# (19) World Intellectual Property Organization International Bureau





## (43) International Publication Date 26 July 2001 (26.07.2001)

**PCT** 

# (10) International Publication Number WO 01/53436 A1

(51) International Patent Classification7: C10L 1/18, 1/06

(21) International Application Number: PCT/SE00/00139

(22) International Filing Date: 24 January 2000 (24.01.2000)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant and

(72) Inventor: GOLUBKOV, Angelica [SE/SE]; Fjällvägen 3b, S-181 31 Lidingö (SE).

(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL,

IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### **Published:**

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



#### (54) Title: MOTOR FUEL FOR SPARK IGNITION INTERNAL COMBUSTION ENGINES

(57) Abstract: A motor fuel for standard spark ignition internal combustion engines consisting of: min 84.9% by volume of hydrocarbon component of  $C_3$ - $C_{12}$  fraction, without restriction on the presence of hydrocarbons of arbitrary structure and of sulfur, max 15% by volume of fuel grade ethanol, and min 0.1% by volume of oxygen-containing substance, chosen from the following classes of organic compounds; alcohols, ketones, ethers, esters, aldols, ketone esters and heterocyclics. As the source of the hydrocarbon component for motor fuel compositions, the present invention enables the use of standard gasolines and other hydrocarbon liquids obtained in petroleum refining, processing of natural gas, synthesis-gas, and coke production. The fuel composition formulated in accordance with the formula of the present invention enables a lowering of the dry vapour pressure equivalent of the motor fuel, an increase in the anti-knock index, a decrease in the level of toxic emissions in the exhaust and a decrease in the fuel consumption. The properties of the motor fuels reached in the embodiment of this invention and production method are also disclosed. The present invention expands the possibilities for the use of renewable resources for motor fuel production.

## MOTOR FUEL FOR SPARK IGNITION INTERNAL COMBUSTION ENGINES

## Field of the invention

5

15

25

This invention relates to motor fuel for spark ignition internal combustion engines. The motor fuel consists of a hydrocarbon liquid, ethanol, and components for adjusting the dry vapor pressure equivalent (DVPE) of the resulting fuel composition. The ethanol and DVPE adjusting components used to obtain the fuel composition are derived preferably from renewable raw materials.

Additionally, this invention relates to motor fuel meeting standard requirements for spark ignition internal combustion engines operating with gasoline.

### 10 Background of the invention

Gasoline is a 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.

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

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.

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.

US Patent No. 2,365,009 dated 1944 describes the combination of  $C_{1-5}$  alcohols and  $C_{3-5}$  hydrocarbons for use as a fuel.

In US Patent No. 4,818,250 granted in 1989 the author proposes the use of limonene obtained from citrus and other plants as a motor fuel, or as a component in blends with gasoline.

5

10

15

20

be produced from renewable resources.

In US Patent No. 5,607,486 granted in 1997 the author discloses novel engine fuel additives comprising terpenes, aliphatic hydrocarbons, and lower alcohols.

Currently *tert*-butyl ethers are widely used as components of gasolines. Motor fuels comprising *tert*-butyl ethers are described in US Patent No. 4,468,233 granted in 1984. The major part of these ethers is obtained from petroleum refining, but they can equally

Ethanol is the 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 its turn derives from carbon dioxide under the influence of solar energy.

The combustion of ethanol produces significantly less harmful substances in comparison to the combustion of gasoline. However, the use of motor fuel consisting mainly of ethanol requires specially designed engines. At the same time many producers of spark ignition internal combustion engines operating on gasoline confirm the possibility of operating standard engines with a motor fuel comprising a mixture of gasoline and not more than 10% by volume of ethanol. Such a mixture of gasoline and ethanol is presently sold in USA under the trademark "gasohol".

European regulations concerning gasolines allow the addition to gasoline of up to 5% by volume of ethanol.

The major disadvantage of mixtures of ethanol and gasoline is that for mixtures up to 15% by volume of ethanol there is an increase in the dry vapor pressure equivalent compared with that of the original gasoline.

Figure 1 shows the behavior of the dry vapor pressure equivalent (DVPE) as a function of the ethanol content of mixtures of ethanol and gasoline A92 summer, and gasoline

10

15

20

25

PCT/SE00/00139

A95 summer and winter, at 37.8°C. The gasolines are standard gasolines purchased at gas stations in USA and Sweden. The gasoline A92 originated from USA, and the gasolines A95 from Sweden. The ethanol is fuel grade ethanol produced by Williams, USA. The DVPE of the mixtures was determined, according to the standard ASTM D 5191 method at SGS laboratory in Stockholm, Sweden.

For the range of concentrations by volume of ethanol between 5-10%, which is of particular interest for use as a motor fuel for standard spark ignition engines, the data in fig.1 shows, that the DVPE of mixtures of gasoline and ethanol, can exceed the DVPE of source gasoline by more than 10%. Since the oil 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 gasolines becomes impossible.

It is known that the DVPE of mixtures of gasolines and ethanol can be adjusted. US Patent No. 5,015,356 granted on May 14, 1991 proposes reformulating gasoline by removing both the volatile and non-volatile components from C<sub>4</sub>-C<sub>12</sub> gasoline to yield either C<sub>6</sub>-C<sub>9</sub> or C<sub>6</sub>-C<sub>10</sub> intermediate gasolines. The fuels of this invention better facilitate the addition of alcohol over current gasolines because of their lower dry vapor pressure equivalent (DVPE). The disadvantage of this method of adjusting the DVPE of mixtures of gasoline and ethanol is that to obtain such a mixture it is necessary to produce special gasoline which affects the supply chain and results in increased prices for the motor fuel.

It is known that some chemical compounds decrease DVPE when added to gasoline or to its mixture with ethanol.

The author of US Patent No. 5,433,756 granted on July 18, 1995 discloses chemical clean-combustion-promoter compounds comprising, in addition to gasoline, ketones, nitroparaffin, and also alcohols other than ethanol. The author notes that the composition of the catalytic clean-combustion-promoter disclosed in the patent reduces the DVPE of gasoline fuel. Nothing is mentioned in this patent about the impact of the clean-combustion-promoter composition on the DVPE of mixtures of gasoline and ethanol.

US 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 between 20-70% alcohol, between 2.5-20% ketone and ether, between 0.03-20% aliphatic and silicon compounds, between 5-20% toluene, and between 4-45% mineral spirits. The alcohols are methanol and 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 the following:

5

- 10 the need for large quantities of the additive, namely not less than 15% by volume of the mixture; and
  - the use of silicon compounds, producing silicon oxide when combusting, which results in increased engine wear.

The motor fuel DVPE adjustment method which is the closest to this invention is described in US Patent No. 5,697,987 granted on December 16, 1997. The patent discloses a spark ignition motor fuel composition consisting essentially of a hydrocarbon component of C<sub>5</sub>-C<sub>7</sub> straight-chained or branched alkanes essentially free of olefins, aromatics, benzene and sulfur, in which the hydrocarbon component has a minimum anti-knock index of 65, according to ASTM D 2699 and D 2700 and a maximum DVPE of 15 psi, according to ASTM D 5191; a fuel grade alcohol; and a cosolvent 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 65 and a maximum DVPE of 15 psi. In this fuel composition the co-solvent for the hydrocarbon component and ethanol is biomass-derived 2-methyltetrahydrofuran.

The disadvantages of this way of adjusting the dry vapor pressure equivalent of mixtures of hydrocarbon liquid and ethanol are the following:

- it is possible to use only hydrocarbon components C<sub>5</sub>-C<sub>7</sub> which are straight-chained or branched alkanes, free of unsaturated compounds, namely olefins, benzene, and

other aromatics, free of sulfur and as follows from the description of the invention, the hydrocarbon component is a coal gas condensate or natural gas condensate;

5

- it is possible to use as a co-solvent of the hydrocarbon component and ethanol only one particular class of chemical compounds containing oxygen, namely ethers, including short-chained and heterocyclic;
- the need to use a large quantity of ethanol, not less than 25%;
- the need to use a large quantity of co-solvent, not less than 20% of 2-methyltetrahydrofuran; and
- the need to modify the spark ignition internal combustion engine when operating
   with such fuel composition as proposed in the above invention, and specifically the need to change the software of the on-board computer or replace the on-board computer itself.

### Summary of the invention

5

Accordingly, a need exists for alternative motor fuels for standard spark ignition internal combustion engines which allow such engines to have the same maximum performance as when operating with standard gasoline currently on the market.

There is a need for using up to 10% by volume of fuel grade ethanol in the compositions of the alternative motor fuels.

There is a need for using compounds obtained from renewable raw material as components of the alternative motor fuels.

There is a need to be able to adjust the dry vapor pressure equivalent (DVPE) and the anti-knock index (octane number), as well as other performance parameters of motor fuels in accordance with the requirements set forth by the quality standards for motor fuel for spark ignition internal combustion engines.

All of these needs are satisfied by the present invention.

The present invention for obtaining the motor fuel enables the use of  $C_3$ - $C_{12}$  hydrocarbon fractions, including narrower ranges within this range, without restriction

on the presence of saturated and unsaturated hydrocarbons, aromatics, and sulfur. 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 carbonization, natural gas, and synthesis gas.

5

10

15

The present invention enables the use of up to 15% by volume of ethanol in mixtures with the aforesaid hydrocarbon component to obtain the motor fuel, and to maintain the dry vapor pressure equivalent of the resulting fuel composition or to lower it in comparison to the level of the dry vapor pressure equivalent of the source hydrocarbon component, by means of adding to the motor fuel composition at least one oxygencontaining organic compound, chosen from the group of substances disclosed in the claims of the present invention.

The present invention enables the adjustment of the dry vapor pressure equivalent, the anti-knock index and other performance parameters of the motor fuel, the reduction of the fuel consumption and the reduction of toxic substances in the engine exhaust emissions by adding to the fuel composition compounds containing oxygen bound in the following functional groups:

and chosen from the following classes of organic compounds: alcohols, ketones, ethers.

20 esters, aldols a.k.a. hydroxy-aldehydes and hydroxy-ketones, ketone esters, and heterocyclics.

10

In a first embodiment of the invention to obtain a motor fuel suitable for operation of a standard spark ignition internal combustion engine it is necessary to use the aforesaid hydrocarbon component in the amount of at least 84.9% by volume of the fuel composition, ethanol in the amount of not more than 15% by volume of the fuel composition, and additional oxygen-containing components in the amount of at least 0.1% by volume of the fuel composition.

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 it is necessary to mix the aforesaid hydrocarbon component, ethanol, and additional oxygencontaining component in a way to secure the following properties of the resulting fuel composition:

- density at 15°C and at normal atmospheric pressure not less than 690 kg/m<sup>3</sup>;
- oxygen content, based on the amount of oxygen-containing components, not more than 7% w/w of the motor fuel composition;
- anti-knock index (octane number) not lower than anti-knock index (octane number)
   of the source hydrocarbon component, preferably for 0.5(RON+MON) to be not less than 80;
  - dry vapor pressure equivalent (DVPE) not higher than DVPE of the source hydrocarbon component, preferably within limits from 20kPa to 120kPa;
- 20 acid content, not more than 0.1% by mass HAc;
  - pH, minimum 5 and maximum 9;
  - aromatic hydrocarbons content, not more than 40% by volume, including benzene; 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 of the liquid evaporated at 70°C, min

25% by volume;

8

- volume of the liquid evaporated at 100°C, min 50% by volume;

- volume of the liquid evaporated at 150°C, min 75% by volume;

- volume of the liquid evaporated at 180°C, min 95% by volume;

- residue of distillation, max 2% by volume;

5 - final boiling point, max 205°C;

- sulfur content, not more than 50mg/kg;

- resins content, not more than 2mg/100ml.

According to a preferred embodiment of the invention to obtain motor fuel suitable for operating a standard spark ignition internal combustion engine the aforesaid hydrocarbon component should be first mixed with ethanol, followed by the addition of the additional oxygen-containing compound or compounds to the mixture. Afterwards, the resulting fuel composition should be kept at a temperature not lower than -35°C, for at least one hour.

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

As examples demonstrating the efficiency of the present invention the following fuel compositions are presented.

## 20 Examples

10

15

The examples of motor fuel compositions for spark ignition internal combustion engines described below 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.

25 1. A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of a hydrocarbon component, which in

25

this composition is a standard gasoline, with fuel grade ethanol, by means of preparation of a three-component mixture with an additional oxygen-containing component, which in this composition are alcohols.

Additionally, composition 1 demonstrates the possibility of adjusting the anti-knock index (octane number) of the motor fuel.

To prepare the formulations of this composition, a standard gasoline purchased in Sweden at OKQ8 gasoline stations, fuel grade ethanol produced by Williams, USA, and technical grade alcohols produced in Russia were used.

The source gasoline A95 summer had the following specification:

- range of hydrocarbons, including saturated and

unsaturated and aromatics  $C_4$ - $C_{12}$ ;

- 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 89.8

The gasoline A95 summer of composition 1 was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F. 4-cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

CO 2.198g/km;
 HC 0.245g/km;
 NO<sub>x</sub> 0.252g/km;

- CO<sub>2</sub> 230.0g/km;

- NMHC 0.283g/km;

Fuel consumption, F<sub>c</sub> 1/100km 9.95

The initial mixture contained 90% by volume of gasoline A95 summer, and 10% by volume of ethanol. The mixture was characterized as follows:

- oxygen content

3.68% w/w;

- DVPE, according to ASTM D 5191

74.5kPa;

5 - anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

92.2

The mixture of 90% by volume of gasoline A95 summer, and 10% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69.

The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 1:

	-	CO	-9.1%;
	-	НС	-4.5%;
	-	$NO_x$	7.3%;
15	-	$CO_2$	4.0%;
	-	NMHC	-4.4%;
	_	Fuel consumption, F <sub>c</sub> 1/100km	3.6%

Formulation 1-1 containing 86.2% by volume of gasoline A95 summer, 6.9% by volume of ethanol, and 6.9% by volume of butanol had the following properties:

20 oxygen content

3.8% w/w;

- DVPE, according to ASTM D 5191

69kPa;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

91.8

Formulation 1-2 containing 85% by volume of gasoline A95 summer, 10% by volume of ethanol, and 5% by volume of 2-ethylhexanol had the following properties:

4.34% w/w; - oxygen content

69kPa; - DVPE, according to ASTM D 5191 5

- anti-knock index 0.5(RON+MON), according to

10

92.5 ASTM D 2699-86 and ASTM D 2700-86

Formulation 1-3 containing 86.3% by volume of gasoline A95 summer, 6.3% by volume of ethanol, and 7.4% by volume of n-amyl alcohol had the following properties:

3.76% w/w; - oxygen content

69kPa; - DVPE, according to ASTM D 5191

anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86 90.8

Formulation 1-4 contained 87% by volume of gasoline A95 summer, 6.5% by 15 volume of ethanol, and 6.5% by volume of isoamyl alcohol. It demonstrated the possibility of maintaining the dry vapor pressure equivalent at the same level as the source gasoline, whilst increasing the octane number, decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the initial mixture of gasoline and ethanol. It had the following properties: 20

 $754.1 \text{ kg/m}^3$ ; density at 15°C, according to ASTM D 4052

- initial boiling point, according to ASTM D 86 26.6°C;

> 45.2% by volume; vaporizable portion at 70°C

> 56.4% by volume; vaporizable portion at 100°C

88.8% by volume; vaporizable portion at 150°C 25

12

	vaporizable portion at 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;
5	- oxygen content, according to ASTM D4815	3.63% w/w;
	- acidity, according to ASTM D1613 mass % HAc	0.007;
	- pH, according to ASTM D1287	8.9;
	- sulfur content, according to ASTM D 5453	16mg/kg;
	- gum content, according to ASTM D381	<1mg/100ml;
10	- water content, according to ASTM D6304	0.12% w/w;
	- aromatics, according to SIS 155120,	
	including benzene	30.3% by volume;
	benzene alone, according to	
	EN 238	0.8% by volume;
15	- 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
20	The motor fuel formulation 1-4 was tested in accordance 2000 NEDC EC 98/69. The testing was performed on the 1987, with the engine B230F, No. LG4F20-87, gave the f with the reference fuel for composition 1:	car Volvo 240 DL, model
		8%;

- HC

-8.5%;

-	$NO_x$	5.3%;
-	CO <sub>2</sub>	2.8%;
-	NMHC	-9%;
-	Fuel consumption, F <sub>c</sub> l/100km	3.1%.

- To prepare all the above formulations of this fuel composition, firstly, gasoline A95 was mixed with ethanol, to which mixture was then added the corresponding alcohol. The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.
- 2. A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of a hydrocarbon component, which in this composition is a standard gasoline, with fuel grade ethanol, by means of a preparation of a three-component mixture with an additional oxygen-containing component, which in this composition are ketones.
- Additionally, the present composition demonstrates the possibility of adjusting the anti-knock index (octane number) of the motor fuel.

To prepare the formulations of this composition a standard gasoline purchased in Sweden at Shell gasoline stations, fuel grade ethanol produced by Sekab, Sweden. and technical grade ketones produced in Russia were used.

89.5kPa;

- The source gasoline A95 winter had the following properties:
  - range of hydrocarbons, including

- DVPE, according to ASTM D 5191

saturated and unsaturated  $C_4$ - $C_{10}$ ;

- anti-knock index 0.5(RON+MON), according to

25 ASTM 2699-86 and ASTM 2700-99 89.4

14

The gasoline A95 winter of composition 2 was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

	-	СО	2.13g/km;
	-	НС	0.280g/km;
	-	NO <sub>x</sub>	0.265g/km;
10	-	$CO_2$	227.0g/km;
	-	NMHC	0.276g/km;
	-	Fuel consumption, F <sub>c</sub> 1/100km	9.84

5

20

The initial mixture contained 90% by volume of gasoline A95 winter, and 10% by volume of ethanol. The mixture was characterized as follows:

- oxygen content
- DVPE, according to ASTM D 5191
- anti-knock index 0.5(RON+MON), according to
ASTM D 2699-86 and ASTM D 2700-86
92.7

The mixture of 90% by volume of gasoline A95 winter, and 10% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 2:

	- CO	-15%;
25	- HC	-7.3%;
	- NO <sub>x</sub>	15.5%;

PCT/SE00/00139

15

- CO <sub>2</sub>	2.42%;
- NMHC	-0.5%;
- Fuel consumption, F <sub>c</sub> l/100km	4.7%

Formulation 2-1 containing 86% by volume of gasoline A95 winter, 7% by volume of ethanol, and 7% by volume of 3-heptanone had the following properties:

-	oxygen content	3.79% w/w;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

WO 01/53436

92.6

Formulation 2-2 containing 88% by volume of gasoline A95 winter, 5% by volume of ethanol, and 7% by volume of diisopropyl ketone had the following properties:

_	oxygen content	3.02% w/w;
-	oxygen content	3.02% w/w

- anti-knock index 0.5(RON+MON), according to

Formulation 2-3 containing 88% by volume of gasoline A95 winter, 5% by volume of ethanol, and 7% by volume of 2-octanone had the following properties:

-	oxygen content	2.91% w/w;
---	----------------	------------

- anti-knock index 0.5(RON+MON), according to

Formulation 2-4 contained 85.5% by volume of gasoline A95 winter, 7.5% by volume of ethanol, and 7% by volume of this diisobutyl ketone. It demonstrated the possibility of decreasing the dry vapor pressure equivalent, increasing the octane

number, decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the initial mixture of gasoline and ethanol. It had the following properties:

	-	density at 15°C, according to ASTM D 4052	719.2kg/m <sup>3</sup> ;
5	-	initial boiling point, according to ASTM D 86	29°C;
		vaporizable portion at 70°C	47.6% by volume;
		vaporizable portion at 100°C	55.6% by volume;
		vaporizable portion at 150°C	84.2% by volume;
		vaporizable portion at 180°C	97.5% by volume;
10		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	3.75% w/w;
	-	acidity, according to ASTM D1613 mass % HAc	0.004;
15	-	pH, according to ASTM D1287	6.6;
	-	sulfur content, according to ASTM D 5453	18mg/kg;
	-	gum content, according to ASTM D381	lmg/100ml;
	-	water content, according to ASTM D6304	0.03% w/w;
	-	aromatics, according to SIS 155120,	
20		including benzene	30.2% by volume;
		benzene alone, according to	
		EN 238	0.7% by volume;
	-	DVPE, according to ASTM D 5191	90.3kPa;

WO 01/53436

5

15

PCT/SE00/00139

17

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

93

The motor fuel formulation 2-4 was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 2:

	-	CO	-21%;
	-	НС	-9%;
	-	NO <sub>x</sub>	12.8%;
10	-	$CO_2$	2.38%;
	-	NMHC	-6.4%;
	_	Fuel consumption, F <sub>c</sub> 1/100km	3.2%.

To prepare all the above formulations of this fuel composition, firstly, gasoline A95 was mixed with ethanol, to which mixture was then added the corresponding ketone. The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.

- A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of hydrocarbon components (HCC).
   which in this composition are a standard gasoline, a hydrocarbon fraction of reformulated gasoline, and a hydrocarbon fraction of natural gas condensate, with biochemical technical grade ethanol, by means of a preparation of a three-component mixture with an additional oxygen-containing component, which in this composition are ethers.
- Additionally, the composition 3 demonstrates the possibility of adjusting the antiknock index (octane number) and other performance properties of the motor fuel.

20

To prepare the formulations of this composition a standard gasoline purchased in Sweden at Shell gasoline stations, reformulated gasoline produced in Sweden by Preem Petroleum AB, and a hydrocarbon fraction of natural gas condensate produced in Russia were used.

5 Additionally, ethanol and ethers of biochemical origin produced in Russia were used.

The hydrocarbon component (HCC) for this motor fuel composition was prepared, initially, by mixing of 85% by volume of gasoline A95 winter and 15% by volume of gas condensate hydrocarbon liquid. After preparation the hydrocarbon component (HCC) was allowed to stand for 24 hours. The resulting component was characterized as follows:

- range of hydrocarbons, including saturated and

unsaturated  $C_3$ - $C_{10}$ ;

- DVPE, according to ASTM D 5191 114kPa;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86 91.5

The hydrocarbon component (HCC) of composition 3 was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

	- CO	2.033g/km;
	- НС	0.279g/km;
25	- NO <sub>x</sub>	0.297g/km;
	- CO <sub>2</sub>	229.5g/km;
	- NMHC	0.255g/km;

PCT/SE00/00139

5

10

19

-	Fuel consumption, F <sub>c</sub> 1/100	km 9.89

The initial mixture comprising 95% by volume of the aforesaid hydrocarbon component (HCC), and 5% by volume of ethanol was characterized as follows:

oxygen content 2% w/w;
DVPE, according to ASTM D 5191 120.5kPa;
anti-knock index 0.5(RON+MON), according to
ASTM 2699-86 and ASTM 2700-86 93

The initial mixture comprising 95% by volume of the aforesaid hydrocarbon component (HCC), and 5% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 3:

	-	СО	-6.98%;
	-	НС	-7.3%;
15	-	$NO_x$	12.1%;
	•	$CO_2$	1.1%;
	-	NMHC	-5.3%;
	_	Fuel consumption, F <sub>c</sub> 1/100km	2.62%

Formulation 3-1 containing 90% by volume of HCC, 5% by volume of ethanol, and 5% by volume of dissobutyl ether had the following properties:

-	oxygen content	2.68% w/w;
-	DVPE, according to ASTM D 5191	116.5kPa;
-	anti-knock index 0.5(RON+MON), according to	
	ASTM D 2699-86 and ASTM D 2700-86	93.8

Formulation 3-2 containing 90% by volume of HCC, 5% by volume of ethanol, and 5% by volume of *tert*-butyl isobutyl ether had the following properties:

- oxygen content	2.68% w/w;
- DVPE, according to ASTM D 5191	116.1kPa;

5 - anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86 93.6

Formulation 3-3 containing 90% by volume of HCC, 5% by volume of ethanol, and 5% by volume of ethyl isobornyl ether had the following properties:

	- oxygen content	2.55% w/w;
10	- DVPE, according to ASTM D 5191	113.8kPa;
	- anti-knock index 0.5(RON+MON), a	ccording to
	ASTM D 2699-86 and ASTM D 270	0-86 93.5

Formulation 3-4 contained 85% by volume of HCC, 8% by volume of ethanol, and 7% by volume of diisoamyl ether. It demonstrated the possibility of decreasing the dry vapor pressure equivalent, increasing the octane number, decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the initial mixture of gasoline and ethanol. It had the following properties:

	- density at 15°C, according to ASTM D 4052	$690.4 \text{kg/m}^3;$
	- initial boiling point, according to ASTM D 86	20.5°C;
20	vaporizable portion at 70°C	47.6% by volume;
	vaporizable portion at 100°C	65.3% by volume;
	vaporizable portion at 150°C	93.4% by volume;
	vaporizable portion at 180°C	97.1% by volume;
	final boiling point	199.6°C;

	evaporation residue	1.3% by volume;
	loss by evaporation	0.7% by volume;
	- oxygen content, according to ASTM D4815	3.97% w/w;
	- acidity, according to ASTM D1613 mass % HAc	0.001;
5	- pH, according to ASTM D1287	7.0;
	- sulfur content, according to ASTM D 5453	18mg/kg;
	- gum content, according to ASTM D381	2mg/100ml;
	- water content, according to ASTM D6304	0.01% w/w;
	aromatics, according to SIS 155120,	
10	including benzene	30.9% by volume;
	benzene alone, according to	
	EN 238	0.7% by volume;
	- DVPE, according to ASTM D 5191	115.1kPa;
	- anti-knock index 0.5(RON+MON), according	
15	ASTM D 2699-86 and ASTM D 2700-86	93.2;
	The motor fuel formulation 3-4 was tested in accordant 2000 NEDC EC 98/69. The testing was performed on the 1987, with the engine B230F, No. LG4F20-87, gave the with the reference fuel for composition 3:	ne car Volvo 240 DL, model
20	- CO	-14%;
	- НС	-7.3%;
	- NO <sub>x</sub>	no change;
	- CO <sub>2</sub>	2.6%;

15

20

25

22

- NMHC -8.6%;

Fuel consumption, F<sub>c</sub> l/100km 2.7%.

To prepare all the above formulations of this fuel composition, firstly, the hydrocarbon component (HCC) was mixed with ethanol, to which mixture was then added the corresponding ether. The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.

4. A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of hydrocarbon components, which in this composition are a standard gasoline, a hydrocarbon fraction of reformulated gasoline, and a hydrocarbon fraction derived from synthesis-gas, with biochemical technical grade ethanol, by means of preparation of a three-component mixture with an additional oxygen-containing component, which in this composition are esters.

Additionally, composition 4 demonstrates the possibility of adjusting the anti-knock index (octane number) and other performance properties of the motor fuel.

To prepare the formulations of this composition a standard gasoline purchased in Sweden at Shell gasoline stations, reformulated gasoline produced in Sweden by Preem Petroleum AB, and hydrocarbon fraction derived from synthesis-gas produced in Russia were used. Additionally, ethanol and esters of biochemical origin produced in Russia were used.

The hydrocarbon component (HCC) for this composition was prepared by, initially. mixing 50% by volume of gasoline A95 winter, 35% by volume of reformulated gasoline, and 15% by volume of hydrocarbon liquid derived from synthesis-gas. After mixing the hydrocarbon component was allowed to stand for 24 hours. The resulting component was characterized as follows:

- range of hydrocarbons, saturated
  and unsaturated, including aromatics

  C<sub>4</sub>-C<sub>11</sub>;
- DVPE, according to ASTM D 5191 69.5kPa;

23

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

5

25

92.2

The hydrocarbon component (HCC) of composition 4 was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

	-	CO	2.175g/km;
10	-	НС	0.269g/km;
	-	NO <sub>x</sub>	0.305g/km;
	-	CO <sub>2</sub>	230.8g/km;
	-	NMHC	0.243g/km;
	-	Fuel consumption, F <sub>c</sub> 1/100km	9.96

The initial mixture comprising 95% by volume of the aforesaid hydrocarbon component (HCC), and 5% by volume of ethanol was characterized as follows:

- oxygen content 1.85% w/w;

- DVPE, according to ASTM D 5191 77.5kPa;

- anti-knock index 0.5(RON+MON), according to

20 ASTM 2699-86 and ASTM 2700-86 93.3

The initial mixture comprising 95% by volume of the aforesaid hydrocarbon component (HCC), and 5% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 4:

- CO -4.6%:

69kPa;

24

	24	
	- HC	-1.8%;
	- NO <sub>x</sub>	-5.6%;
	- CO <sub>2</sub>	1.4%;
	- NMHC	-5.2%;
5	- Fuel consumption, F <sub>c</sub> 1/100km	2.8%
	Formulation 4-1 containing 88.5% by volume of hydrovolume of ethanol, and 7% by volume of isobuty properties:	-
	- oxygen content	3.88% w/w;
10	- DVPE, according to ASTM D 5191	71.2kPa;
	- anti-knock index 0.5(RON+MON), according to	
	ASTM D 2699-86 and ASTM D 2700-86	94.5
15	Formulation 4-2 containing 88% by volume of hydrolume of ethanol, and 7% by volume of <i>n</i> -amyl ac properties:	
	- oxygen content	3.82% w/w;
	- DVPE, according to ASTM D 5191	69.7kPa;
	- anti-knock index 0.5(RON+MON), according to	
	ASTM D 2699-86 and ASTM D 2700-86	93.5
20	Formulation 4-3 containing 88% by volume of hydvolume of ethanol, and 7% by volume of isoam properties:	
	- oxygen content	3.82% w/w;

- DVPE, according to ASTM D 5191

WO 01/53436

5

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

93.7

Formulation 4-4 contained 87.5% by volume of hydrocarbon component, 5.5% by volume of ethanol, and 7% by volume of isoamyl propionate. It demonstrated the possibility of maintaining the dry vapor pressure equivalent and the fuel consumption at the same level as the source hydrocarbon component (HCC), whilst increasing the octane number and decreasing the level of toxic emissions in the exhaust in comparison with the initial mixture of gasoline and ethanol. It had the following properties:

10	- density at 15°C, according to ASTM D 4052	$752.4 \text{kg/m}^3$ ;
	- initial boiling point, according to ASTM D 86	31.9°C;
	vaporizable portion at 70°C	42.6% by volume;
	vaporizable portion at 100°C	53.2% by volume;
	vaporizable portion at 150°C	84.7% by volume;
15	vaporizable portion at 180°C	97.3% by volume;
	final boiling point	200.2°C;
	evaporation residue	1.3% by volume;
	loss by evaporation	0.1% by volume;
	- oxygen content, according to ASTM D4815	3.83% w/w;
20	- acidity, according to ASTM D1613 mass % HAc	0.003;
	- pH, according to ASTM D1287	6.7;
	- sulfur content, according to ASTM D 5453	14mg/kg;
	- gum content, according to ASTM D381	lmg/100ml;
	- water content, according to ASTM D6304	0.02% w/w;

26

aromatics, according to SIS 155120,

including benzene 30.6% by volume;

benzene alone, according to

EN 238 0.7% by volume;

5 - DVPE, according to ASTM D 5191 69.5kPa;

- anti-knock index 0.5(RON+MON), according to

15

20

25

ASTM D 2699-86 and ASTM D 2700-86 95

The motor fuel formulation 4-4 was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 4:

-	CO	-9.2%;
-	НС	-0.8%;
-	NO <sub>x</sub>	no change;
-	$CO_2$	0.05%;
_	NMHC	-6.3%;

Fuel consumption, F<sub>c</sub> l/100km 0.02%.

To prepare all the above formulations of this fuel composition, firstly, the hydrocarbon component was mixed with ethanol, to which mixture was then added the corresponding ester. The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.

5. A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of a hydrocarbon component, being in this composition a standard gasoline, with fuel grade ethanol, by means of a preparation

of multi-component mixtures with additional oxygen-containing components, which in this composition are alcohols and aldols.

Additionally, composition 5 demonstrates the possibility of adjusting the anti-knock index (octane number) of the motor fuel.

To prepare the formulations of this composition a standard gasoline and fuel grade ethanol from Williams, USA and also alcohols and aldols produced in Russia were used.

The source gasoline A92 summer was characterized as follows:

- range of hydrocarbons, saturated

and unsaturated, including aromatics C<sub>5</sub>-C<sub>12</sub>;

- DVPE, according to ASTM D 5191 40kPa;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86 86.4

The gasoline A92 summer of composition 5 from USA, was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

20 - CO 2.393g/km;
- HC 0.301g/km;
- NO<sub>x</sub> 0.265g/km;
- CO<sub>2</sub> 230.8g/km;
- NMHC 0.276g/km;

25 - Fuel consumption, F<sub>c</sub> 1/100km 10.03

20

28

The initial mixture consisting of 90% by volume of the source gasoline A92, and of 10% by volume of ethanol was characterized as follows:

oxygen content 3.68% w/w;
DVPE, according to ASTM D 5191 47.5kPa;
anti-knock index 0.5(RON+MON), according to
ASTM 2699-86 and ASTM 2700-86 89.3

The mixture of 90% by volume of gasoline A92 summer, and 10% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 5:

	-	CO	-12.1%;
	-	НС	-4.6%;
	-	NO <sub>x</sub>	18.3%;
15	-	$CO_2$	3.6%;
		NMHC	-4.2%;
	-	Fuel consumption, F <sub>c</sub> 1/100km	4.9%

Formulation 5-1 containing 86.6% by volume of gasoline A92 summer, 7.35% by volume of ethanol, 4.82% by volume of 2-ethylhexanol, and 1.23% by volume of diacetone alcohol had the following properties:

oxygen content 3.77% w/w;
DVPE, according to ASTM D 5191 44kPa;
anti-knock index 0.5(RON+MON), according to
ASTM D 2699-86 and ASTM D 2700-86 88.2

Formulation 5-2 containing 84.9% by volume of gasoline A92 summer, 15% by volume of ethanol, and 0.1% by volume of diacetone alcohol had the following properties:

- oxygen content

5.54% w/w;

5 - DVPE, according to ASTM D 5191

39.5kPa;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

90.1

Formulation 5-3 containing 85% by volume of gasoline A92 summer, 8% by volume of ethanol, and 7% by volume of isobutyl aldol had the following properties:

- oxygen content

4.91% w/w;

- DVPE, according to ASTM D 5191

40kPa:

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

89

Formulation 5-4 contained 88.5% by volume of gasoline A92 summer, 4.5% by volume of ethanol, and 7% by volume of diacetone alcohol. It demonstrated the possibility of decreasing the dry vapor pressure equivalent, increasing the octane number, decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the initial mixture of gasoline and ethanol. It had the following properties:

nad the following properties.

- density at 15°C, according to ASTM D 4052

 $755.5 \text{kg/m}^3$ ;

- initial boiling point, according to ASTM D 86

26.8°C;

vaporizable portion at 70°C

42.3% by volume;

vaporizable portion at 100°C

53.8% by volume;

25 vaporizable portion at 150°C

87.5% by volume;

30

	vaporizable portion at 180°C	97.4% by volume;	
	final boiling point	188.8°C;	
	evaporation residue	1.5% by volume;	
	loss by evaporation	1.5% by volume;	
5	- oxygen content, according to ASTM D4815	4.04% w/w;	
	- acidity, according to ASTM D1613 mass % HAc	0.011;	
	- pH, according to ASTM D1287	6.2;	
	- sulfur content, according to ASTM D 5453	17mg/kg;	
	- gum content, according to ASTM D381	<1mg/100ml;	
10	- water content, according to ASTM D6304	0.13% w/w;	
	aromatics, according to SIS 155120,		
	including benzene	31.2% by volume;	
	benzene alone, according to		
	EN 238	0.7% by volume;	
15	- DVPE, according to ASTM D 5191	42.5kPa;	
	- anti-knock index 0.5(RON+MON), according to		
	ASTM D 2699-86 and ASTM D 2700-86	89.4	
20	The motor fuel formulation 5-4 was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 5:		
	- CO -16	5.3%;	

- HC

-7.4%;

20

-	$NO_x$	12.6%;
-	CO <sub>2</sub>	3.2%;
-	NMHC	-5.8%;
_	Fuel consumption, F <sub>c</sub> l/100km	4.3%.

- To prepare all the above formulations of this fuel composition, firstly, gasoline A92 was mixed with ethanol, to which mixture was then added the corresponding alcohol and aldol (hydroxy-ketone or hydroxy-aldehyde). The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.
  - 6. A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of hydrocarbon components, being in this composition a hydrocarbon liquid of C<sub>6</sub>-C<sub>11</sub> fraction, with fuel grade ethanol, by means of a preparation of a three-component mixture of an additional oxygen-containing component, which in this composition are ketone esters.

Additionally, the present composition demonstrates the possibility of adjusting the anti-knock index (octane number) of the motor fuel.

To prepare the formulations of this composition a hydrocarbon liquid of  $C_6$ - $C_{11}$  fractions purchased from Merck, Germany, fuel grade ethanol produced by Sekab. Sweden, and keto-ethers purchased from Merck, Germany were used.

The source technical grade hydrocarbon liquid had the following properties:

- range of hydrocarbons, including saturated and

unsaturated and aromatics  $C_6$ - $C_{11}$ ;

- DVPE, according to ASTM D 5191 20kPa;

25 - anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86 78.7

20

The hydrocarbon component (HCC) of composition 6 was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

	- (	CO	2.631g/km;
	- ]	НС	0.348g/km;
	- 1	$NO_x$	0.313g/km;
10	- (	CO <sub>2</sub>	235.1g/km;
	- ]	NMHC	0.308g/km;
	- ]	Fuel consumption, F <sub>c</sub> l/100km	10.68

The initial mixture consisting of 90% by volume of the aforesaid hydrocarbon liquid, and of 10% by volume of ethanol was characterized as follows:

15	- oxygen content	3.65% w/w;
	- DVPE, according to ASTM D 5191	31.8kPa;
	- anti-knock index 0.5(RON+MON), according to	
	ASTM 2699-86 and ASTM 2700-86	83.9

The initial mixture comprising 90% by volume of the aforesaid hydrocarbon component (HCC), and 10% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 6:

	- CO	-4.8%;
25	- НС	-1.3%;
	- NO <sub>x</sub>	26.3%:

33

-	$CO_2$	4.4%;
-	NMHC.	-0.6%;
_	Fuel consumption, F <sub>c</sub> 1/100km	5.7%

Formulation 6-1 containing 85% by volume of hydrocarbon component, 5% by volume of ethanol, and 10% by volume of ethyl acetoacetate had the following properties:

- oxygen content 6.87% w/w;

- DVPE, according to ASTM D 5191 20kPa;

- anti-knock index 0.5(RON+MON), according to

5

15

10 ASTM D 2699-86 and ASTM D 2700-86 80

Formulation 6-2 contained 85% by volume of hydrocarbon component, 10% by volume of ethanol, and 5% by volume of *tert*-butyl acetoacetate. It demonstrated the possibility of maintaining the dry vapor pressure equivalent at the same level as the source hydrocarbon component, whilst increasing the octane number, decreasing the level of toxic emissions in the exhaust and decreasing the fuel consumption in comparison with the initial mixture of gasoline and ethanol. It had the following properties:

	- density at 15°C, according to ASTM D 4052	760.6kg/m <sup>3</sup> ;
	- initial boiling point, according to ASTM D 86	52°C;
20	vaporizable portion at 70°C	29.4% by volume:
	vaporizable portion at 100°C	76.2% by volume;
	vaporizable portion at 150°C	83.9% by volume;
	vaporizable portion at 180°C	98% by volume;
	final boiling point	201.6°C;
25	evaporation residue	1.4% by volume;

34

	loss by evaporation	0.05% by volume;
	- oxygen content, according to ASTM D4815	5.54% w/w;
	- acidity, according to ASTM D1613 mass % HAc	0.08;
	- pH, according to ASTM D1287	7.5;
5	- sulfur content, according to ASTM D 5453	0mg/kg;
	- gum content, according to ASTM D381	0mg/100ml;
	- water content, according to ASTM D6304	0.01% w/w;
	- aromatics, according to SIS 155120,	
	including benzene	5% by volume;
10	benzene alone, according to	
	EN 238	0% by volume;
	- DVPE, according to ASTM D 5191	20kPa;
	- anti-knock index 0.5(RON+MON), according to	
	ASTM D 2699-86 and ASTM D 2700-86	85.2
15	The motor fuel formulation 6-2 was tested in accordant 2000 NEDC EC 98/69. The testing was performed on the 1987, with the engine B230F, No. LG4F20-87, gave the with the reference fuel for composition 6:	the car Volvo 240 DL, model
	- CO	-12.3%;
20	- HC	-8.1%;
	- NO <sub>x</sub>	no change;
	- CO <sub>2</sub>	2.4%;
	- NMHC	-6.7%;

WO 01/53436

5

10

15

20

25

- Fuel consumption, F<sub>c</sub> 1/100km

4.2%.

To prepare all the above formulations of this fuel composition, firstly, the hydrocarbon component was mixed with ethanol, to which mixture was then added the corresponding ketone ester. The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.

7. A motor fuel composition demonstrating the possibility of lowering the dry vapor pressure equivalent (DVPE) of a mixture of hydrocarbon components, which in this composition are a standard gasoline and hydrocarbon liquid obtained in chemical-recovery carbonization, with biochemical technical grade ethanol, by preparation of three-component mixture of an additional oxygen-containing component, which in this composition are oxygen-containing heterocyclic compounds.

Additionally, the present composition demonstrates the possibility of adjusting the anti-knock index (octane number) and other performance parameters of the motor fuel.

To prepare the formulations of this fuel composition a standard gasoline purchased in Sweden at Shell gasoline stations and a hydrocarbon liquid obtained from the off-gases of chemical-recovery carbonization, produced in Russia were used. Also, ethanol obtained from the biochemical processing of wood hydrolysates, and oxygen-containing heterocyclic compounds derived from vegetation were used. Both the ethanol and heterocyclic compounds were supplied from Russia.

The hydrocarbon component for the present motor fuel composition was prepared by, initially, mixing of 75% by volume of gasoline A95 winter, 15% by volume of reformulated gasoline and 10% by volume of hydrocarbon liquid obtained in chemical-recovery carbonization. After mixing the hydrocarbon component was allowed to stand for 24 hours. The resulting component was characterized as follows:

- range of hydrocarbons, including saturated and unsaturated, including aromatics

C3-C12;

36

- DVPE, according to ASTM D 5191 92.5 kPa;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86

5

25

90.2

The hydrocarbon component (HCC) of composition 7 was used as a reference fuel to conduct the tests in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, cylinder volume 2.32 liter, No. LG4F20-87, power 83 kW at 90 revolutions/second, torque 185 Nm at 46 revolutions/second, and gave the following operating results for the exhaust emissions:

10	- CO	2.133g/km;
	- HC	0.241g/km;
	- NO <sub>x</sub>	0.255g/km;
	- CO <sub>2</sub>	226.7g/km;
	- NMHC	0.250g/km;
15	- Fuel consumption, F <sub>c</sub> 1/100km	9.5

The initial mixture comprising 90% by volume of the aforesaid hydrocarbon component, and 10% by volume of ethanol was characterized as follows:

- oxygen content 3.65% w/w;

- DVPE, according to ASTM D 5191 99kPa;

20 - anti-knock index 0.5(RON+MON), according to

ASTM 2699-86 and ASTM 2700-86 92.7

The initial mixture comprising 90% by volume of the aforesaid hydrocarbon component (HCC), and 10% by volume of ethanol was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 7:

37

	- CO	-18.3%;
	- HC	-8.9%;
	- NO <sub>x</sub>	8.6%;
	- CO <sub>2</sub>	2.24%;
5	- NMHC	-6.7%;
	- Fuel consumption, F <sub>c</sub> 1/100km	2.8%

Formulation 7-1 containing 89.5% by volume of hydrocarbon component, 3.5% by volume of ethanol, and 7% by volume of furfuryl alcohol had the following properties:

10 - oxygen content 4.24% w/w;

- DVPE, according to ASTM D 5191 92kPa;

- anti-knock index 0.5(RON+MON), according to

ASTM D 2699-86 and ASTM D 2700-86 92.2

Formulation 7-2 containing 89.5% by volume of hydrocarbon component, 4% by volume of ethanol, and 7.5% by volume of diethyl furfural had the following properties:

- oxygen content 4.4% w/w;

- DVPE, according to ASTM D 5191 92.5kPa;

- anti-knock index 0.5(RON+MON), according to

25

20 ASTM D 2699-86 and ASTM D 2700-86 92.7

Formulation 7-3 contained 89.5% by volume of hydrocarbon component, 5% by volume of ethanol, and 5.5% by volume of tetrahydrofurfuryl alcohol. It demonstrated the possibility of maintaining the dry vapor pressure equivalent and the fuel consumption at the same level as the source hydrocarbon component (HCC), whilst increasing the octane number and decreasing the level of toxic

WO 01/53436

emissions in the exhaust in comparison with the initial mixture of gasoline and ethanol. It had the following properties:

	-	density at 15°C, according to ASTM D 4052	765.3kg/m <sup>3</sup> ;
	-	initial boiling point, according to ASTM D 86	25.2°C;
5		vaporizable portion at 70°C	40.4% by volume;
		vaporizable portion at 100°C	53.5% by volume;
		vaporizable portion at 150°C	85.5% by volume;
		vaporizable portion at 180°C	98.7% by volume;
		final boiling point	203.6°C;
10		evaporation residue	1.1% by volume;
		loss by evaporation	0.3% by volume;
	-	oxygen content, according to ASTM D4815	4.16% w/w;
	-	acidity, according to ASTM D1613 mass %HAc	0.002;
	-	pH, according to ASTM D1287	7.4;
15	-	sulfur content, according to ASTM D 5453	16mg/kg;
	-	gum content, according to ASTM D381	2mg/100ml;
	-	water content, according to ASTM D6304	0.025% w/w;
		aromatics, according to SIS 155120,	
		including benzene	31.5% by volume;
20		benzene alone, according to	
		EN 238	0.7% by volume;
	-	DVPE, according to ASTM D 5191	89.7kPa;
	-	anti-knock index 0.5(RON+MON), according to	

39

ASTM D 2699-86 and ASTM D 2700-86

5

15

20

93.1

The motor fuel formulation 7-3 was tested in accordance with the test method EU 2000 NEDC EC 98/69. The testing was performed on the car Volvo 240 DL, model 1987, with the engine B230F, No. LG4F20-87, gave the following results compared with the reference fuel for composition 7:

	- CO	-30.3%;
	- HC	-13.5%;
	- NO <sub>x</sub>	-3.5;
	- CO <sub>2</sub>	no change;
10	- NMHC	-14.5%;
	- Fuel consumption, F <sub>c</sub> l/100km	no change.

To prepare all the above formulations of this fuel composition, the primary, the hydrocarbon component was mixed with ethanol, to which mixture was then added the corresponding heterocyclic. The motor fuel obtained was then allowed to stand before testing between 1 and 24 hours at a temperature not lower than -35°C. All the formulations were prepared without the use of any mixing devices.

The foregoing description and examples of the preferred embodiment 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.

5

### THE CLAIMS DEFINING THE INVENTION

The claims defining the invention are the following:

- 1. A motor fuel for spark ignition internal combustion engines, comprising a hydrocarbon component, ethanol, and other oxygen-containing compounds, in which for the adjustment of the dry vapor pressure equivalent, anti-knock index and other performance properties the fuel composition is formulated as:
  - a hydrocarbon component of C<sub>3</sub>-C<sub>12</sub> fractions;
  - a fuel grade ethanol; and
- at least one more, other than ethanol, organic compound containing oxygen bound in any of the following functional groups:

- 2. A motor fuel as in claim 1, wherein the hydrocarbon component fractions comprise any subrange of  $C_3$ - $C_{12}$ ;
- A motor fuel as in claim 2, wherein the hydrocarbon component fractions have no
   restriction on the presence of saturated and unsaturated hydrocarbons, including aromatics;

5

- 4. A motor fuel as in claim 3, wherein the hydrocarbon component fractions have no restriction on the presence of sulfur;
- 5. A motor fuel as in claim 4, wherein the source of the hydrocarbon component fractions are standard gasolines, hydrocarbon liquids obtained from petroleum refining, from natural gas, from off-gas of chemical-recovery carbonization, from synthesis-gas processing, and any mixture of the same;
  - 6. A motor fuel as in claim 5, wherein with main substance content of the ethanol is not less than 95% by volume;
- 7. A motor fuel as in claim 6, wherein to lower the dry vapor pressure equivalent of the resulting fuel composition in comparison to the dry vapor pressure equivalent of the mixture of the initial hydrocarbon component and ethanol, and to increase the anti-knock index, and to adjust the other performance properties are used oxygen-containing substances, originating from the following classes of organic compounds; alcohols, ketones, ethers, esters, aldols a.k.a. hydroxy-aldehydes and hydroxy-ketones, ketone esters and heterocyclics.
  - 8. A motor fuel as in claim 7, wherein to prepare the motor fuel suitable for the operation of a standard spark ignition internal combustion engine are used:
    - hydrocarbon component in the amount of at least 84.9% by volume of the fuel composition;
- ethanol in an amount of not more than 15% by volume of the fuel composition:
  - an additional oxygen-containing component, or additional oxygen-containing components to the total amount of not less than 0.1% by volume of the fuel composition.
- 9. A motor fuel as in claim 8, wherein after adding together the components of the25 fuel, the fuel composition is characterized as follows:
  - density at 15°C, according to ASTM D 4059, min 690kg/m<sup>3</sup>;
  - oxygen content, according to ASTM D 4815, max 7% w/w;
  - dry vapor pressure equivalent (DVPE), according to

42

	ASTM D 5191: min	20kPa;
	max	120kPa;
	- acids content, according to ASTM D 1613,	
	mass % HAc, max	0.1;
5	- pH, according to ASTM D 1287 min	5;
	max	9;
	- aromatics, according to SIS 155120,	
	including benzene, max	40% by volume;
	benzene alone, according to EN 238, max	1% by volume;
10	- sulfur content, according to ASTM D 5453, max	50mg/kg;
	- gum content, according to ASTM D 381, max	2mg/100ml;
	- water content, according to ASTM D 6304, max	0.25% w/w;
	- distillation, according to ASTM D86	
	- initial boiling point, min	20°C;
15	- vaporizable portion at 70°C, min	25% by volume;
	- vaporizable portion at 100°C, min	50% by volume;
	- vaporizable portion at 150°C, min	75% by volume;
	- vaporizable portion at 180°C, min	95% by volume;
	- final boiling point, max	205°C;
20	- evaporation residue, max	2% by volume;
	- anti-knock index 0.5(RON+MON), according	
	to ASTM D 2699-86 and ASTM D 2700-86, min	80;

- 10. A motor fuel as in claim 9, wherein there is a reduction in the emission of toxic substances into the atmosphere during the operation of a standard spark ignition internal combustion engine;
- 11. A motor fuel as in claim 10, wherein there is a lower fuel consumption during the
   operation of a standard spark ignition internal combustion engine in comparison with the corresponding fuel containing only hydrocarbon component fractions and ethanol;
  - 12. A motor fuel as in claim 11, wherein to prepare the fuel composition with lowest impact on environment it is necessary to maximize the use of components originating from renewable raw material.

10

15

13. A process for the production of the motor fuel of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, wherein the fuel compositions of the present invention are prepared by successively adding to the hydrocarbon component, first ethanol, then the additional oxygen-containing compound or compounds at a temperature not lower than -35°C. After mixing the resulting fuel composition should be allowed to stand before use for at least one hour.

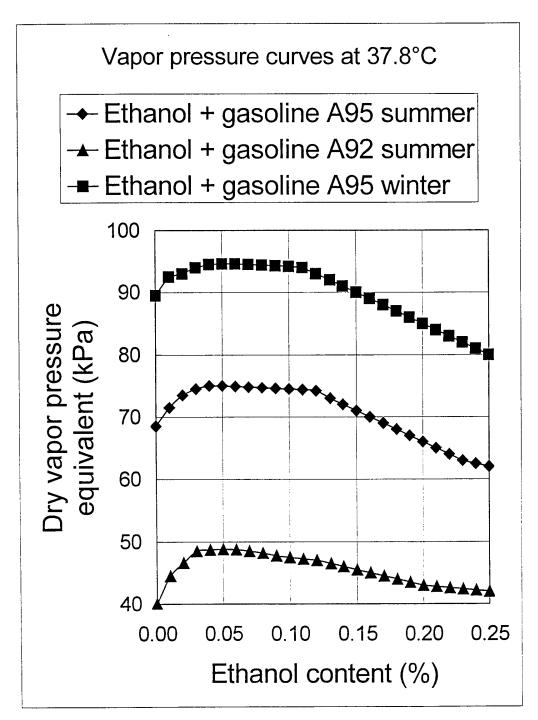


Figure 1

International application No.

PCT/SE 00/00139

### A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C10L 1/18, C10L 1/06
According to International Patent Classification (IPC) or to both national classification and IPC

#### **B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

#### IPC7: C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

#### SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.	DOCUMENTS	CONSIDERED	TO BE	E RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Х	WO 9421753 A1 (VEBA OEL AKTIENGESELLSCHAFT), 29 Sept 1994 (29.09.94)	1-13
х	US 4541836 A (EDMOND J. DERDERIAN), 17 Sept 1985 (17.09.85)	1-13
X	US 4207076 A (FRANCIS S. BOVE ET AL), 10 June 1980 (10.06.80)	1-13
X	FR 2500844 A (SOCIETE D'ETUDES ET DE REALISATIONS), 3 Sept 1982 (03.09.82)	1-13

X	Further documents are listed in the continuation of Box	. C.	See patent family annex.		
*	Special categories of cited documents:	"T"	later document published after the international filing date or priority		
"A"	document defining the general state of the art which is not considered to be of particular relevance		date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E"	erlier document but published on or after the international filing date	"X"			
"L"			considered novel or cannot be considered to involve an inventive step when the document is taken alone		
	special reason (as specified)  "Y" document of particular relevance: 1  O" document referring to an oral disclosure, use, exhibition or other considered to involve an inventive				
″0″			considered to involve an inventive step when the document is combined with one or more other such documents, such combination		
"P"	hair a phriomata a rese		being obvious to a person skilled in the art		
	the priority date claimed	<b>"&amp;"</b>	document member of the same patent family		
Dat	e of the actual completion of the international search	Date	of mailing of the international search report		
11	Sept 2000		1 3 -09- 2000		
Name and mailing address of the ISA/		Authorized officer			
Swedish Patent Office					
		Anna Siölund/FÖ			

Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

Facsimile No. + 46 8 666 02 86

International application No.
PCT/SE 00/00139

Category*	Citation of document with indication where accessing the state of the	Delegation 11 31
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Х	STN International, File CAPLUS, CAPLUS accession No. 1990:615167, Document No. 113:215167, Vicente Rodriques: "Octane-improvers for gasoline containing oxygenated organic compounds"; & Span. ES 2012729 A6 19900401, 10 pp.	1-13
	<del></del>	
X	Journal of the Institute of Energy, Volume 66, 1993, F Karaosmanoglu et al, "The effects of blending agents on alcohol-gasoline fuels" page 9 - page 12	1-13
	<del></del>	
X	File WPI, Derwent accession no. 1991-118025, TANG CHANGGAN: "Fume-reducing, oil-saving antiknock agent for ships and vehicles - contains ethanol isopropanol and butanol and is added to gasoline and diesel oil NoAbstract"; & CN1044489 A 19900808 DW 99117	1-13
	<del></del>	
X	GB 2090612 A (INSTITUT FRANCAIS DU PETROLE), 14 July 1982 (14.07.82)	1-13
X	US 4398920 A (JEAN-CLAUDE GUIBET ET AL), 16 August 1983 (16.08.83)	1-13
X	WO 9935215 A2 (WENZEL, DEBORAH), 15 July 1999 (15.07.99)	1-13
X	EP 0171440 A1 (UNION RHEINISCHE BRAUNKOHLEN KRAFTSTOFF AKTIENGESELLSCHAFT), 19 February 1986 (19.02.86)	1-13
X	EP 0121089 A2 (UNION RHEINISCHE BRAUNKOHLEN KRAFTSTOFF AKTIENGESELLSCHAFT), 10 October 1984 (10.10.84)	1-13

International application No.

PCT/SE 00/00139

		FC1/3L 00/	00105
C (Continu	nation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relev	ant passages	Relevant to claim No
A	File WPI, Derwent accession no. 1981-005120, INST NAT MOTOARE TERMICE BUCURESTI: "Combustible compsn is homogeneous mixt. of benzene, methanol, water, butanol and2-ethyl-hexanol"; & R075851 A 19810228 DW 198131		1-13
A	STN International, File CAPLUS, CAPLUS access- no. 1983:129039, Document No. 98:129039, Verdeti, Doina D. et al: "Fuel mixture"; & RO 71636 B 19810328, 2 pp.	ion	1-13
	SA/210 (continuation of second sheet) (July 1992)		

International application No. PCT/SE0000139

Box I	Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)		
This inter	This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:		
1.	Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:		
2.	Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  see next sheet		
3.	Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).:		
Box II	Observations where unity of invention is lacking (Continuation of item 2 of first sheet)		
1.	As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.		
2.	As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.		
3.	As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:		
4.	No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:		
Remark	The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.		

International application No. PCT/SE00/00139

The claims are so broadly formulated that a meaningful international search cannot be carried out for the whole scope of the claims. The search has therefore been focused on those parts of the claims which appear to be supported and disclosed in the description.

Form PCT/ISA/210 (extra sheet) (July1992)

Information on patent family members

International application No. PCT/SE 00/00139

cited in	nt document i search report		Publication date		tent family member(s)	Publication date
WO	9421753	A1	29/09/94	DE	4308053 A,C	15/09/94
US	4541836	A	17/09/85	AT AU DE EP SE AU BR CA IN	30924 T 2221683 A 3467590 D 0162122 A,B 0162122 T3 564852 B 8306714 A 1221539 A 161559 A	15/12/87 14/06/84 00/00/00 27/11/85 27/08/87 17/07/84 12/05/87 26/12/87
US	4207076	A	10/06/80	AU AU BR DE FR GB PH	533410 B 5580180 A 7908370 A 3004115 A 2449722 A,B 2043098 A,B 14791 A	24/11/83 28/08/80 09/09/80 04/09/80 19/09/80 01/10/80 09/12/81
FR	2500844	A	03/09/82	NONE		
GB	2090612	A	14/07/82	BR DE FR OA BR DE DE FR GB OA OA	8108488 A 3150989 A,C 2497223 A,B 6975 A 8108111 A 8108559 A 3149170 A,C 3150988 A,C 2498622 A,B 2090611 A,B 2090613 A,B 6976 A 6982 A	19/10/82 05/08/82 02/07/82 31/07/83 21/09/82 19/10/82 29/07/82 05/08/82 30/07/82 14/07/82 14/07/82 31/07/83 31/08/83
US	4398920	A	16/08/83	BE CA DE DK DK FR FR GB IT JP NL NO NO SE ZA FR	889067 A 1157646 A 3122243 A 148747 B,C 248581 A 2483944 A,B 2488272 A 2077290 A,B 1168090 B 8122189 D 57025390 A 8102772 A 155582 B,C 811915 A 8103562 A 8103842 A 2487846 A,B	03/12/81 29/11/83 24/12/81 16/09/85 10/12/81 11/12/81 12/02/82 16/12/81 20/05/87 00/00/00 10/02/82 04/01/82 12/01/87 10/12/81 30/06/82 05/02/82

Information on patent family members

International application No.
PCT/SE 00/00139

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
WO	9935215	A2	15/07/99	AU EP WO US	2316299 A 0999957 A 9956991 A 5903890 A	26/07/99 17/05/00 11/11/99 11/05/99
EP	0171440	A1	19/02/86	SE DE AT DE	0171440 T3 3330165 A,C 35823 T 3472802 D	07/03/85 15/08/88 00/00/00
EP	0121089	A2	10/10/84	SE AT DE	0121089 T3 43625 T 3478465 D	15/06/89 00/00/00