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

(11) EP 2 287 276 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.02.2011 Bulletin 2011/08

(21) Application number: **09173482.2**

(22) Date of filing: **20.10.2009**

(51) Int Cl.:
C10L 1/10 *(2006.01)* ***C10L 1/14*** *(2006.01)*
C10L 10/00 *(2006.01)* ***C10L 10/02*** *(2006.01)*
C10L 10/06 *(2006.01)* ***C10L 3/00*** *(2006.01)*
F02B 51/00 *(2006.01)* ***F02B 47/04*** *(2006.01)*
F02M 25/00 *(2006.01)*

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

(30) Priority: **28.07.2009 PL 38865709**

(27) Previously filed application:
28.07.2009 PL 38865709

(71) Applicant: **Przedsiebiorstwo Wielobranzowe Prima Sp.zo.o.**
05-660 Warka (PL)

(72) Inventor: **MAJCHER, Maciej**
66-235, Torzyn (PL)

(74) Representative: **Kaminski, Piotr**
Kaminski Sobajda & Partners
Patent and Trademark Attorneys
Ul. Dworkowa 2/67
00-784 Warszawa (PL)

(54) Modifier of combustion of liquid and gaseous fuels in combustion engines.

(57) Object of the invention is the modifier of combustion of liquid and gaseous fuels, such as fuel for marine engines, diesel oil, petrol, light and heavy oil, mazout and other hydrocarbons, in combustion engines, **characterised in that** it contains from 10 to 30 wt. % of carrier, preferably water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 80 wt. % of at least one aliphatic alcohol, from 5 to 15 wt. % of carbamide or its derivatives, and from 5 to 15 wt. % of monoacetylferrocene. Object of the invention is also a method of modifying a process of fuel combustion and a use of the combustion modifier.

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Description

[0001] Object of the invention is a modifier of combustion of liquid and gaseous fuels, such as fuel for marine engines, diesel oil, petrol, light and heavy oil, mazout and other hydrocarbons, in combustion engines, a method of modifying a process of combustion of fuels and a use of the modifier of fuel combustion.

[0002] Processes of combustion of liquid and gaseous fuels in combustion engines are still being improved. In particular, all methods that allow to increase a process yield and limitation of emission of harmful substances to atmosphere are investigated. Additives of various types that modify processes taking place during combustion of fuels are known. In particular, preventing from carbon black and other sludge banks settling in e.g. in exhaust systems of combustion engines, is desirable.

[0003] Ferrocene derivatives belong to a group of metal organic compounds from a group of cyclopentadienyl complexes. Complexes with iron II constitute a sandwich system, in which two ligands are bound with a metal cation located between them. Derivatives of such type are known and are used as catalysts of chemical processes.

[0004] From Japanese patent specification JP2000247990, a use of cyclopentadiene complexes in chemical synthesis, e.g. during preparation of aromatic amines, is known.

[0005] From Swiss patent CH 599464, a use of ferrocene as a catalyst of processes of combustion to be used as an additive to fuels used in engines, e.g. motor car engines, is known.

[0006] Object of the invention is a modifier of combustion of liquid and gaseous fuels, such as fuel for marine engines, diesel oil, petrol, light and heavy oil, mazout and other hydrocarbons in combustion engines, **characterised in that** it contains from 10 to 30 wt. % of carrier, preferably water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 80 wt. % of at least one aliphatic alcohol, from 5 to 15 wt. % of carbamide or its derivatives and from 5 to 15 wt. % of monoacetylferrocene.

[0007] The modifier contains from 10 to 30 wt. % of water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 40 wt. % of isopropanol, from 20 to 40 wt. % of n-butanol, from 5 to 15 wt. % of carbamide and from 5 to 15 wt. % of monoacetylferrocene.

[0008] The modifier contains 20 wt. % of water or hydrocarbon distillate of a fraction of the 180 - 380°C range, 30 wt. % of isopropanol, 30 wt. % of n-butanol, 10 wt. % of carbamide and 10 wt. % of monoacetylferrocene.

[0009] Object of the invention is also a method of modifying a process of combustion of liquid and gaseous fuels, such as fuel for marine engines, diesel oil, petrol, light and heavy oil, mazout and other hydrocarbons, in combustion engines, **characterised in that** the modifier of combustion containing from 10 to 30 wt. % of carrier, preferably water or hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 80 wt. % of at least one aliphatic alcohol, from 5 to 15 wt. % of carbamide or its derivatives, and from 5 to 15 wt. % of monoacetylferrocene, is metered as optionally additionally diluted, the diluent preferably being a carrier, either is metered as liquid directly to the fuel or to the aeration system of combustion chamber of the engine, preferably through pumping together with air to fuel mixture fed to the combustion chamber of the engine, the modifier being metered as diluted with a carrier, preferably at the ratio 2.5 - 3.8 mL modifier per 1 L water or the hydrocarbon fraction of the 180 - 380°C range.

[0010] The modifier contains from 10 to 30 wt. %, preferably 20 wt. % of carrier, from 20 to 40 wt. %, preferably 30 wt. % of isopropanol, from 20 to 40 wt.%, preferably 30 wt. % of n-butanol, from 5 to 15 wt. %, preferably 10 wt. % of carbamide and from 5 to 15 wt. %, preferably 10 wt. % of monoacetylferrocene.

[0011] In case of metering the modifier to the aeration system, it is metered by means of spraying.

[0012] From 1.8 to 10 mL of the modifier per 100 L of fuel as diesel oil or from 5 to 47 mL of the modifier per 1000 kg of fuel for marine engines or from 10 to 100 mL of the modifier per 1000 litres of liquid fuels, such as mazout and heavy oil, is metered in the method, and the given amounts refer to the modifier composition prior to the additional dilution.

[0013] Object of the invention is also a use of the modifier of combustion defined above for increasing a yield of combustion of liquid and gaseous fuels, reducing their consumption and as a catalyst in combustion process in engines, and for decreasing emission of undesirable gases, in particular carbon monooxide, to atmosphere and also for after-burning carbon black, exhaust gases and other impurities present in the combustion chamber, for example dusts and coal tar-type substances, as well as for purifying the combustion chamber and exhaust system from sludge banks.

[0014] Object of the invention is also an application of the modifier of combustion of liquid and gaseous fuels, containing a carrier, preferably water or hydrocarbon distillate of a fraction of the 180 - 380°C range, at least one aliphatic alcohol, carbamide or its derivatives and monoacetylferrocene, for increasing a yield of combustion of liquid and gaseous fuels, reducing its consumption and as a catalyst in combustion process in engines, and for decreasing emission of undesirable gases, in particular carbon monooxide, to atmosphere and also for after-burning carbon black, exhaust gases and other impurities present in the combustion chamber, for example dusts and coal tar-type substances, as well as for purifying the combustion chamber and exhaust system from sludge banks.

[0015] The above-mentioned composition of the modifier can be adjusted to a type of fuel used and a type of engine powered with that fuel. Accordingly, amounts of individual components can be changed. In addition to the ratios mentioned-above, the modifier can also contain 15 to 25 wt. % of carrier, 25 to 35 wt. % of isopropanol, 25 to 35 wt. % of n-

butanol, 8 to 12 wt. % of carbamide and 8 to 12 wt. % of monoacetylferrocene.

[0016] The modifier of combustion according to the invention can in particular be used in chambers of self igniting diesel-oil, low-speed and high-speed engines powered with low-octane or high-octane (92, 95, 98) petrol, light and heavy diesel oil, mazout, gas e.g. methane or propane-butane. The modifier can also be used together with fuels of a different type, selection or composition modification of which will be familiar for a skilled in the art. As fuels to which the modifier of the invention can be utilised, suitable hydrocarbon fractions utilised for fuelling combustion engines, e.g. a fraction derived from crude oil distillation within the fraction of the 180 - 360°C range, e.g. diesel oil, can be used. It can also be a fraction of the 220 - 340°C range. Hydrocarbon fractions can also be used as an additional diluent for combustion modifier composition, when it is metered in the liquid state directly to the fuel. When the modifier is metered in a sprayed form to an aeration system of the engine (to a carburettor), it is water which is used as a carrier and a diluent for the modifier composition. A use of a different type of carriers and diluents having similar properties i.e. not interfering into chemical processes during fuel combustion when using a modifier, is also possible.

[0017] Aim of the invention was to develop a universal modifier of combustion of all fuel types in combustion engines having different construction, to act as a catalyst that limits settling carbon black and coal tar type substances, ensures its after-burning and reduces emission of undesirable substances, e.g. carbon monoxide, solids and hydrocarbons to atmosphere and - at the same time - enhances a yield of combustion processes by reducing consumption of the respective fuels.

[0018] Unexpectedly, it has been found that modifier components - as a result of its specific quantitative and qualitative selection - make it possible to carry out the combustion process in engines in a stable and safe way. A use of a specific ferrocene derivative (monoacetylferrocene) in combination with alcohols and carbamide has made it possible to fully control existing processes and ensured a universal character of the modifier, suitable to be used with various fuels. What is more important, general operational parameters of engines used in tests have not been deteriorated. On the other hand, several advantages resulting from a use of the modifier of combustion according to the invention, in particular limitation of emission of harmful exhaust gas components to atmosphere, were observed.

[0019] One of the most prospective directions when utilising the modifier of combustion of the invention is its application for modifying the process of fuel combustion in marine engines, motor-cars of any type, construction equipment, diesel locomotives, in engines that supply electric energy generators, mining machines and aircraft reaction engines. The performed study has demonstrated that the reduction in relative consumption during modified fuel combustion for natural gas GZ-50 is not less than 12 %, for diesel oil - 12 %, and for mazout and fuel for marine engines - 10 -15%. A decrease in fuel consumption was also observed for other hydrocarbon fractions used as a liquid and gaseous fuel.

[0020] Experiments concerning practical implementation of the modifier of the invention i.e. a composition of the modifier (for example according to Example 1) have evidenced that in some cases there is a possibility of fuel saving up to 12% and even up to 25%, a direct influence of the modifier on saving of fuel consumption necessary to perform definite work amounting to 8-12 %, while the remaining contribution to saving being an indirect factor, e.g. resulting from purifying the engine and systems of feeding and exhausting. An extra effectiveness of processes was achieved through introducing a slight modification of aeration system of the combustion chamber, not involving any construction changes in the feeding system. A use of the modifier of the invention results in good condition of exhaust system as a result of e.g. its purification without necessity of introducing substantial changes in engine construction.

[0021] It is also crucial that the modifier acts in all engine sections i.e. in the area of fuel feeding to the engine, in the engine itself, and in the exhaust system, where it causes a decrease in contamination of oil with fuel combustion products, and also in oil filtration system, thanks to which advantageous changes occur within the whole mentioned area and then after-burning of exhaust gas, dust and sludge banks takes place.

[0022] The modifier according to the invention can be successfully used in combustion engines and in jet engines of any type, for various fuels such as aircraft fuel, petrol, light and heavy diesel oils, marine engines fuel, mazout, hydrocarbons of various types, and their compositions in a mixture with petroleum-based synthetic fuels, optionally processed or not, and all low-grade fuels. The invention is also applicable for gaseous and liquid fuels such as methane, propane - butane, synthesis gas, as well as for various contaminated mixtures and fuels.

[0023] An application of the modifier according to present invention makes it possible to use low-processed and wet raw materials as fuels.

[0024] The essential component of the modifier according to the invention is a complex being an iron carrier - monoacetylferrocene i.e. cyclopenta-1,3-diene; 1-(1-cyclopenta-2,4- dienylidene) etanolate of ferrum ion 2+. In processes during combustion, presence of hydroxyl groups in a reaction medium is of crucial importance. The modifier contains also carbamide or its derivatives, such as alkylurea of $R_1R_2N(CO)NR_1R_2$ type, where R_1, R_2, R_3, R_4 are the same or different and are C_1-C_6 alkyl groups, e.g. methylene or ethylene groups.

[0025] Aliphatic alcohols used in the modifier according to the invention can have linear or branched chains. The modifier of the invention should include at least one alcohol (a carrier of OH groups). Preferably, the alcohol is selected from a group of C_2 - C_{11} alcohols, more preferably C_3-C_8 alcohols, in particular C_3-C_6 alcohols. Examples of alcohols used are: ethanol, propanol, isopropanol, n-butanol, pentanol, heptanol and octanol. By selecting the alcohol, a ratio of

hydroxyl groups to a number of carbon atoms in a chain is changed, thereby changing the ratio of hydroxyl groups to a mass of other modifier components. Advantageous effects are obtained when using alcohols of moderate chain length, e.g. isopropanol and n-butanol. Thus, a mixture of the two alcohols in the modifier is preferably used. On the other hand, the modifier can contain only one alcohol of the mentioned group or a mixture of three or four alcohols.

[0026] A mixture of the modifier may also include additives, which do not influence its properties. e.g. dyes, to make a distinction between various types of the modifier.

[0027] One can assume that during combustion processes, complex ligands based on an N-radical having a complexing centre constituted by an iron ion with built-in hydroxyl groups and hydrocarbon chains in a suitable position are formed in the reaction mixture.

[0028] Roughly speaking, one can define these compounds as derivatives of $C_5H_5FeC_5H_4COC_mH_n$.type, but it is only a pictorial formula and there is no possibility to isolate such compounds from the reaction mixture.

[0029] In the method according to the invention, the modifier composition is optionally diluted with water or a hydrocarbon fraction, and only then it is metered. The modifier is either directly added to the fuel (e.g. to a fuel container) and does not contain water, or it is fed through a metering system to an air suction system i.e. to a carburettor premixing chamber (through a feeding channel), where the modifier is metered by spraying as an aqueous solution.

[0030] In Figures (Figs. 1-4) results of comparison of testing of exhaust gas components for the basic fuel (diesel oil) and for the modifier-added fuel of the composition of Example 1 are shown. The tests were carried out with a use of SULZER 6A20/24 engine. The modifier diluted at the ratio of 2.8 mL modifier : 1 L diluent (carrier) was used. The modifier was metered directly to the fuel or to the engine aeration chamber at the amount from 4.6 mL to 5mL of modifier per 100 L and per 1000 L of diesel oil feeding the engine.

[0031] Fig. 1 presents comparison of values of emission of not-burnt hydrocarbons (THC) in exhaust gas when feeding with the basic fuel and the fuel with the added modifier of the invention, Fig. 2 - comparison of values of emission of carbon monooxide in exhaust gas when feeding with the basic fuel and the fuel with the added modifier of the invention, Fig.3 - comparison of values of emission of carbon black in exhaust gas when feeding with the basic fuel and the fuel with the added modifier of the invention, Fig. 4 - comparison of values of emission of solid particles in exhaust gas when feeding with the basic fuel and the fuel with the added modifier of the invention.

Example 1

[0032] A modifier of the following composition: 20 wt. % of carrier, 30 wt. % of isopropanol, 30 wt. % of n-butanol, 10 wt. % of carbamide and 10 wt. % of monoacetyloferrocene has been prepared. Sample I a was a modifier, in which water was used as a carrier, sample 1b was a modifier with an added hydrocarbon distillate of a fraction of the 180 - 380°C range as a carrier.

Example 2

[0033] In an analogous way, samples 2a and 2b were prepared. The modifier composition was the following: 30 wt. % of carrier (water or hydrocarbon distillate), 35 wt. % of isopropanol, 25 wt. % of n-butanol, 5 wt. % of carbamide, 5 wt. % of monoacetyloferrocene.

Example 3

[0034] In an analogous way, samples 3a and 3b were prepared; the modifier was of the following composition: 20 wt. % of carrier (water or hydrocarbon distillate), 50 wt. % of isopropanol, 15 wt. % of carbamide and 15 wt. % of monoacetyloferrocene.

Example 4

[0035] The modifier of Example 1 - sample 1a was diluted with water at the ratio of 3 mL catalyst composition per 1 L water. The resulting solution was metered to the aeration chamber of the engine. Sample 1b was diluted with hydrocarbon fraction 180÷360 at the analogous ratio and was metered as liquid to a fuel container. Amounts of the metered modifier amounted to 5 mL per 100 L diesel oil (recalculated to modifier before being diluted). Diluting the modifier carrier only provided uniform metering and more easy handling with liquids. Testing of modifier efficiency was carried out using test engines PERKINS 1104C-44 and SULZER 6A20/24.

[0036] In Table I below comparison of testing of emission of engine SULZER 6A20/24 for the basic fuel with the added modifier of Example I and for the basic fuel (standard diesel oil) with no additives, is presented. Emission of hydrocarbons (HC) and carbon monooxide (CO) was considerably lower in case of the modifier-added fuel. Results of comparison for engine SULZER are presented also in Fig. 1-4, which show, what advantages as regards emission of exhaust gas were

achieved by using the modifier of Example 1.

[0037] In tests carried out for PERKINS 1104C-44-type engine, a presence of the modifier additive in diesel oil (basic fuel) resulted in a decrease in power output of the engine within the whole range of engine speed. The observed power output decrease at 2200 rpm was 7% as compared to the conventionally used diesel oil. At the same time, a decrease in fuel consumption from 4 to 12% depending on a modifier composition was observed. Calculations of general efficiency of engine for the conventional fuel and the fuel with added modifier did not exhibit any significant differences. This results from modifier properties, which cause a slight decrease in engine power output, but at the same time reduce fuel consumption. It was also observed that using the fuel with the added modifier resulted in a reduced emission of carbon monooxide and solid particles, in particular at low engine speeds. A decrease in carbon monooxide emission was within the range of 70÷90%. A level of hydrocarbons emission decreased about 30%.

[0038] In tests with a use of SULZER 6A20/24 engine, testing of exhaust gas and calibration procedures and analytical equipment control conformed to Norm PN-EN ISO 8178 (01.1999). Testing was carried out on a marine piston diesel engine of SULZER 6A20/24 type. A spectrophotometric analyzer of exhaust gas was used. No influence of the fuel with the added modifier of the invention on change in mechanical or energy performance of engine was observed. At the same time, an advantageous influence of the combustion modifier on levels of emission of harmful exhaust gas components was observed. A level of reduction of emission of solid particles lies within the range of 53÷73%. Emission of insoluble fraction of organic compounds was reduced by 35÷62%. Also a decrease in emission of solid particles within the range of 40÷62% was observed. A decrease in emission of not-burnt hydrocarbons amounted to 19÷40% Values of listed parameters depended on the engine load. A decrease in emission of carbon monooxide was very considerable at low engine load and amounted to 38.6% (for the remaining ranges it amounted to 1÷9%).

[0039] The fuel with the added modifier of the invention in figures (fig. 1-4) was denoted with a trade name "Reduxco".

Table 1

Component		Basic fuel	Modified fuel
NOx unit weighed emission	g/kWh	16.71	17.40
CO unit weighed emission	g/kWh	1.30	1.06
HC unit weighed emission	g/kWh	1.33	0.97
SOx unit weighed emission	g/kWh	0.05	0.05

Claims

1. Modifier of combustion of liquid and gaseous fuels, such as fuel for marine engines, diesel oil, petrol, light and heavy oil, mazout and other hydrocarbons, in combustion engines, **characterised in that** it contains from 10 to 30 wt. % of carrier, preferably water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 80 wt. % of at least one aliphatic alcohol, from 5 to 15 wt. % of carbamide or its derivatives, and from 5 to 15 wt. % of monoacetylferrocene.

2. Modifier according to claim 1, **characterised in that** it contains from 10 to 30 wt. % of water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 40 wt. % of isopropanol, from 20 to 40 wt. % of n-butanol, from 5 to 15 wt. % of carbamide and from 5 to 15 wt. % of monoacetylferrocene.

3. Modifier according to claim 1, **characterised in that** it contains 20 wt. % of water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, 30 wt. % of isopropanol, 30 wt. % of n-butanol, 10 wt. % of carbamide and 10 wt. % of monoacetylferrocene.

4. Method of modifying a process of combustion of liquid and gaseous fuels, such as fuel for marine engines, diesel oil, petrol, light and heavy oil, mazout and other hydrocarbons, in combustion engines, **characterised in that** the modifier of combustion containing from 10 to 30 wt. % of carrier, preferably water or a hydrocarbon distillate of a fraction of the 180 - 380°C range, from 20 to 80 wt. % of at least one aliphatic alcohol, from 5 to 15 wt. % of carbamide or its derivatives, and from 5 to 15 wt. % of monoacetylferrocene, is metered as optionally additionally diluted, a diluent preferably being a carrier, either in the liquid state, directly to the fuel or to an aeration system of an engine combustion chamber, preferably by pumping together with air to a fuel mixture fed to the engine combustion chamber, the modifier being metered as diluted with the carrier, preferably at the ratio of 2.5 - 3.8 mL modifier per 1 L water or the hydrocarbon fraction of the range 180 - 380°C.

5. Method according to claim 4, **characterised in that** the modifier of combustion contains from 10 to 30 wt. %, preferably 20 wt. % of carrier, from 20 to 40 wt. %, preferably 30 wt. % of isopropanol, from 20 to 40 wt. %, preferably 30 wt. % of n-butanol, from 5 to 15 wt. %, preferably 10 wt. % of carbamide and from 5 to 15 wt. %, preferably 10 wt. % of monoacetylferrocene.

6. Method according to claim 4, **characterised in that** in case of metering of the modifier to the aeration system, it is metered by spraying.

7. Method according to claim 4 **characterised in that** from 1.8 to 10 mL of modifier per 100 L of fuel as diesel oil, or from 5 to 47 mL of modifier per 1000 kg of fuel for marine engines, or from 10 to 100 mL modifier per 1000 L of liquid fuels, such as mazout and heavy oil, is metered, and the given amounts of the modifier refer to its composition prior to the additional dilution.

8. Use of the modifier of combustion defined in claim 1 for increasing a yield of combustion of liquid and gaseous fuels, for reducing its consumption, as a catalyst in combustion engines, and for reducing emission of undesirable gases, in particular carbon monooxide, to atmosphere, as well as for after-burning carbon black, exhaust gases and other impurities present in the combustion chamber, for example dusts and coal tar-type substances, as well as for purifying the combustion chamber and exhaust system from sludge banks.

9. Use of the modifier of combustion of liquid and gaseous fuels, containing a carrier, preferably water or a hydrocarbon distillate of a fraction of the range from 180 to 380°C, at least one aliphatic alcohol, carbamide or its derivatives, and monoacetylferrocene, for increasing a yield of combustion of liquid and gaseous fuels, for reducing its consumption, as a catalyst in combustion engines, and for reducing emission of undesirable gases, in particular carbon monooxide, to atmosphere, as well as for after-burning of carbon black, exhaust gases and other impurities present in the combustion chamber, for example dusts and coal tar-type substances and for purifying the combustion chamber and exhaust system from sludge banks.

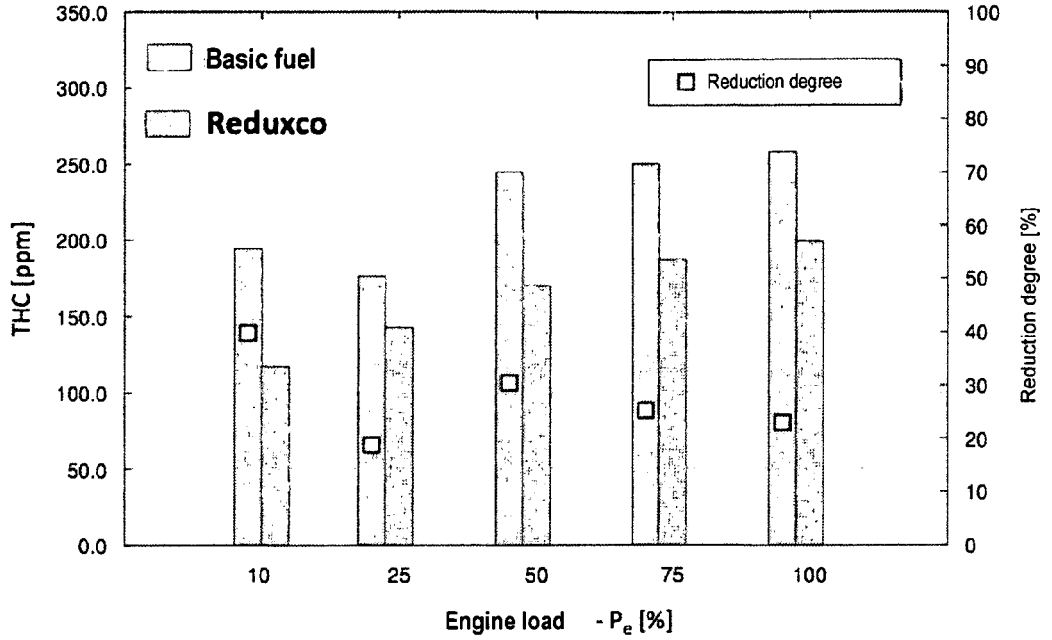
Basic fuel
Reduxco
Reduction degree
THC [ppm]
Reduction degree [%]
350.0
300.0
250.0
200.0
150.0
100.0
50.0
0.0
100
90
80
70
60
50
40
30
20
10
0
10
25
50
75
100
Engine load - P_e [%]

Fig. 1

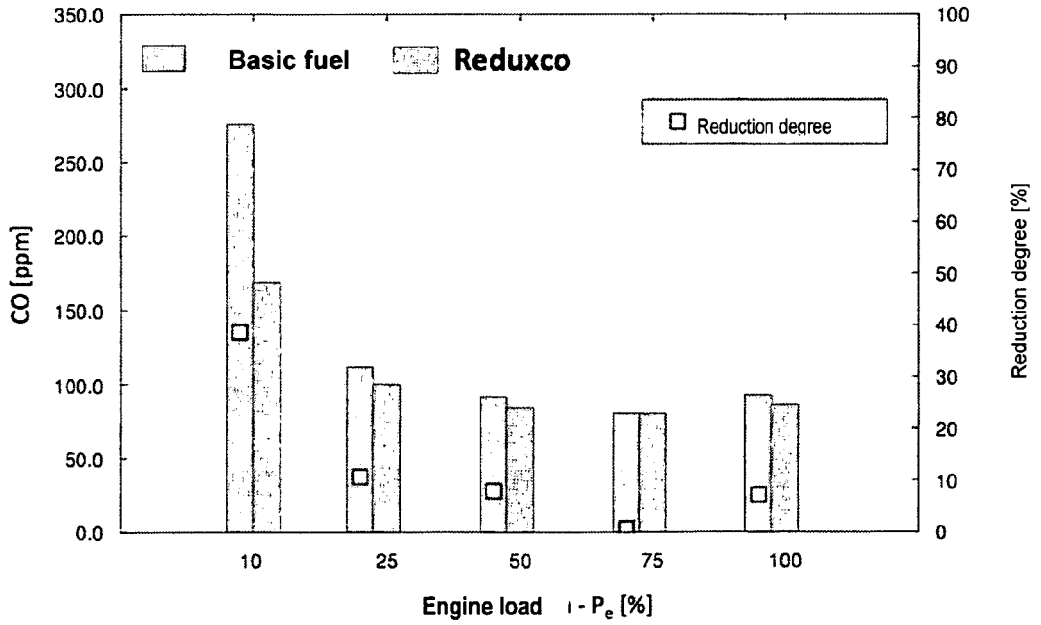
Basic fuel
Reduxco
Reduction degree
CO [ppm]
Reduction degree [%]
350.0
300.0
250.0
200.0
150.0
100.0
50.0
0.0
100
90
80
70
60
50
40
30
20
10
0
10
25
50
75
100
Engine load - P_e [%]

Fig. 2

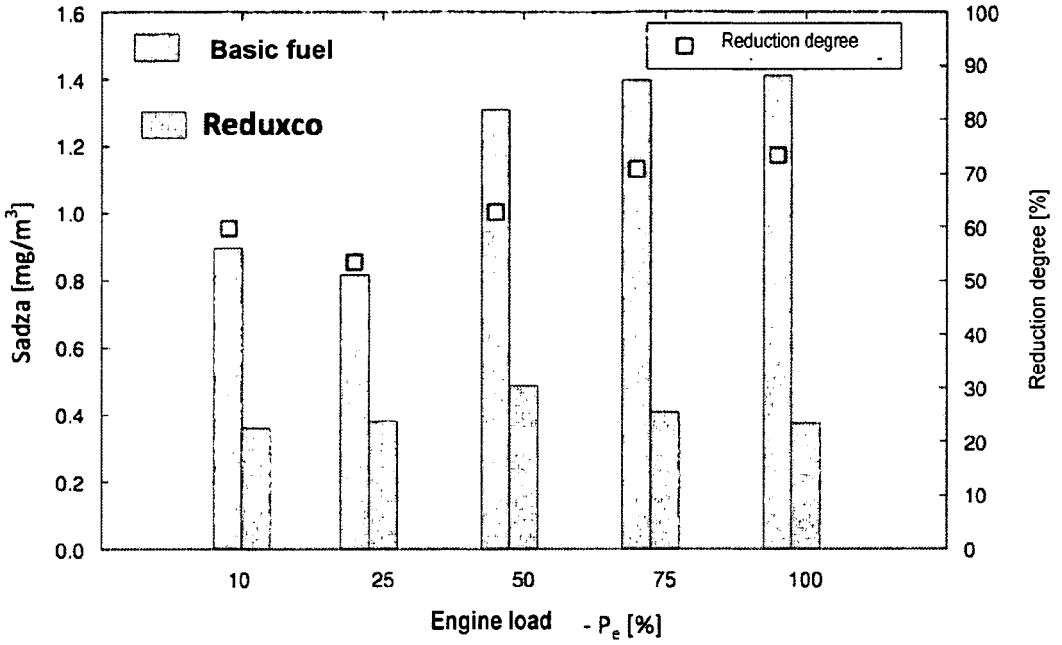
Basic fuel
Reduxco
Reduction degree
Sadza [mg/m3]
Reduction degree [%]
Engine load - Pe [%]
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
100
90
80
70
60
50
40
30
20
10
0
10
25
50
75
100

Fig. 3

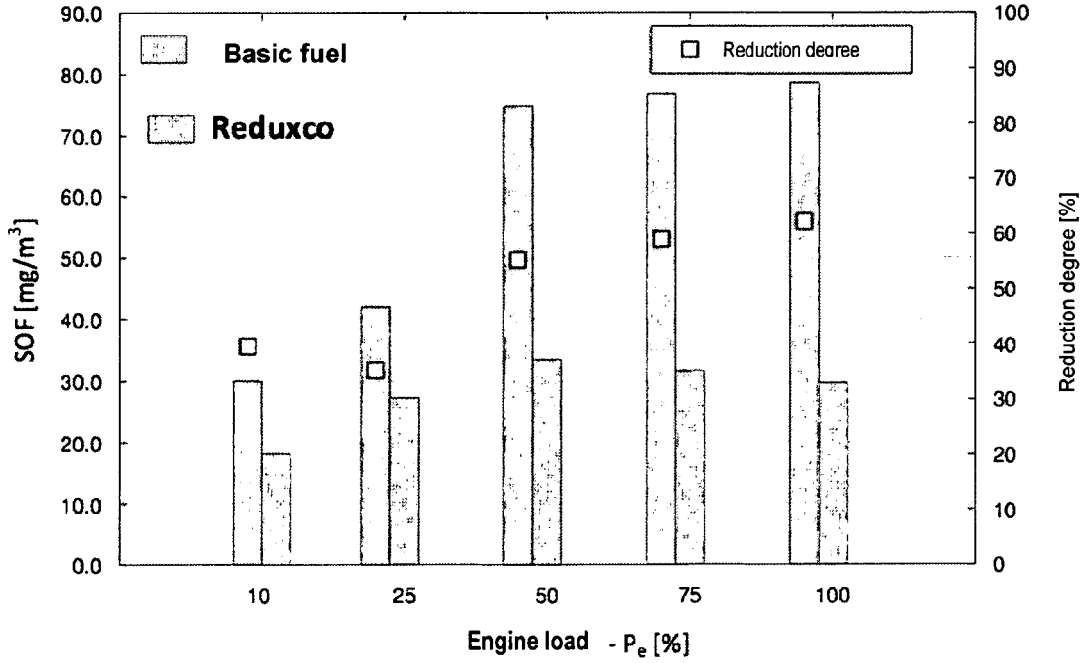
Basic fuel
Reduxco
Reduction degree
SOF [mg/m3]
Reduction degree [%]
Engine load - Pe [%]
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
100
90
80
70
60
50
40
30
20
10
0
10
25
50
75
100

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 09 17 3482

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	* abstract *	1-8	F02B47/04 F02M25/00
Y	CN 1 114 676 A (YUAN YUMING [CN]) 10 January 1996 (1996-01-10)	9	
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A	US 4 389 220 A (KRACKLAUER JOHN J) 21 June 1983 (1983-06-21) * claims 1-3 *	1,4,8,9	
A	WO 95/06805 A1 (PLATINUM PLUS INC [US]; VALENTINE JAMES M [US]) 9 March 1995 (1995-03-09) * claims 1,2,4,5,8,11,13-15; figure 1 *	1	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	24 November 2010	de La Morinerie, B

CATEGORY OF CITED DOCUMENTS

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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