopropyl toluene = 77 : 9.2 : 0.3 : 0.1 : 10.4 : 3

% by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 89.9$

[0142] The following fuels demonstrate the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing motor fuel based on US A98 summer gasoline.

[0143] The US A98 gasoline had the following specification:

DVPE = 48.2 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 92.2$

[0144] The comparative fuel 3-4 contained US A98 summer gasoline and ethanol and had the following properties for the various compositions:

A98 : Ethanol = 95 : 5 % by volume

DVPE = 56.3 kPa

$0.5(\text{RON} + \text{MON}) = 93.0$

A98 : Ethanol = 90 : 10 % by volume

DVPE = 55.8 kPa

$0.5(\text{RON} + \text{MON}) = 93.6$

[0145] The fuel 3-6 contained US A98 summer gasoline (a), ethanol (b), the oxygen-containing additives (c), and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A98 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 93.3$

A98 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Isooctane = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 93.9$

A98 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : m-Isopropyltoluene = 75.5 : 9.2 : 0.3 : 0.1 : 14.9 % by volume

DVPE = 47.5 kPa

$0.5(\text{RON} + \text{MON}) = 94.4$

A98 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha : Isooctane = 75 : 9.2 : 0.3 : 0.1 : 8.4 : 7 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 93.6$

A98 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha : m-Isopropyl toluene = 75 : 9.2 : 0.3 : 0.1 : 10.4 : 5

% by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 48.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.7$

A98 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha : Alkylate = 75 : 9.2 : 0.3 : 0.1 : 7.9 : 7.5 % by volume

The boiling temperature for the naphtha is 100-200°C.

The boiling temperature for the alkylate is 100-130°C.

DVPE = 48.2 kPa

$0.5(\text{RON} + \text{MON}) = 93.6$

[0146] The following fuels demonstrated the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing motor fuel based on US summer A95 gasoline.

[0147] The US summer A95 gasoline had the following specification:

DVPE = 47.0 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 90.9$

[0148] The US summer A95 gasoline was used as a reference fuel for the testing performed according to EU2000

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NEDC EC 98/69 test cycle on a 1987 Volvo 240 DL with a B230F, 4-cylinder, 2.32 litre engine (No. LG4F20-87) developing 83 kW at 90 revolutions/second and a torque of 185 Nm at 46 revolutions/second.

[0149] The testing performed as above demonstrated for the US summer A95 gasoline the following results:

CO (carbon monoxide)	2.406g/km;
HC (hydrocarbons)	0.356g/km;
NO _x (nitrogen oxides)	0.278g/km;
CO ₂ (carbon dioxide)	232.6g/km;
NMHC*	0.258g/km;
Fuel consumption, F _c 1/100km	9.93

* Non-methane hydrocarbons.

[0150] The comparative fuel 3-7 contained US A95 summer gasoline and ethanol and had the following properties for the various compositions:

A95 : Ethanol = 95 : 5 % by volume

DVPE = 55.3 kPa

0.5(RON + MON) = 91.5

A95 : Ethanol = 90 : 10 % by volume

DVPE = 54.8 kPa

0.5(RON + MON) = 92.0

[0151] Testing of the reference gasoline-alcohol mixture (RFM3) comprising 90 % by volume of US A95 summer grade gasoline and 10 % by volume of ethanol performed on a 1987 Volvo 240 DL with a B230F, 4-cylinder, 2.32 litre engine (No. LG4F20-87) in accordance with the standard test method EU 2000 NEDC EC 98/69 demonstrated the following results, as compared to summer US A95 gasoline:

CO	-12.5%;
HC	-4.8%;
NO _x	+2.3%;
CO ₂	+3.7%;
NMHC*	-4.0%;
Fuel consumption, F, 1/100km	+3.1%
"-" represents a reduction in emission, while "+" represents an increase in emission.	

[0152] The fuel 3-9 contained US A95 summer gasoline (a), ethanol (b), the oxygen-containing additives (c), and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A95 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

The boiling temperature for the naphtha is 100-200°C

DVPE = 47.0 kPa

0.5(RON + MON) = 91.6

A95 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Isooctane = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

DVPE = 47.0 kPa

0.5(RON + MON) = 92.2

A95 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : m-Isopropyltoluene = 75 : 9.2 : 0.3 : 0.1 : 15.4 % by volume

DVPE = 46.8 kPa

0.5(RON + MON) = 93.0

A95 : Ethanol : Tetrahydrofurfuryl alcohol : Cyclooctatetraene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 46.6 kPa

0.5(RON + MON) = 92.5

A95 : Ethanol : 4-Methyl-4-oxytetrahydropyran : Allocymene = 80 : 9.5 : 0.5 : 10 % by volume

DVPE = 46.7 kPa

0.5(RON + MON) = 92.1

[0153] The motor fuel compositions below demonstrate that it is not always necessary to reduce the excess DVPE of the motor fuel caused by the presence of ethanol to the level of DVPE of the source gasoline. In some cases it is sufficient just to bring it in compliance with the requirements of the regulations in force for the corresponding gasoline. The DVPE level for the US summer grade gasoline is 7 pSi, which corresponds to 48.28 kPa.

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A95 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 76.5 : 9.2 : 0.3 : 0.1 : 7 : 6,9 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 48.2 kPa

0.5(RON + MON) = 91.7

A95 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha : Isooctane = 76.5 : 9.2 : 0.3 : 0.1 : 7 : 6.9 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 48.2 kPa

0.5(RON + MON) = 92.2

A95 : Ethanol : Isoamyl alcohol : Isobutyl alcohol : m-Isopropyltoluene = 77 : 9.2 : 0.3 : 0.1 : 13.4 % by volume

DVPE = 48.2 kPa

0.5(RON + MON) = 92.9

[0154] The fuel formulation 3-10 contained 76 % by volume of US A95 summer gasoline, 9.2 % by volume of ethanol, 0.25 % by volume of isoamyl alcohol, 0.05 % by volume of isobutyl alcohol, 11.5 % by volume of naphtha with boiling temperature of 100-200°C, and 3 % by volume of isopropyltoluene. Formulation 3-10 was tested to demonstrate how the invention enables the production of ethanol-containing gasoline entirely meeting the requirements of the standards in force, firstly for the level of the DVPE and also for the other parameters. At the same time this gasoline secures a decrease of toxic emissions in the exhaust and lower fuel consumption in comparison to the mixture RFM 3 of source US A95 summer gasoline with 10% of ethanol. Formulation 3-10 had the following specific properties:

density at 15°C, according to ASTM D4052	774.9kg /m ³ ;
initial boiling point, according to ASTM D 86	36.1°C;
vaporisable portion - 70°C	33.6 % by volume;
vaporisable portion - 100°C	50.8 % by volume;
vaporisable portion - 150°C	86.1 % by volume;
vaporisable portion - 190°C	97.0 % by volume;
final boiling point	204.8°C;
evaporation residue	1.5 % by volume;
loss by evaporation	1.5 % by volume;
oxygen content, according to ASTM D4815	3.37% w/w;
acidity, according to ASTM D1613 weight% HAc	0.007;
pH, according to ASTM D1287	7.58;
sulfur content, according to ASTM D 5453	47mg/kg;
gum content, according to ASTM D381	2.8mg/ 100ml;
water content, according to ASTM D6304	0.02% w/w;
aromatics, according to SS 155120, including benzene	31.2 % by volume;
benzene alone, according to EN 238	0.7 % by volume;
DVPE, according to ASTM D 5191	48.0kPa;
anti-knock index 0.5(RON+MON), according to ASTM D 2699-86 and ASTM D 2700-86	92.2

[0155] The motor fuel Formulation 3-10 was tested on a 1987 Volvo 240 DL with a B230F, 4-cylinder, 2.32 litre engine (No. LG4F20-87) in accordance with test method EU 2000 NEDC EC 98/69 as above and gave the following results in comparison (+) or (-)% with the results for the source US A95 summer gasoline:

CO	-15.1%
HC	-5.6%;
NOx	+0.5%;
CO ₂	unchanged;
NMHC	-4.5%;
Fuel consumption, Fc, 1/100km	unchanged.

[0156] Similar results were obtained when the other oxygen-containing compounds substituted the tested oxygen-containing compounds.

[0157] To prepare all the fuel formulations above, initially US summer gasoline was mixed with ethanol, to which mixture was then added the corresponding oxygen-containing additive. The motor fuel composition obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the above formu-

lations were prepared without the use of any mixing devices.

[0158] It was established the possibility of employing of the additive mixture comprising ethanol and oxygen-containing compounds other than ethanol also for adjustment of the vapour pressure of the ethanol-containing motor fuels used in standard internal combustion spark ignition engines based on summer grade gasolines meeting US standards.

Adding C₈-C₁₂ hydrocarbons to the composition of the additive mixture increased the efficiency of the vapour pressure reducing impact of the additive on the excess vapour pressure caused by presence in the gasoline of ethanol.

[0159] Figure 2 shows the behaviour of the dry vapour pressure equivalent (DVPE) as a function of the ethanol content in the mixtures of US summer A92 gasoline and the additive mixture 4 comprising 35 % by volume of ethanol, 1 % by volume of isoamyl alcohol, 0.2 % by volume of isobutanol, 43.8 % by volume of naphtha boiling at temperatures between 100-170°C, and 20% of isopropyl toluene.

Figure 2 demonstrates that employment of this additive mixture in formulation of ethanol-containing gasoline enables the reduction of more than 100% of the excess vapour pressure induced by the presence of ethanol.

[0160] Similar results for DVPE were obtained for US summer grade A95 and A98 gasoline mixed with the additive mixture composed of 35 % by volume of ethanol, 1 % by volume of isoamyl alcohol, 0.2 % by volume of isobutanol, 43.8 % by volume of naphtha boiling at 100-170°C and 20% by volume of isopropyltoluene.

[0161] Similar results were obtained when other oxygen-containing compounds and C₆-C₁₂ hydrocarbons of this invention were used in the proportion established by this invention to formulate the additive mixture, which was then used for preparation of the ethanol-containing gasolines. These gasolines entirely meet the requirements for the motor fuels used in standard internal combustion spark ignition engines.

[0162] Moreover, the additive mixture comprising ethanol, the oxygen-containing compound other than ethanol, and C₆-C₁₂ hydrocarbons in the proportion and composition of the present invention, can be used as an independent motor fuel for the engines adopted for operation on ethanol.

EXAMPLE 4

[0163] Example 4 demonstrates the possibility of reducing the dry vapour pressure equivalent of the ethanol-containing motor fuel for the cases when the hydrocarbon base of the fuel is a non-standard gasoline with a dry vapour pressure equivalent according to ASTM D-5191 at a level of 110 kPa (about 16 psi).

[0164] To prepare the mixtures of this composition lead-free winter gasoline A92, A95, and A98 purchased in Sweden from Shell, Statoil, Q8OK and Preem and gas condensate (GK) purchased in Russia from Gazprom were used.

[0165] The hydrocarbon component (HCC) for the motor fuel compositions was prepared by mixing about 85 % by volume of winter A92, A95 or A98 gasoline with about 15 % by volume of gas condensate hydrocarbon liquid (GC).

[0166] To prepare the hydrocarbon component (HCC) for the fuel formulations 4-1 to 4-10 of this motor fuel composition, about 85 % by volume of winter A92, A95 or A98 gasoline was first mixed with the gas condensate hydrocarbon liquid (GC). The obtained hydrocarbon component (HCC) was then allowed to stand for 24 hours. The resulting gasoline contained aliphatic and alicyclic C₃-C₁₂ hydrocarbons, including saturated and unsaturated ones.

[0167] Fig. 1 demonstrates the behaviour of the DVPE of the ethanol-containing motor fuel based on winter A98 gasoline and gas condensate. The ethanol-containing motor fuel based on winter A92 and A98 gasoline and gas condensate (GC) demonstrated similar behaviour.

[0168] Gasoline comprising 85 % by volume of winter gasoline A92 and 15 % by volume of gas condensate (GC) had the following properties:

DVPE = 110.0 kPa

Anti-knock index 0.5(RON + MON)=87.9

[0169] The comparative fuel 4-1 contained A92 winter gasoline, gas condensate (GC) and ethanol and had the following properties for the various compositions:

A92 : GC : Ethanol= 80.75 : 14.25 : 5 % by volume

DVPE = 115.5 kPa

0.5(RON + MON) = 89.4

A92 : GC : Ethanol= 76.5 : 13.5 : 10 % by volume

DVPE = 115.0 kPa

0.5(RON + MON) = 90.6

[0170] The fuel 4-3 contained winter A92 gasoline, gas condensate (GC), ethanol, the oxygen-containing additive and C₆-C₁₂ hydrocarbons and had the following properties for the various compositions:

A92 : GC : Ethanol : Isobutanol : Isopropylbenzene = 68 : 12 : 9.5 : 0.5 : 10 % by volume

DVPE = 108.5 kPa

0.5(RON + MON) = 91.7

A92 : GC : Ethanol : Tert-butylethyl ether : Naphtha = 68 : 12 : 9.5 : 0.5 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 108.5 kPa

$0.5(\text{RON} + \text{MON}) = 90.6$

A92 : GC : Ethanol : Isoamylmethyl ether : Toluene = 68 : 12 : 9.5 : 0.5 : 10 % by volume

DVPE = 107.5 kPa

$0.5(\text{RON} + \text{MON}) = 91.6$

[0171] The fuel compositions below demonstrate that the invention enables the reduction of the excess DVPE of the non-standard gasoline to the level of the corresponding standard gasoline. The DVPE for the standard A92 winter gasoline is 90 kPa.

A92 : GC : Ethanol : Isoamyl alcohol : Naphtha : Alkylate = 55 : 10 : 9.5 : 0.5 : 12.5 : 12.5 % by volume

The boiling temperature for the naphtha is 100-200°C.

The boiling temperature for the alkylate is 100-130°C.

DVPE = 90.0 kPa

$0.5(\text{RON} + \text{MON}) = 90.6$

A92 : GC : Ethanol : Isoamyl alcohol : Naphtha : Ethylbenzene = 55 : 10 : 9.5 : 0.5 : 15 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 89.8 kPa

$0.5(\text{RON} + \text{MON}) = 90.9$

A92 : GC : Ethanol : Isoamyl alcohol : Naphtha : Isopropyltoluene = 55 : 10 : 9.5 : 0.5 : 20 : 5 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 90.0 kPa

$0.5(\text{RON} + \text{MON}) = 90.6$

[0172] The following compositions demonstrate the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing fuel mixtures based on about 85 % by volume of winter A98 gasoline and about 15 % by volume of gas condensate.

[0173] The gasoline comprising 85 % by volume of winter A98 gasoline and 15 % by volume of gas condensate (GC) had the following specification:

DVPE = 109.8 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 92.0$

[0174] The comparative fuel 4-4 contained A98 winter gasoline, gas condensate (GC) and ethanol and had the following properties for the various compositions:

A98 : GC : Ethanol = 80.75 : 14.25 : 5 % by volume

DVPE = 115.3 kPa

$0.5(\text{RON} + \text{MON}) = 93.1$

A98 : GC : Ethanol = 76.5 : 13.5 : 10 % by volume

DVPE = 114.8 kPa

$0.5(\text{RON} + \text{MON}) = 94.0$

[0175] The fuel 4-6 contained A98 winter gasoline, gas condensate, ethanol, the oxygen-containing additives, and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A98 : GC : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 68 : 12 : 9.2 : 0.6 : 0.2 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 107.4 kPa

$0.5(\text{RON} + \text{MON}) = 93.8$

A98 : GC : Ethanol : Ethylisobutyl ether : Myrzene = 72 : 13 : 9.5 : 0.5 : 5 % by volume

DVPE = 110.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.6$

A98 : GC : Ethanol : Isobutanol : Isooctane = 68 : 12 : 5 : 5 : 10 % by volume

DVPE = 102.5 kPa

$0.5(\text{RON} + \text{MON}) = 93.5$

[0176] The motor fuel compositions below demonstrate that the invention enables the reduction of the excess DVPE of non-standard gasoline to the level of DVPE of the corresponding standard gasoline. The DVPE for the standard winter A98 gasoline is 90.0 kPa.

A92 : GC : Ethanol : Isoamyl alcohol : Naphtha : Alkylate = 55 : 10 : 9.5 : 0.5 : 12.5 : 12.5 % by volume

The boiling temperature for the naphtha is 100-200°C.

The boiling temperature for the alkylate is 100-130°C.

DVPE = 89.8 kPa

$0.5(\text{RON} + \text{MON}) = 94.0$

A92 : GC : Ethanol : Isoamyl alcohol : Naphtha : Isopropylbenzene = 55 : 10 : 9.5 : 0.5 : 15 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 89.6 kPa

$0.5(\text{RON} + \text{MON}) = 94.2$

A92 : GC : Ethanol : Isobutanol : Naphtha : Isopropyltoluene = 55 : 10 : 5 : 5 : 20 : 5 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 88.5 kPa

$0.5(\text{RON} + \text{MON}) = 94.1$

[0177] The following compositions demonstrate the possibility of adjusting the dry vapour pressure equivalent (DVPE) of the ethanol-containing fuel mixtures based on about 85 % by volume of winter A95 gasoline and about 15 % by volume of gas condensate.

[0178] The gasoline comprising 85 % by volume of winter A98 gasoline and 15 % by volume of gas condensate (GC) had the following specification:

DVPE = 109.5 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 90.2$

[0179] The hydrocarbon component (HCC) comprising 85 % by volume of winter gasoline and 15 % by volume of gas condensate (GC) was used as a reference fuel for testing as described above and gave the following results:

CO	2.033 g/km;
HC	0.279 g/km;
NO _x	0.279 g/km;
CO ₂	229.5 g/km;
NMHC	0.255 g/km;
Fuel consumption, Fc, 1/ 100km	9.89

[0180] The fuel 4-7 contained A95 winter gasoline, gas condensate (GC) and ethanol and had the following properties for the various compositions:

A95 : GC : Ethanol = 80.75 : 14.25 : 5 % by volume

DVPE = 115.0 kPa

$0.5(\text{RON} + \text{MON}) = 91.7$

A95 : GC : Ethanol = 76.5 : 13.5 : 10 % by volume

DVPE = 114.5 kPa

$0.5(\text{RON} + \text{MON}) = 92.5$

[0181] The reference fuel mixture (RFM4) comprising 80.75% of winter A95 gasoline, 14.25% of gas condensate (GC) and 5% of ethanol was tested as described above and gave the following results in comparison (+) or (-)% with the results for the gasoline comprising 85 % by volume of winter gasoline A95 and 15 % by volume of gas condensate (GC):

CO	-6.98%
HC	-7.3%;
NO _x	+12.1%;
CO ₂	+ 1.1%;
NMHC	-5.3%;
Fuel consumption, Fc, 1/100km	+2.62%.

[0182] The fuel 4-9 contained A95 winter gasoline, gas condensate (GC), ethanol, the oxygen-containing additives, and C₆-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A95 : GC : Ethanol : Isoamyl alcohol : Isobutyl alcohol : Naphtha = 68 : 12 : 9.2 : 0.6 : 0.2 : 10 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 107.0 kPa

$0.5(\text{RON} + \text{MON}) = 92.1$

A95 : GC : Ethanol : Isobutanol : Cyclooctatetraene = 72 : 13 : 9.5 : 0.5 : 5 % by volume

DVPE = 108.5 kPa

$0.5(\text{RON} + \text{MON}) = 92.6$

[0183] The motor fuel compositions below demonstrate that the invention enables the reduction of the excess vapour pressure equivalent (DVPE) of the non-standard gasoline to the level of the corresponding standard gasoline. The DVPE of the standard winter gasoline A95 is 90.0 kPa.

A95 : GC : Ethanol : Isoamyl alcohol : Isobutanol : Naphtha : Alkylate = 55 : 10 : 9.2 : 0.6 : 0.2 : 12.5 : 12.5 % by

volume

The boiling temperature for the naphtha is 100-200°C.

The boiling temperature for the alkylate is 100-130°C.

DVPE = 89.5 kPa

$0.5(\text{RON} + \text{MON}) = 92.4$

A95 : GC : Ethanol: Isoamyl alcohol : Naphtha : Tert-butylxylene = 55 : 10 : 9.5 : 0.5 : 20 : 5 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 89.8 kPa

$0.5(\text{RON} + \text{MON}) = 92.5$

A95 : GC : Ethanol: Isobutanol : Naphtha : Isopropylbenzene = 55 : 10 : 5 : 5 : 20 : 5 % by volume

The boiling temperature for the naphtha is 100-200°C.

DVPE = 89.9 kPa

$0.5(\text{RON} + \text{MON}) = 92.2$

[0184] The motor fuel 4-10 contained 55% by volume of A95 winter gasoline, 10% by volume of gas condensate (GC), 5% by volume of ethanol, 5% by volume of tert-butanol, 20% by volume of naphtha with boiling temperature of 100-200°C and 5% by volume of isopropyltoluene. Formulation 4-10 was tested to demonstrate how the invention enables the formulation of ethanol-containing gasoline entirely meeting requirements of the standards in force, firstly in respect of the dry vapour pressure equivalent limit, and also for the other parameters of the fuel, even when the source hydrocarbon component (HCC) has a DVPE considerably higher than the requirements of the standards. At the same time this ethanol-containing gasoline decreases the level of toxic emissions in the exhaust and decreases the fuel consumption in comparison with the above-described mixture RFM 4. The formulation 4-10 had the following specific properties:

density at 15°C, according to ASTM D4052	698.6 kg/m ³ ;
initial boiling point, according to ASTM D 86	20.5°C;
vaporisable portion - 70°C	47.0 % by volume;
vaporisable portion - 100°C	65.2 % by volume;
vaporisable portion - 150°C	92.4 % by volume;
vaporisable portion - 180°C	97.3 % by volume;
final boiling point	189.9°C;
evaporation residue	0.5 % by volume;
loss by evaporation	1.1 % by volume;
oxygen content, according to ASTM D4815	3.2% w/w;
acidity, according to ASTM D1613 weight% HAc	0.001;
pH, according to ASTM D 1287	7.0;
sulfur content, according to ASTM D 5453	18 mg/kg;
gum content, according to ASTM D381	2 mg/100ml;
water content, according to ASTM D6304	0.01% w/w;
aromatics, according to SS 155120, including benzene	30.9 % by volume;
benzene alone, according to EN 238	0.7 % by volume;
DVPE, according to ASTM D 5191	90.0 kPa;
anti-knock index $0.5(\text{RON} + \text{MON})$, according to ASTM D 2699-86 and ASTM D 2700-86	92.3

[0185] The motor fuel Formulation 4-10 was tested as above and gave the following results in comparison (+) or (-) % with the results for the motor fuel comprising 85 % by volume of winter A95 gasoline and 15 % by volume of gas condensate:

CO	-14.0%
HC	-8.6%;
NO _x	unchanged;
CO ₂	+ 1.0%;
NMHC	-6.7%;
Fuel consumption, Fc, 1/100km	+2.0%.

[0186] Similar results are obtained when other oxygen-containing additives of the invention are substituted for the

oxygen-containing additives of the examples 4-1 to 4-10.

[0187] To prepare all the above fuel formulations 4-1 to 4-10 of this motor fuel composition, the hydrocarbon component (HCC), which is a mixture of winter gasoline and gas condensate (GC), was initially mixed with ethanol, to which mixture then was added the corresponding oxygen-containing additive and C₆-C₁₂ hydrocarbons. The motor fuel composition obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the above formulations were prepared without the use of any mixing devices.

[0188] The inventive fuel formulations demonstrated the possibility of adjusting the vapour pressure of the ethanol-containing motor fuels for the standard internal combustion spark ignition engines based on non-standard gasolines having a high vapour pressure.

EXAMPLE 5

[0189] Example 5 demonstrates the possibility of reducing the dry vapour pressure equivalent of the ethanol-containing motor fuel for the cases when the hydrocarbon base of the fuel is a reformulated gasoline with dry vapour pressure equivalent according to ASTM D-5191 at a level of 27.5 kPa (about 4 psi).

[0190] To prepare the mixtures of this composition lead-free reformulated gasoline purchased in Sweden from Preem and in Russia from Lukoil, and the Petroleum benzine purchased from Merck in Germany were used.

[0191] The hydrocarbon component (HCC) for the motor fuel compositions was prepared by mixing about 85 % by volume of winter A92, A95 or A98 gasoline with about 15 % by volume of gas condensate hydrocarbon liquid (GC).

[0192] The source gasolines comprised aliphatic and alicyclic C₆-C₁₂ hydrocarbons, including saturated and unsaturated.

[0193] Fig. 1 demonstrates the behaviour of the DVPE of the ethanol-containing motor fuel based on reformulated gasoline A92 and Petroleum benzine. Similar behaviour was observed for the ethanol-containing motor fuel based on reformulated A95 and A98 gasoline, and Petroleum benzine.

[0194] It should be pointed out that addition of ethanol to the reformulated gasoline induces a higher vapour pressure increase compared to the addition of ethanol to the standard gasoline.

[0195] Gasoline comprising 80 % by volume of reformulated gasoline A92 and 20 % by volume of Petroleum benzine (PB) had the following properties:

DVPE = 27.5 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 85.5$

[0196] The comparative fuel 5-1 contained A92 reformulated gasoline, Petroleum benzine (PB) and ethanol and had the following properties for the various compositions:

A92 : PB : Ethanol = 76 : 19 : 5 % by volume

DVPE = 36.5 kPa

$0.5(\text{RON} + \text{MON}) = 89.0$

A92 : PB : Ethanol = 72 : 18 : 10 % by volume

DVPE = 36.0 kPa

$0.5(\text{RON} + \text{MON}) = 90.7$

[0197] The fuel 5-3 contained reformulated A92 gasoline, Petroleum benzine (PB), ethanol, the oxygen-containing additives and also C₈-C₁₂ hydrocarbons and had the following properties for the various compositions:

A92 : PB : Ethanol : Isoamyl alcohol : Naphtha = 60 : 15 : 9.2 : 0.8 : 15 % by volume

The boiling temperature for the naphtha is 140-200°C.

DVPE = 27.5 kPa

$0.5(\text{RON} + \text{MON}) = 89.3$

A92 : PB : Ethanol : n-Butanol : Naphtha : Xylene = 60 : 15 : 9.2 : 0.8 : 7.5 : 7.5 % by volume

The boiling temperature for the naphtha is 140-200°C.

DVPE = 27.5 kPa

$0.5(\text{RON} + \text{MON}) = 91.2$

A92 : PB : Ethanol : Tetrahydrofurfuryl alcohol : Isopropylbenzene = 60 : 15 : 9 : 1 : 15 % by volume

DVPE = 27.5 kPa

$0.5(\text{RON} + \text{MON}) = 91.3$

[0198] The fuel compositions below demonstrate the possibility of adjusting the dry vapour pressure equivalent of the ethanol-containing gasolines based on reformulated A98 gasoline and Petroleum benzine (PB).

[0199] The motor fuel comprising 80 % by volume of reformulated gasoline A98 and 20 % by volume of Petroleum benzine (PB) had the following properties:

DVPE = 27.3 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 88.0$

[0200] The comparison fuel 5-4 contained A98 reformulated gasoline, Petroleum benzine (PB) and ethanol and had

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the following properties for the various compositions:

A98 : PB : Ethanol = 76 : 19 : 5 % by volume

DVPE = 36.3 kPa

$0.5(\text{RON} + \text{MON}) = 91.0$

A98 : PB : Ethanol = 72 : 18 : 10 % by volume

DVPE = 35.8 kPa

$0.5(\text{RON} + \text{MON}) = 92.5$

[0201] The fuel 5-6 contained A98 reformulated gasoline, Petroleum benzine (PB), ethanol, the oxygen-containing additives, and C₈-C₁₂ hydrocarbons (d) and had the following properties for the various compositions:

A98 : PB : Ethanol: Isoamyl alcohol : Naphtha = 60 : 15 : 9.2 : 0.8 : 15 % by volume

The boiling temperature for the naphtha is 140-200°C.

DVPE = 27.0 kPa

$0.5(\text{RON} + \text{MON}) = 91.7$

A98 : PB : Ethanol: Linalool : Allocymene = 60 : 15 : 9 : 1 : 15 % by volume

DVPE = 26.0 kPa

$0.5(\text{RON} + \text{MON}) = 93.0$

A98 : PB : Ethanol : Methylcyclohexanol : Limonene = 60 : 15 : 9.5 : 1 : 14.5 % by volume

DVPE = 25.4 kPa

$0.5(\text{RON} + \text{MON}) = 93.2$

[0202] The motor fuel compositions below demonstrate the possibility of adjusting the dry vapour pressure equivalent of the ethanol-containing fuel mixture based on about 80 % by volume of reformulated A95 gasoline and about 20 % by volume of the Petroleum benzine (PB). Gasoline comprising 80 % by volume of the reformulated A95 gasoline and 20 % by volume of the Petroleum benzine (PB) had the following properties:

DVPE = 27.6 kPa

Anti-knock index $0.5(\text{RON} + \text{MON}) = 86.3$

[0203] The hydrocarbon component (HCC) comprising 80 % by volume of reformulated gasoline and 20 % by volume of Petroleum benzine (PB) was used as a reference fuel for testing on a 1987 Volvo 240 DL with a B230F, 4-cylinder, 2.32 litre engine (No. LG4F20-87) in accordance with test method EU 2000 NEDC EC 98/69 and gave the following results:

CO	2.631 g/km;
HC	0.348 g/km;
NO _x	0.313 g/km;
CO ₂	235.1 g/km;
NMHC	0.308 g/km;
Fuel consumption, Fc, 1/100km	10.68

[0204] The fuel 5-7 contained A95 reformulated gasoline, Petroleum benzine (PB) and ethanol and had the following properties for the various compositions:

A95 : PB : Ethanol = 76 : 19 : 5 % by volume

DVPE = 36.6 kPa

$0.5(\text{RON} + \text{MON}) = 90.2$

A95 : PB : Ethanol = 72 : 18 : 10 % by volume

DVPE = 36.1 kPa

$0.5(\text{RON} + \text{MON}) = 91.7$

[0205] The reference fuel mixture (RFM5) comprising 72 % by volume of reformulated A95 gasoline, 18 % by volume of Petroleum benzine (PB) and 10 % by volume of ethanol was tested on a 1987 Volvo 240 DL with a B230F, 4-cylinder, 2.32 litre engine (No. LG4F20-87) in accordance with test method EU 2000 NEDC EC 98/69 as above and gave the following results in comparison (+) or (-)% with the results for the gasoline comprising 80 % by volume of reformulated gasoline A95 and 20 % by volume of Petroleum benzine (GC):

CO	-4.8%
HC	-1.3%;
NO _x	+26.3%;
CO ₂	+4.4%;
NMHC	-0.6%;

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(continued)

Fuel consumption, Fc, 1/100km	+5.7%.
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[0206] The fuel 5-9 contained A95 reformulated gasoline, Petroleum benzine (PB), ethanol, the oxygen-containing additives, and C₈-C₁₂ hydrocarbons and had the following properties for the various compositions:

A95 : PB : Ethanol: Isoamyl alcohol : Naphtha = 60 : 15 : 9.2 : 0.8 : 15 % by volume

The boiling temperature for the naphtha is 140-200°C.

DVPE = 27.1 kPa

0.5(ROn + MON) = 91.4

A95 : PB : Ethanol: Tetrahydrofurfuryl alcohol : Tert-butylcyclohexane = 60 : 15 : 9.2 : 0.8 : 15 % by volume

DVPE = 26.5 kPa

0.5(ROn + MON) = 90.7

A95 : PB : Ethanol: 4-Methyl-4-hydroxytetrahydropyran : Isopropyltoluene = 60 : 15 : 9.2 : 0.8 : 15 % by volume

DVPE = 26.1 kPa

0.5(ROn + MON) = 92.0

[0207] The motor fuel 5-10 contained 60% by volume of A95 reformulated gasoline, 15% by volume of Petroleum benzine (PB), 10% by volume of ethanol, 5% by volume of 2,5-Dimethyltetrahydrofuran and 10% by volume of isopropyltoluene. Formulation 5-10 was tested to demonstrate how the invention enables the formulation of ethanol-containing gasoline with a low vapour pressure, wherein the presence in the motor fuel composition of ethanol does not induce an increase of dry vapour pressure equivalent in comparison to the source hydrocarbon component (HCC). Moreover, this gasoline secures a decrease of toxic emissions in the exhaust and a decrease of the fuel consumption in comparison with the above mixture RFM 5. The formulation 5-10 had the following specific properties:

density at 15°C, according to ASTM D4052	764.6 kg/m ³ ;
initial boiling point, according to ASTM D 86	48.9°C;
vaporisable portion - 70°C	25.3 % by volume;
vaporisable portion - 100°C	50.8 % by volume;
vaporisable portion - 150°C	76.5 % by volume;
vaporisable portion - 190°C	95.6 % by volume;
final boiling point	204.5°C;
evaporation residue	1.4 % by volume;
loss by evaporation	0.5 % by volume;
oxygen content, according to ASTM D4815	4.6% w/w;
acidity, according to ASTM D 1613 weight% HAc	0.08;
pH, according to ASTM D1287	7.5;
sulfur content, according to ASTM D 5453	39 mg/kg;
gum content, according to ASTM D381	1.5 mg/100ml;
water content, according to ASTM D6304	0.1% w/w;
aromatics, according to SS 155120, including benzene	38 % by volume;
benzene alone, according to EN 238	0.4 % by volume;
DVPE, according to ASTM D 5191	27.2 kPa;
anti-knock index 0.5(ROn+MON), according to ASTM D 2699-86 and ASTM D 2700-86	91.8

[0208] The motor fuel Formulation 5-10 was tested as described previously and gave the following results in comparison (+) or (-)% with the results for the motor fuel comprising 80 % by volume of reformulated A95 gasoline and 20 % by volume of Petroleum benzine:

CO	-12.3%
HC	-6.2%;
NOx	unchanged;
CO ₂	+2.6%;
NMHC	-6.4%;
Fuel consumption, Fc, 1/ 100km	+3.7%

[0209] Similar results are obtained when other oxygen-containing additives of the invention substitute the oxygen-containing additives of the examples 5-1 to 5-10.

[0210] To prepare all the above fuel formulations 5-1 to 5-10 of this motor fuel composition, initially the hydrocarbon component (HCC) which is a mixture of reformulated gasoline and Petroleum benzine (PB) was mixed with ethanol, to which mixture then was added the corresponding oxygen-containing additive and C₈-C₁₂ hydrocarbons. The motor fuel composition obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the above formulations were prepared without the use of any mixing devices.

[0211] The invention demonstrated the possibility of adjusting the vapour pressure of the ethanol-containing motor fuels for the standard internal combustion spark ignition engines based on non-standard gasolines having a low vapour pressure.

[0212] Figure 2 shows the behaviour of the dry vapour pressure equivalent (DVPE) when mixing the hydrocarbon component (HCC), comprising 80 % by volume of reformulated A92 gasoline and 20 % by volume of Petroleum benzine, with the oxygen-containing additive mixture 5, comprising 40 % by volume of ethanol, 20 % by volume of 3,3,5-trimethylcyclohexanone, and 20 % by volume of naphtha with boiling temperature 130-170°C and 20 % by volume of tert-butyltoluene. The graph demonstrates that the use of the additive of this invention enables obtaining ethanol-containing gasolines, the vapour pressure of which does not exceed the vapour pressure of the source hydrocarbon component (HCC).

[0213] Similar DVPE behaviour was demonstrated when mixing the above oxygen-containing additive with hydrocarbon component (HCC) comprising 20 % by volume of Petroleum benzine (GC) and 80 % by volume of A95 or A98 reformulated gasoline.

[0214] Similar results were obtained when other oxygen-containing compounds and C₈-C₁₂ hydrocarbons of this invention were used in the proportion of the invention to formulate the oxygen-containing additive, which was then used for preparation of the ethanol-containing gasolines.

[0215] These gasolines have a vapour pressure equivalent (DVPE) not higher than the DVPE of the source hydrocarbon component (HCC). At the same time the anti-knock index for all ethanol-containing gasolines prepared in accordance with this invention was higher than that of the source hydrocarbon component (HCC).

[0216] The foregoing description and examples of preferred embodiments of this invention should be taken as illustrating, rather than as limiting, the present invention as defined by the claims. As will be readily appreciated, numerous variations and combinations of the features set forth above can be used without departing from the present invention as set forth in the claims. All such modifications are intended to be included within the scope of the following claims.

Claims

1. A method of reducing the vapour pressure of a C₃-C₁₂ hydrocarbon-based motor fuel mixture for conventional spark ignition internal combustion engines containing 0.1 to 20% by volume of ethanol, not more than 0.25% by weight of water according to ASTM D 6304, and not more than 7% by weight of oxygen according to ASTM D 4815, by at least 80 % of the ethanol induced vapour pressure increase, and more preferably to the vapour pressure of the C₃-C₁₂ hydrocarbon component (a) alone, wherein, in addition to the C₃-C₁₂ hydrocarbon component (a) and an ethanol component (b), an oxygen-containing component (c) is present in the fuel mixture in an amount from 0.05 up to 15% by volume of the total volume of the fuel mixture; the component (c) being selected from at least one of the following types of compounds:

- alkanol, having from 3 to 10 carbon atoms;
- dialkyl ether, having from 6 to 10 carbon atoms;
- ketone, having from 4 to 9 carbon atoms;
- alkyl ester of alkanolic acid, having from 5 to 8 carbon atoms;
- hydroxyketone, having from 4 to 6 carbon atoms;
- ketone ester of alkanolic acid, having from 5 to 8 carbon atoms;
- oxygen-containing heterocyclic compound selected from the following: tetrahydrofurfuryl alcohol, tetrahydrofurfuryl acetate, dimethyltetrahydro-furan, tetramethyltetrahydrofuran, methyl tetrahydropyran, 4-methyl-4-oxytetrahydropyran, and the mixtures hereof; and

wherein a component (d), selected from at least one C₆-C₁₂ hydrocarbon, is present in the fuel mixture in an amount such that the ratio (b):((c)+(d)) is from 1:200 to 200:1 by volume.

2. The method of claim 1, **characterised in that** the oxygen-containing component (c) and component (d) are added to the ethanol component (b), which mixture of (c), (b) and (d) is subsequently added to the hydrocarbon component (a).

3. The method of claim 1, **characterised in that** the ethanol component (b) is added to the hydrocarbon component (a) to which mixture of (b) and (a) the oxygen-containing component (c) is added, thereby obtaining a mixture of (a), (b) and (c), to which mixture component (d) is added.

4. The method of any of the preceding claims, **characterised in that** the C₃-C₁₂ hydrocarbon component (a) is selected from the group consisting of a non-reformulated standard type gasoline, a hydrocarbon liquid from petroleum refining, a hydrocarbon liquid from natural gas, a hydrocarbon liquid from an off-gas of chemical-recovery carbonisation, a hydrocarbon liquid from synthesis gas processing, or mixtures thereof, a non-reformulated standard type gasoline being preferred.

5. The method of any of the preceding claims, **characterised in that** the fuel composition obtained exhibits the following characteristics;

- (i) a density at 15°C, according to ASTM D 4052 of at least 690 kg /m³;
- (ii) a dry vapour pressure equivalent according to ASTM D 5191 from 20 kPa to 120 kPa;
- (iii) an acids content according to ASTM D 1613 of no greater than 0.1 weight % HAC;
- (iv) a pH according to ASTM D 1287 from 5 to 9;
- (v) an aromatics content according to SS 155120 of no greater than 40% by volume, wherein benzene is present in amounts according to EN 238 no greater than 1% by volume;
- (vi) a sulphur content according to ASTM D 5453 of no greater than 50 mg/kg;
- (vii) a gum content according to ASTM D 381 of no greater than 2 mg/100 ml;
- (viii) distillation properties according to ASTM D86 wherein initial boiling point is at least 20°C; a vaporisable portion at 70°C is at least 25% by volume; a vaporisable portion at 100°C is at least 50% by volume; a vaporisable portion at 150°C is at least 75% by volume; a vaporisable portion at 190°C is at least 95% by volume; a final boiling point no greater than 205°C; and an evaporation residue no greater than 2% by volume; and
- (ix) an anti-knock index 0.5 (RON+MON) according to ASTM D 2699-86 and ASTM D 2700-86 of at least 80.

6. The method of any of the preceding claims, **characterised in that** hydrocarbon component (d) is selected from benzene, toluene, xylene, ethylbenzene, isopropylbenzene, isopropyltoluene, diethylbenzene, isopropylxylene, tert-butylbenzene, tert-butyltoluene, tert-butylxylene, cyclooctadiene, cyclooctotetraene, limonene, isooctane, isononane, isodecane, isooctene, myrcene, allocymene, tert-butylcyclohexane and mixtures hereof.

7. The method of any of the preceding claims, **characterised in that** hydrocarbon component (d) is selected from a C₈-C₁₁ fraction.

8. The method of any of the preceding claims, **characterised in that** hydrocarbon component (d) is selected from a fraction boiling at 100-200°C, obtained in the distillation of oil, bituminous coal resin, or synthesis gas processing products.

9. The method of any of the preceding claims, **characterised in that** the ratio of (b):((c)+(d)) is from 1: 10 to 10:1 by volume.

Patentansprüche

1. Verfahren zum Vermindern des Dampfdrucks eines C₃-C₁₂ Motorentreibstoffgemisches auf Kohlenwasserstoffbasis für herkömmliche funkengezündete Verbrennungsmotoren, enthaltend 0,1 bis 20 Vol.-% Ethanol, nicht mehr als 0,25 Gew.-% Wasser gemäß ASTM D 6304 und nicht mehr als 7 Gew.-% Sauerstoff gemäß ASTM D 4815, um mindestens 80 % des durch das Ethanol verursachten Dampfdruckanstiegs, und stärker bevorzugt des Dampfdrucks des C₃-C₁₂ Kohlenwasserstoffbestandteils (a) allein, wobei zusätzlich zu dem C₃-C₁₂ Kohlenwasserstoffbestandteil (a) und einem Ethanolbestandteil (b) ein Sauerstoff enthaltender Anteil (c) in dem Treibstoffgemisch in einer Menge von 0,05 bis 15 Vol.-% des Gesamtvolumens des Treibstoffgemisches vorhanden ist; wobei Bestandteil (c) aus wenigstens einer der folgenden Arten von Verbindungen ausgewählt ist:

- Alkanol mit 3 bis 10 Kohlenstoffatomen;
- Dialkylether mit 6 bis 10 Kohlenstoffatomen;
- Keton mit 4 bis 9 Kohlenstoffatomen;
- Alkylester von Alkansäure mit 5 bis 8 Kohlenstoffatomen;

- Hydroxyketon mit 4 bis 6 Kohlenstoffatomen;
- Ketonester von Alkansäure mit 5 bis 8 Kohlenstoffatomen;
- Sauerstoff enthaltende heterocyclische Verbindungen, ausgewählt aus den folgenden: Tetrahydrofurfurylalkohol, Tetrahydrofurfurylacetat, Dimethyltetrahydrofuran, Tetramethyltetrahydrofuran, Methyltetrahydropyran, 4-Methyl-4-oxytetrahydropyran und Gemischen davon; und

wobei ein aus mindestens einem C₆-C₁₂ Kohlenwasserstoff ausgewählter Bestandteil (d) in dem Treibstoffgemisch in einer solchen Menge vorhanden ist, dass das Volumenverhältnis (b): ((c)+(d)) 1:200 bis 200:1 beträgt.

2. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Sauerstoff enthaltende Bestandteil (c) und der Bestandteil (d) dem Ethanolbestandteil (b) zugegeben werden, wobei das Gemisch aus (c), (b) und (d) nachfolgend dem Kohlenwasserstoffbestandteil (a) zugegeben wird.

3. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Ethanolbestandteil (b) dem Kohlenwasserstoffbestandteil (a) zugegeben wird, dem Gemisch aus (b) und (a) der Sauerstoff enthaltende Bestandteil (c) zugegeben wird, wobei ein Gemisch aus (a), (b) und (c) erhalten wird, und diesem Gemisch Bestandteil (d) zugegeben wird.

4. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** der C₃-C₁₂ Kohlenwasserstoffbestandteil (a) aus nicht reformuliertem Standardbenzin, einer Kohlenwasserstoffflüssigkeit aus der Erdölraffinerie, einer Kohlenwasserstoffflüssigkeit aus Erdgas, einer Kohlenwasserstoffflüssigkeit aus einem Abgas einer chemischen Rückgewinnung bei der Verkohlung, einer Kohlenwasserstoffflüssigkeit aus einer Synthesegasverarbeitung oder Gemischen davon ausgewählt ist, wobei nicht reformuliertes Standardbenzin bevorzugt ist.

5. Verfahren gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die erhaltene Treibstoffzusammensetzung die folgenden Merkmale aufweist:

- (i) eine Dichte bei 15°C gemäß ASTM D 4052 von mindestens 690 kg/m³;
- (ii) ein trockenes Dampfdruckequivalent gemäß ASTM D 5191 von 20 kPa bis 120 kPa;
- (iii) einen Säuregehalt gemäß ASTM D 1613 von nicht mehr als 0,1 Gew.-% HAc;
- (iv) einen pH-Wert gemäß ASTM D 1287 von 5 bis 9;
- (v) einen Aromatengehalt gemäß SS 155120 von nicht mehr als 40 Vol.-%, wobei Benzol gemäß EN 238 in Mengen von nicht mehr als 1 Vol.-% vorhanden ist;
- (vi) einen Schwefelgehalt gemäß ASTM D 5453 von nicht mehr als 50 mg/kg;
- (vii) einen Gummigehalt gemäß ASTM D 381 von nicht mehr als 2 mg/100 ml;
- (viii) Destillationseigenschaften gemäß ASTM D 86, wobei der Anfangssiedepunkt mindestens 20°C beträgt, der verdampfbare Anteil bei 70°C mindestens 25 Vol.-% beträgt, der verdampfbare Anteil bei 100°C mindestens 50 Vol.-% beträgt; der verdampfbare Anteil bei 150°C mindestens 75 Vol.-% beträgt; der verdampfbare Anteil bei 190°C mindestens 95 Vol.-% beträgt; der Endsiedepunkt nicht größer als 205°C ist; und der Verdampfungsrückstand nicht mehr als 2 Vol.-% beträgt; und
- (ix) eine Klopfestigkeit von 0,5 (RON+MON) gemäß ASTM D 2699-86 und ASTM D 2700-86 von mindestens 80.

6. Verfahren gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** der Kohlenwasserstoffbestandteil (d) aus Benzol, Toluol, Xylol, Ethylbenzol, Isopropylbenzol, Isopropyltoluol, Diethylbenzol, Isopropylxylol, tert-Butylbenzol, tert-Butyltoluol, tert-Butylxylol, Cyclooctadien, Cyclooctatetraen, Limonen, Isooctan, Isononan, Isodecan, Isoocten, Myrcen, Allocymen, tert-Butylcyclohexan und Gemischen davon ausgewählt ist.

7. Verfahren gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** der Kohlenwasserstoffbestandteil (d) aus einer C₈-C₁₁ Fraktion ausgewählt ist.

8. Verfahren gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** der Kohlenwasserstoffbestandteil (d) aus einer bei 100 bis 200°C siedenden Fraktion ausgewählt ist, welche beim Destillieren von Öl, Kokskohlenharz oder Synthesegasverarbeitungsprodukten erhalten wird.

9. Verfahren gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Volumenverhältnis von (b):((c)+(d)) 1:10 bis 10:1 beträgt.

Revendications

1. Procédé de réduction de la pression de vapeur d'un mélange de carburant pour moteur à base d'hydrocarbures en C₃ à C₁₂ pour des moteurs conventionnels à combustion interne à allumage par étincelle, contenant de 0,1 à 20 % en volume d'éthanol, pas plus de 0,25 % en poids d'eau conformément à la norme ASTM D 6304, et pas plus de 7 % en poids d'oxygène conformément à la norme ASTM D 4815, d'au moins 80 % de l'augmentation de pression de vapeur induite par l'éthanol, et de manière davantage préférée jusqu'à la pression de vapeur du composant hydrocarbures en C₃ à C₁₂ (a) seul, dans lequel, en plus du composant hydrocarbures en C₃ à C₁₂ (a) et d'un composant éthanol (b), un composant contenant de l'oxygène (c) est présent dans le mélange de carburant en une quantité allant de 0,05 à 15 % en volume du volume total du mélange de carburant ; le composant (c) étant choisi parmi au moins l'un des types suivants de composés :

- un alcanol, ayant de 3 à 10 atomes de carbone ;
- un éther de dialkyle, ayant de 6 à 10 atomes de carbone ;
- une cétone, ayant de 4 à 9 atomes de carbone ;
- un alkyl ester d'acide alcanoïque, ayant de 5 à 8 atomes de carbone ;
- une hydroxy-cétone, ayant de 4 à 6 atomes de carbone ;
- un cétoester d'acide alcanoïque, ayant de 5 à 8 atomes de carbone ;
- un composé hétérocyclique contenant de l'oxygène choisi parmi ce qui suit : l'alcool tétrahydrofurfurylique, l'acétate de tétrahydrofurfuryle, le diméthyl-tétrahydrofurane, le tétraméthyl-tétrahydrofurane, le méthyltétrahydropyrane, le 4-méthyl-4-oxytétrahydropyrane, et les mélanges de ceux-ci ; et

dans lequel un composant (d), choisi parmi au moins un hydrocarbure en C₆ à C₁₂, est présent dans le mélange de carburant en une quantité telle que le rapport (b):((c)+(d)) va de 1:200 à 200:1 en volume.

2. Procédé selon la revendication 1, **caractérisé en ce que** le composant contenant de l'oxygène (c) et le composant (d) sont ajoutés au composant éthanol (b), lequel mélange de (c), (b) et (d) est ultérieurement ajouté au composant hydrocarbures (a).

3. Procédé selon la revendication 1, **caractérisé en ce que** le composant éthanol (b) est ajouté au composant hydrocarbures (a), auquel mélange de (b) et (a) est ajouté le composant contenant de l'oxygène (c), obtenant ainsi un mélange de (a), (b) et (c), auquel mélange est ajouté le composant (d).

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le composant hydrocarbures en C₃ à C₁₂ (a) est choisi dans le groupe constitué par une essence de type standard non reformulée, un liquide d'hydrocarbures provenant du raffinage du pétrole, un liquide d'hydrocarbures provenant du gaz naturel, un liquide d'hydrocarbures provenant d'un dégagement gazeux d'une carbonisation de récupération chimique, un liquide d'hydrocarbures provenant d'un traitement de gaz de synthèse, ou un mélange de ceux-ci, une essence de type standard non reformulée étant préférée.

5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la composition de carburant obtenue présente les caractéristiques suivantes :

- (i) une masse volumique à 15°C, selon la norme ASTM D 4052, d'au moins 690 kg/m³ ;
- (ii) un équivalent de pression de vapeur sèche, selon la norme ASTM D 5191, de 20 kPa à 120 kPa ;
- (iii) une teneur en acides, selon la norme ASTM D 1613, non supérieure à 0,1 % en poids de HAc ;
- (iv) un pH, selon la norme ASTM D 1287, de 5 à 9 ;
- (v) une teneur en aromatiques, selon la norme SS 155120, non supérieure à 40 % en volume, le benzène étant présent en des quantités, selon la norme EN 238, non supérieures à 1 % en volume ;
- (vi) une teneur en soufre, selon la norme ASTM D 5453, non supérieure à 50 mg/kg ;
- (vii) une teneur en gomme, selon la norme ASTM D 381, non supérieure à 2 mg/100 mL ;
- (viii) des propriétés de distillation, selon la norme ASTM D 86, dans lesquelles le point d'ébullition initial est d'au moins 20°C ; une portion vaporisable à 70°C représente au moins 25 % en volume ; une portion vaporisable à 100°C représente au moins 50 % en volume ; une portion vaporisable à 150°C représente au moins 75 % en volume ; une portion vaporisable à 190°C représente au moins 95 % en volume ; un point d'ébullition final non supérieur à 205°C ; et un résidu d'évaporation non supérieur à 2 % en volume ; et
- (ix) un indice d'octane 0,5(RON + MON), selon la norme ASTM D 2699-86 et la norme ASTM D 2700-86, d'au moins 80.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le composant hydrocarbure(s) (d) est choisi parmi le benzène, le toluène, le xylène, l'éthylbenzène, l'isopropylbenzène, l'isopropyltoluène, le diéthylbenzène, l'isopropylxylène, le tert-butylbenzène, le tert-butyltoluène, le tert-butylxylène, le cyclooctadiène, le cyclooctotétraène, le limonène, l'isooctane, l'isononane, l'isodécane, l'isooctène, le myrcène, l'allocymène, le tert-butylcyclohexane et les mélanges de ceux-ci.
7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le composant hydrocarbure(s) (d) est choisi à partir d'une fraction en C₈ à C₁₁.
8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le composant hydrocarbure(s) (d) est choisi à partir d'une fraction bouillant à 100-200°C, obtenue par distillation du pétrole, d'une résine de charbon bitumineux ou de produits de traitement de gaz de synthèse.
9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le rapport (b):((c)+(d)) va de 1:1 à 10:1 en volume.

Vapor pressure curves at 37.8°C

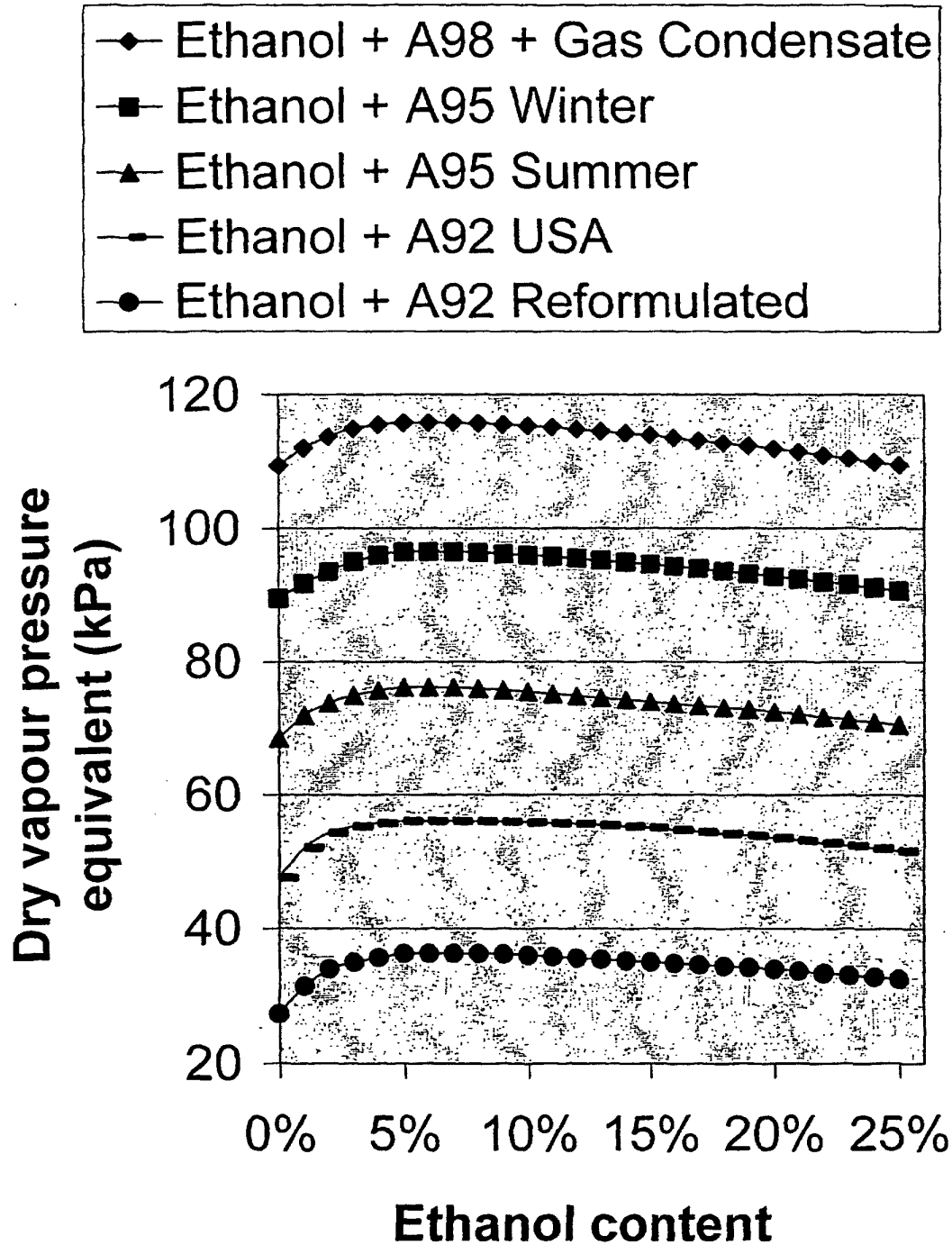


Figure 1

Vapor pressure curves at 37.8°C

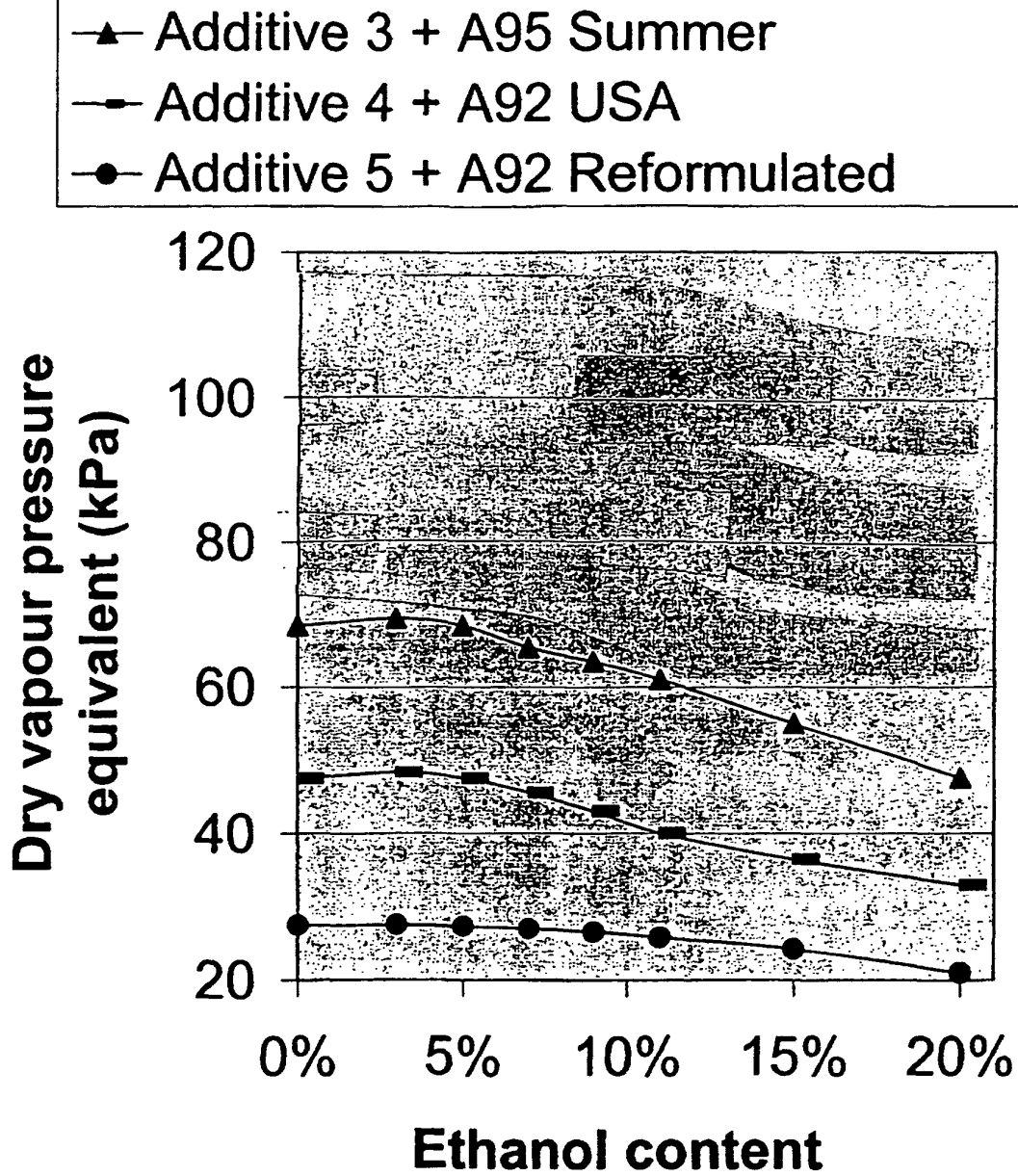


Figure 2