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CA 2272331 C 2009/05/12

(11)(21) **2 272 331**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 1997/11/11
(87) Date publication PCT/PCT Publication Date: 1998/05/28
(45) Date de délivrance/Issue Date: 2009/05/12
(85) Entrée phase nationale/National Entry: 1999/05/17
(86) N° demande PCT/PCT Application No.: GB 1997/003084
(87) N° publication PCT/PCT Publication No.: 1998/022556
(30) Priorité/Priority: 1996/11/18 (GB9623934.8)

(51) Cl.Int./Int.Cl. *C10L 1/06* (2006.01),
C10L 1/02 (2006.01)
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(54) Titre : COMPOSITIONS COMBUSTIBLES
(54) Title: FUEL COMPOSITION

(57) **Abrégé/Abstract:**

Unleaded aviation fuel compositions having a Motor Octane Number of at least 98, for use in piston driven aircraft comprising triptane and at least one other saturated liquid aliphatic hydrocarbon having from 5 to 10 carbon atoms. The compositions preferably contain triptane, iso-pentane and either one or any combination of iso-octane, toluene and methyl tertiary butyl ether.



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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10L 1/06, 1/02	A1	(11) International Publication Number: WO 98/22556 (43) International Publication Date: 28 May 1998 (28.05.98)
(21) International Application Number: PCT/GB97/03084 (22) International Filing Date: 11 November 1997 (11.11.97) (30) Priority Data: 9623934.8 18 November 1996 (18.11.96) GB (71) Applicant (for all designated States except US): BP OIL INTERNATIONAL LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): CLARK, Alisdair, Quentin [GB/GB]; 18 Britten Close, Ash, Aldershot, Hants GU12 6LS (GB). (74) Agent: WILSON, Michael, John; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury on Thames, Middlesex TW16 7LN (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FUEL COMPOSITION (57) Abstract Unleaded aviation fuel compositions having a Motor Octane Number of at least 98, for use in piston driven aircraft comprising triptane and at least one other saturated liquid aliphatic hydrocarbon having from 5 to 10 carbon atoms. The compositions preferably contain triptane, iso-pentane and either one or any combination of iso-octane, toluene and methyl tertiary butyl ether.		

FUEL COMPOSITION

The present invention relates to fuel compositions and in particular aviation gasolines possessing a high octane number suitable for use in piston-driven aircraft.

If a gasoline engine is run on a fuel which has an octane number lower than the minimum requirement for the engine, knocking will occur. Straight run
5 gasoline has a low motor octane number but may be boosted to the required motor octane number of 82-88 for automotive use by the addition of octane boosters such as tetraethyl lead either alone or with refinery components such as reformate, alkylate, cracked spirit or chemical streams such as toluene, xylene, methyl tertiary butyl ether or ethanol. Aircraft piston-driven engines operate under extreme
10 conditions to deliver the desired power e.g. high compression ratios. Due to the severity of the conditions e.g. with turbo charging or super charging the engine, aviation piston-driven engines require fuel of a minimum octane level higher than that for automotive internal combustion gasoline engines, in particular at least 98-100. The base fuel of an aviation gasoline has a motor octane number of 90-93.
15 To boost the motor octane number sufficiently to the required level, tetraethyl lead is added to the aviation base fuel. The fuel may contain the organolead and also other octane boosters, such as those described above. Industrial and Engineering Chemistry Vol. 36 No. 12 p1079-1084 dated 1944 describes the use of triptane (2,2,3-trimethylbutane) in combination with tetraethyl lead in aviation gasoline.
20 However, the presence of tetraethyl lead is the key to achieving high octane quality in aviation gasolines.

In modern day formulations tetraethyl lead is always used to boost the octane quality of the aviation gasoline to the desired level. However due to environmental concerns of the effect of lead and its compounds attempts are being
25 made to find an alternative to the use of tetraethyl lead in aviation gasoline.

Conventional octane boosters such as ethers, aromatics, such as toluene, and non-lead metal compounds can boost the motor octane number of unleaded motor gasoline sufficiently high enough to achieve the desired value but they do not boost the motor octane number of an unleaded aviation gasoline sufficiently high enough to ensure satisfactory performance or suffer from other significant technical limitations.

US 5470358 describes the use of aromatic amines to boost the motor octane number of unleaded aviation gasoline to at least 98 but many aromatic amines are known to be toxic. They have high boiling points, no supercharge properties and high freezing points; they are also prone to produce gums.

There remains a need for an unleaded aviation gasoline of sufficiently high octane number suitable for use in piston driven aircraft

According to the present invention there is provided an unleaded aviation fuel composition, having a Motor Octane Number of at least 98, and usually a final Boiling Point of less than 170°C, and preferably a Reid Vapour Pressure at 37.8°C of between 38-60 kPascals, which comprises:

component (a) at least one hydrocarbon having the following formula I



wherein R is hydrogen or methyl and component (b) at least one saturated liquid aliphatic hydrocarbon having 4 to 10 in particular 5 or 6 carbon atoms optionally with at least one other saturated liquid aliphatic hydrocarbon having from 5 to 10 carbon atoms wherein at least 30% by volume of the total composition is a hydrocarbon of formula I.

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

The composition may comprise apart from a component (I), the hydrocarbon of formula I, a component (II) which is at least one of the known octane boosters described above especially an oxygenate octane booster, usually an ether, usually of Motor Octane Number of at least 96-105 e.g. 98-103. The ether octane booster is usually a dialkyl ether, in particular an asymmetric one, preferably wherein each alkyl has 1-6 carbons, in particular one alkyl being a branched chain

alkyl of 3-6 carbons in particular a tertiary alkyl especially of 4-6 carbons such as tert-butyl or tert-amyl, and with the other alkyl being of 1-6 e.g. 1-3 carbons, especially linear, such as methyl or ethyl. Examples of component (II) include methyl tertiary butyl ether, ethyl tertiary butyl ether and methyl tertiary amyl ether.

5 The oxygenate may also be an alcohol of 1-6 carbons e.g. ethanol.

At least one component (I) may be present together with at least one component (II) in a combination. The combination may be, for example, triptane together with methyl tertiary butyl ether. The combination may be in a volume ratio of 40:60 to 99:1 e.g. 50:50 to 90 : 10, preferably 60:40 to 85:15. The volume
10 percentage of ether may be up to 30% of the total composition e.g. 1-30%, such as 1-15% or 5-25%.

The motor octane number of the aviation gasoline of the invention is at least 98, for example 98-103, preferably 99 to 102. Motor Octane Numbers are determined according to ASTM D 2700-92. The hydrocarbons of formula I may
15 also, especially when present in amount of at least 30% by volume, be used to provide gasolines of the invention with a Performance Number (according to ASTM D909) of at least 130 e.g. 130-170.

Triptane or 2,2,3 trimethylpentane may be used in a purity of at least 95% but is preferably used as part of a hydrocarbon mixture obtained, via distillation of
20 a cracked residue, which is an atmospheric or vacuum residue from crude oil distillation, to give a C₄ fraction containing olefin and hydrocarbon, alkylation to produce a C₄₋₉ especially a C₆₋₉ fraction which is distilled to give a predominantly C₈ fraction, which usually contains trimethyl pentanes including 223 trimethyl pentane and/or 233 trimethyl pentane. To produce triptane this fraction can be
25 demethylated to give a crude product comprising at least 5% of triptane, which can be distilled to increase the triptane content in the mixture; such a distillate may comprise at least 10% or 20% of triptane and 2,2,3 trimethylpentane but especially at least 50% e.g. 50-90% the rest being predominantly of other aliphatic C₇ and C₈ hydrocarbons e.g. in amount 10-50% by volume. Alternatively triptane and 2,2,3
30 trimethylpentane may be used in any commercially available form.

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

The amount of the hydrocarbon of Formula I alone or with component II may be present in the composition in an effective amount to boost the Motor
35 Octane Number to at least 98 and may be in a percentage of from 35-92%,

preferably 60-90%, especially 70-90% by volume, based on the total volume of the composition. In particular the compound of formula I is usually in the composition in a percentage of 5-90%, 10-80%, 20-60% more especially 30-50% by volume, based on the total composition, though amounts of the compound of formula I of
5 10-45% are also very valuable; preferred are 20-90% or 40-90% or 50-90% by volume.

The composition also comprises a component (b). Component (b) is at least one saturated aliphatic liquid hydrocarbon of 4 to 10 preferably 5 to 8 in particular 5 or 6 carbon atoms, alone or with at least one saturated aliphatic liquid
10 hydrocarbon (different from component(a)) having from 4 to 10 carbons in particular 5 to 10 carbon atoms, preferably 5 to 8 carbon atoms, especially in combination with one of 4 carbons. Component (b) may comprise a component (III) which is more volatile and has a lower boiling point than component (a) in particular one boiling at least 30°C such as 30-60°C below that of triptane at
15 atmospheric pressure, and especially is itself of Motor Octane Number greater than 88 in particular at least 90 e.g. 88-93 or 90-92. Examples of component (III) include alkanes of 5 carbons in particular iso-pentane, which may be substantially pure or a crude hydrocarbon fraction from alkylate or isomerate containing at least 30% e.g. 30-80% such as 50-70%, the main contaminant being up to 40% mono
20 methyl pentanes and up to 50% dimethyl butanes. Component (III) of boiling point 30-60°C less than that of triptane may be used as sole component (III) but may be mixed with an alkane of boiling point 60-100°C less than that of triptane e.g. n and/or iso butane in blends of 99.5:0.5 to 70:30, e.g. 88:12 to 75:25. Iso-pentane alone or mixed with n-butane is preferred, especially in the above proportions, and
25 in particular with a volume amount of butane in the composition of up to 3.5% e.g. 1-3.5% or 2-3.5%.

Component (b) may also comprise a component (IV) having a boiling point higher than component (a) preferably one boiling at least 20°C more than the compound of formula I e.g. triptane such as 20-60°C more than triptane but less
30 than 170°C and usually is of Motor Octane Number of at least 92 e.g. 92-100; such components (IV) are usually alkanes of 7-10 carbons especially 7 or 8 carbons, and in particular have at least one branch in their alkyl chain, in particular 1-3 branches, and preferably on an internal carbon atom and especially contain at least one -
C(CH₃)₂- group. An example of component (IV) is iso-octane.

35 Component (b) may be a combination of at least one component (III)

together with at least one component (IV). The combination may be, for example, butane or isopentane together with iso-octane, and the combination may be in a volume ratio of 10 : 90 to 90 : 10, preferably 10:50 to 50:90, especially 15:85 to 35:65, in particular with butane or especially isopentane together with iso-octane.
 5 Especially preferred is the combination of isopentane together with iso-octane, in particular, in the above proportions, and optionally butane.

In another preferred embodiment, triptane and isopentane and optionally n-butane are present in the composition of the invention with 80-90% triptane and in particular in relative volume ratios of 80-90:10-15:0-3.5.

10 In a preferred embodiment of this invention component (a) is 2,2,3 trimethylbutane and component (b) is isopentane in combination with iso-octane, preferably in relative volume ratios of 10-80 : 5-25 : 10:80 in particular 30-50 : 5-25 : 35-60 or 15-45 : 10-18 : 45-75 or 60-80 : 10-18 : 10-25. Especially the composition contains 30-80% of triptane and the isopentane and iso-octane are in a
 15 volume ratio of 35-15 : 65-85.

In a further preferred embodiment of this invention the composition comprises component (a) as 2,2,3 trimethylbutane, methyl tertiary butyl ether and component (b) as isopentane in combination with n-butane, preferably in relative volume ratios of 50-90 : 5-30 : 10-15 : 0.1-3.5 in particular 50-80 : 10-25 : 10-
 20 15 : 0.1-3.5.

If desired the composition may comprise an aromatic liquid hydrocarbon of 6-9 e.g. 6-8 or 7-9 carbons, such as xylene or a trimethyl benzene, preferably but toluene, in particular in amounts of up to 30% by volume of the total composition e.g. 1-30% or 5-15%. In this case a preferred embodiment is a composition that
 25 may thus contain 50-95% e.g. 50-80% triptane, 5-25% e.g. 10-25% component (b) e.g. isopentane and 5-30%, for example toluene. The benzene content of the composition is preferably less than 0.1% by volume.

In another preferred embodiment the composition may comprise both the aromatic hydrocarbon and the ether. In this case a preferred composition may
 30 comprise 45-80% triptane 5-30% ether (with a preferred total of both of 70-85%), 10-25% component (b) (III) e.g. iso-pentane (optionally containing butane) and 5-20% toluene, all by volume.

The compositions may also comprise 10-90% e.g. 25-85%, 35-80%, or 35-90% by volume of triptane, 5-75% e.g. 8-55% by volume of a mixture
 35 predominantly of iso C₇ and iso C₈ hydrocarbons, but usually with small amounts

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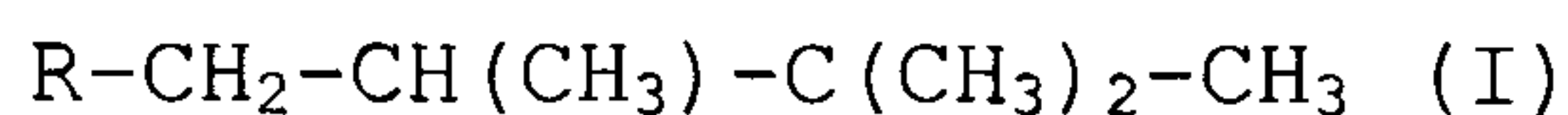
of iso C₆ and iso C₉ hydrocarbons and 5-40% e.g. 8-40% or 5-35% or 8-25% by volume isopentane. The triptane and mixture may be obtained as a distillation fraction obtained by the processing of crude oil and subsequent reactions as
5 described above.

The unleaded aviation gasoline composition of the invention usually has a calorific value (also called Specific Energy) of at least 42 MJ/kg (18075 BTU/lb) e.g. at least 43.5 MJ/kg (18720 BTU/lb) such as 42-46 or 43.5-45
10 MJ/kg. The gasoline usually has a boiling range (ASTM D86) of 25-170°C and is usually such that at 75°C 10-40% by volume is evaporated, at 105°C a minimum of 50% is evaporated, at 135°C a minimum of 90% is evaporated; the final boiling point is usually not more than 170°C
15 preferably 80-130°C. The gasoline usually has a maximum freezing point of -60°C in particular -40°C. The Reid Vapour Pressure of the gasoline at 37.8°C measured according to ASTM D323 is usually 30-60 kPa preferably 38-60 e.g. 38-55 or especially 38-49 or 45-55 kPa.

20 The composition of the invention may contain at least one aviation gasoline additive, for example as listed in ASTM D-910 or DEF-STAN 91-90; examples of additives are anti-oxidants, corrosion inhibitors, anti-icing additives e.g. glycol ethers or alcohols and anti-static additives,
25 especially antioxidants such as one or more hindered phenols; in particular the additives may be present in the composition in amounts of 0.1-100ppm e.g. 1-20ppm, usually of an antioxidant especially one or more hindered phenols. A coloured dye may also be present to differentiate the
30 aviation gasoline from other grades of fuel.

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In one aspect, the invention provides an unleaded aviation fuel having a Motor Octane Number of at least 98, and having a final boiling point of less than 170°C, which comprises: component (a) comprising at least one hydrocarbon
5 having the following formula I:



wherein R is hydrogen or methyl; and component (b) at least one saturated liquid aliphatic hydrocarbon having 5 or 6 carbon atoms, wherein at least 20% by volume of the total
10 composition is a hydrocarbon of formula I, together with at least one aviation gasoline additive selected from the group consisting of an anti-oxidant, a corrosion inhibitor, an anti-icing additive and an anti-static additive.

The compositions of the invention are unleaded and
15 have reduced toxicity, and are suitable for use in aviation gasoline for piston engine aircraft. Aromatic amines e.g. m-toluidine are usually substantially absent.

The invention will be illustrated by way of the following Examples

20 Example 1

An unleaded aviation gasoline was made by mixing 2,2,3 trimethylbutane of 99% purity with iso-pentane and iso-octane to give a composition consisting of 2,2,3 trimethylbutane 40%, isopentane 12%, and iso-octane 48%
25 expressed in volume percentages of the total gasoline.

The motor octane number (MON) of the gasoline was 99.9 as determined by ASTM D2700-92 and the Reid Vapour Pressure was 33 kPa.

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Example 2

An unleaded aviation gasoline contained the gasoline of Ex. 1 with 8 mg/l of

a mixture of 75% 2,6-ditertiary, butyl phenol and 25% tertiary and tri tertiary, butyl phenols, as antioxidant.

Example 3

An unleaded aviation gasoline was made from a crude triptane fraction. A
5 cracked residue from the distillation of crude oil was distilled to give a C₄ fraction
containing olefin and saturates. The fraction was alkylated (i.e. self reacted) to
form a crude C₈ saturate which was distilled to give a fraction boiling 95-120°C,
which contained 223 and 233 trimethyl pentane. This fraction was demethylated
by reduction to give a first fraction containing about 17% triptane and 83% iso C₆-
10 C₉ with a majority of iso C₇ and iso C₈ hydrocarbons. This first fraction was
redistilled to produce a second fraction of 87% triptane and 13% iso C₇ and C₈.

90 parts by volume of this second fraction was mixed with 10 parts of
isopentane to give an unleaded aviation gasoline of MON value 99.1. Addition of
8mg/l of the phenol mixture of Ex.2 gave an oxidation stabilized unleaded aviation
15 gasoline fuel.

Example 4

The process of Example 3 was repeated with the first fraction containing
the 17% triptane redistilled to give a third fraction containing 37% triptane and
63% iso C₇ and C₈. 82 parts by volume of this third fraction were mixed with 18
20 parts of isopentane to give an unleaded aviation gasoline of MON value 98.0.
Addition of the phenol mixture as in Ex.3 gave an oxidation stabilised aviation
gasoline fuel.

Examples 5-9

In these Examples 2,2,3 trimethylbutane (triptane) 99% purity was mixed with iso-
25 pentane and butane, and optionally toluene and/or methyl tertiary butyl ether, to
produce a series of gasoline blends, for making unleaded aviation gasolines.

The formulated gasolines were made by mixing each blend with a phenolic
antioxidant 55% minimum 2,4 dimethyl-6-tertiary butyl phenol 15% minimum 4
methyl-2, 6-ditertiary-butyl phenol with the remainder as a mixture of monomethyl
30 and dimethyl-tertiary butyl phenols (DEF STAN 91-90 RDE/A/610).

In each case the gasolines were tested for Motor Octane Number, and their
Reid Vapour Pressure at 37.8°C and their calorific value, and their distillation
properties and freezing point. In addition for Example 10 the Indicated Mean
Effective Pressure (IMEP) was determined (according to ASTM D909) to give the
35 Supercharge Performance Number. The results are shown in table 1.

Table 1

Example	5	6	7	8	9
Composition % v/v					
Triptane	85.0	73.0	53.0	87.8	87.0
Isopentane	12.0	14.0	14.0	12.0	11.8
Butane	3.0	3.0	3.0	0.2	1.2
Toluene	-	10.0	10.0	-	-
MTBE	-	-	20.0	-	-
Antioxidant mg/l	15	15	24	17	15
Distillation °C					
Initial Boiling Point	43.0	41.0	36.5	47.5	46.5
T10%	63.5	63.5	57.0	68.0	67.0
T40%	77.0	79.0	69.9	76.5	77.0
T50%	78.5	81.5	73.8	78.5	79.0
T90%	80.5	87.5	88.4	80.5	81.0
Final Boiling Point	115.0	116.0	107.7	80.5	90.0
Reid Vapour Pressure kPa	51.3	52.5	58.3	40.4	46.3
MON	99.8	98.3	98.0	99.7	99.8
Freezing point °C	-54	<-80	<-80	-49	-51.5
Supercharge (IMEP)	-	-	-	-	>160
Specific energy MJ/kg	44.5	44.1	42.1	44.5	44.5

T 10% means the temperature at which 10% by volume of the composition has
5 distilled.

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CLAIMS:

1. An unleaded aviation fuel composition, having a Motor Octane Number of at least 98, and having a final boiling point of less than 170°C, which comprises:

5 component (a) comprising at least one hydrocarbon having the following formula I:



wherein R is hydrogen or methyl; and

10 component (b) at least one saturated liquid aliphatic hydrocarbon having 5 or 6 carbon atoms, wherein at least 30% by volume of the total composition is a hydrocarbon of formula I.

2. A composition according to claim 1, wherein the hydrocarbon of formula I is triptane.

15 3. A composition according to claim 1 or 2, having a Reid Vapour Pressure at 37.8°C of 38-60 kPascals.

4. A composition according to claim 3, with a Reid Vapour Pressure of 38-49 kPascals.

20 5. A composition according to any one of claims 1 to 4, wherein component (b) comprises a component (III) which is more volatile and has a lower boiling point than triptane.

6. A composition according to claim 5, wherein component (III) has a Motor Octane Number greater than 88.

25 7. A composition according to claim 5 or 6, wherein component (III) comprises iso-pentane.

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8. A composition according to claim 7, wherein the fuel composition comprises 5-40% by volume of iso-pentane.

9. A composition according to claim 8, which comprises 5-25% by volume of iso-pentane.

5 10. A composition according to any one of claims 7 to 9, wherein component (III) further comprises butane.

11. A composition according to any one of claims 1 to 10, wherein the fuel composition comprises 0.1-3.0% by volume of n-butane.

10 12. A composition according to any one of claims 5 to 11, wherein component (b) comprises in addition to component (III) a component (IV) having a boiling point higher than triptane but less than 170°C.

13. A composition according to claim 12, wherein
15 component (IV) has a Motor Octane Number of at least 92.

14. A composition according to claim 12 or 13, wherein component (IV) is iso-octane.

15. A composition according to any one of claims 1 to 14, wherein the composition comprises up to 30% by volume
20 of an aromatic liquid hydrocarbon of 6-8 carbons.

16. A composition according to claim 15, wherein the composition comprises 5-30% by volume of toluene.

17. A composition according to any one of claims 1 to 16, which comprises as a component (I) said hydrocarbon
25 having the formula I and as a component (II) an oxygenate octane booster.

18. A composition according to claim 17, wherein the component (II) is an ether.

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19. A composition according to claim 18, wherein the ether is methyl tertiary butyl ether.

20. A composition according to claim 19, wherein 35-92% by volume of the total composition is the combined volume of the hydrocarbon of formula I and methyl tertiary butyl ether.

21. A composition according to any one of claims 1 to 9, which comprises 80-90% of triptane, with isopentane and optionally butane.

22. A composition according to claim 1, which comprises 30-80% of triptane, and also isopentane and iso-octane, the volume ratio of isopentane to iso-octane being 35-15:65-85.

23. A composition according to claim 1, which comprises toluene in an amount up to 30% by volume of the total composition.

24. A composition according to claim 23, which comprises 0-15% methyl tertiary butyl ether.

25. A composition according to any one of claims 1 to 24, which has a calorific value of at least 42 MJ/kg.

26. A composition according to claim 25, which has a calorific value of at least 43.5 MJ/kg.

27. A composition according to any one of claims 1 to 26, wherein the Performance Number for supercharging is at least 130.

28. An unleaded aviation fuel having a Motor Octane Number of at least 98, and having a final boiling point of less than 170°C, which comprises:

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component (a) comprising at least one hydrocarbon having the following formula I:



wherein R is hydrogen or methyl; and

5 component (b) at least one saturated liquid aliphatic hydrocarbon having 5 or 6 carbon atoms, wherein at least 20% by volume of the total composition is a hydrocarbon of formula I, together with at least one aviation gasoline additive selected from the group
10 consisting of an anti-oxidant, a corrosion inhibitor, an anti-icing additive and an anti-static additive.

29. A fuel according to claim 28, wherein the antioxidant is one or more hindered phenols.

30. Use of an unleaded aviation fuel according to
15 claim 28 or 29, in an aircraft piston driven engine.

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