

Engine fuel based on a mixture of alcohol and water and containing an additive for improving combustion

Field of the invention

5 The field of the invention is that of fuels for combustion engines. The fuel of the invention belongs to the new fuels with reduced environmental impact, for example those commonly called "e-fuels" when they are made from low-carbon electricity, low-carbon hydrogen, and/or from CO₂. They are considered a solution for the decarbonisation of transportation. The fuel of the invention is essentially composed of a water/alcohol mixture and is thus
10 part of the ecological alternatives for the replacement of fossil fuels. Water represents up to 15% by weight of the mixture. The function of water is to reduce the production of nitrogen oxides in the engine's combustion products. Alcohol is therefore the main component of the fuel. The invention relates to an additive which, when incorporated into the water/alcohol mixture, ensures better ignition and faster combustion of the fuel in the
15 engine.

State of the art

Methanol of the "e-fuels" type represents a credible low environmental impact alternative to replace fossil fuels and biofuels for combustion engines in the near future. The combustion of methanol thus produced leads to a neutral CO₂ balance. Methanol as a fuel
20 has a usable energy density in combustion engines but has a low cetane number. Its ignition in compression ignition engines, such as diesel, is problematic especially at low engine speeds. Different ways to improve the ignition of methanol in a compression ignition engine have been described.

The first means is the co-injection of a pilot fuel or additive with methanol into the engine.
25 For example, patent application CN 214944586 describes the co-injection of a diesel-type pilot fuel with methanol as the primary fuel. The scientific article "Effect of Cetane Improvers on Gasoline, Ethanol, and Methanol Reactivity and the Implications for RCCI Combustion" (SAE International Journal of Fuels and Lubricants Vol. 6, No. 1 (April 2013), pp. 170-187) describes the co-injection of 2-ethylhexyl nitrate (EHN) with a fuel
30 consisting primarily of methanol in the gaseous state. During combustion in a specific RCCI (Reactivity Compression Controlled Ignition) mode, a well-mixed fuel and low-reactivity oxidizer (usually with air) are compressed in the gaseous state but do not reach self-ignition. Later, still during the compression cycle, high reactivity fuel, in this case

EHN, is injected to form a local mixture of low and high reactivity fuel. A EHN weight ratio of 7% co-injected in the presence of gaseous methanol is said to lead to acceptable combustion efficiency compared with a reference fuel consisting of a mixture of isooctane and n-heptane. This type of process has the major disadvantage of requiring co-injection control according to the engine's operating conditions, structural arrangements such as separate tanks and injection systems. Also, the use of a fuel oil as a pilot fuel generates CO₂ emissions with a negative impact on the environment.

The second means is a mixture of fuels with methanol. It is known that alcohols, such as methanol or ethanol, can be mixed in a minority or majority proportion with fossil or synthetic diesel fuels such as dimethyl ether (DME) or with gasoline. In this case again the CO₂ emission balance is negative for the environment.

The third means is the incorporation of an ignition improvement additive in admixture with methanol, possibly also in admixture with diesel fuel. Numerous patent applications, such as CN 103865592 and CN 104232180, describe the incorporation of a cocktail of multifunctional additives in a mixture with methanol, possibly also in a mixture with a fuel oil. These additives have, for example, conservation, anti-corrosion, combustion improvement and detergency functions. These additives generally represent at least 10% of the weight of the fuel. The proportion of methanol in the fuel is between 30% and 90% by weight depending on the weight percentages of additives and diesel fuel present in the fuel.

The combined effects of these additives are only observed in a global way without dosing with precision the necessary quantities. It is therefore not a fuel essentially composed of methanol.

It is moreover known to mix fuels such as diesel, biodiesel and/or alcohol with water (typically up to 15% by weight) to reduce the production of nitrogen oxides in the combustion products of compression or spark ignition engines. However, the addition of water reduces the combustion temperature and flammability of the fuel. US Patent 7,216,607 and the scientific paper "Performance and NO_x Emissions of Spark Ignited Combustion Engines Using Alternative Fuels-Quasi One-Dimensional Modeling II. Methanol Fueled Engine" (Combustion Science and Technology Volume 18, 1978 - Issue 5-6) describe these effects of adding water to fuels.

On another level, in the field of hydrocarbon diesel or bio-diesel fuels, 2-ethylhexyl nitrate (EHN) has long been known to be used as a cetane enhancer in diesel fuel. A higher cetane value ensures lower fuel consumption, reduced particulate matter and NO_x emissions,

faster cold engine start, reduced engine knock and noise, and reduced engine wear. The reaction mechanism of EHN in the presence of a hydrocarbon diesel fuel has been studied for example in the scientific publication "The Autoignition Behavior of Surrogate Diesel Fuel Mixtures and the Chemical Effects of 2-Ethylhexyl Nitrate (2-EHN) Cetane Improver" (vol. 108, section 4: Journal of fuels and lubricants (1999), pp. 1029-1045).
5 However, the reaction mechanism of its diesel fuel cetane improver effect is still poorly understood and its use is based on empirical laws. For this reason, its effectiveness on fuels other than diesel cannot be presumed. This additive is industrially produced and widely used in commercial diesel fuels. More than fifty thousand tons of EHN have been
10 produced per year in Europe since the 1980s. Other alkyl nitrates can also be used as cetane enhancement additives in diesel fuel.

Patent application EP 030 429 describes a fuel comprising a mixture of (A) at least one alcohol having an average molecular weight of less than 160 and (B) at least one other organic compound or mixture of organic compounds which together have a spontaneous
15 ignition temperature of less than 450°C. Compound (B) may be, amongst several possibilities, an organic compound selected from azo compounds, tetrazines, nitroso compounds, nitro compounds, nitrates and hyponitrites, it being understood that this compound (B) is not entirely composed of a C₂-C₈ alkyl nitrate. It should be noted that the sole example of a fuel containing water does not contain any alkyl nitrate.

20 The present invention provides a solution for improving the ignition of a fuel essentially consisting of a mixture of alcohol and water (also referred to in the following as alcohol/water mixture) in combustion engines. This improvement is obtained by adding the EHN additive alone in a small proportion by weight to the alcohol/water mixture. More broadly, other alkyl nitrates, known to have cetane number improving properties similar to
25 EHN for diesel fuel, are also advocated in the context of the present invention for improving the ignition of the alcohol/water mixture. It is unexpected that additives known to increase the cetane number of a diesel or biodiesel hydrocarbon can be so effectively used, at very low weight percentages, to improve the ignition of an alcohol, such as methanol, in admixture with water.

30 **Summary of the invention**

The invention relates to a liquid fuel for a combustion engine of the compression-ignition or spark-ignition type, comprising from about 95.0% to about 99.9% by weight of a mixture of alcohol and water and from about 0.01% to about 5.0% by weight of a

compound for improving the ignition delay of the fuel, the mixture of alcohol and water consisting of about 1% to about 15% by weight of water and about 85% to about 99% by weight of alcohol.

The said compound for improving the ignition delay of the fuel is an alkyl nitrate, which is
5 liquid at room temperature, has low flammability, and is non-toxic and industrially produced.

The said compound, at these low levels in the presence of the alcohol/water mixture, is therefore conventionally assimilated to a fuel additive.

The addition of said liquid compound to the alcohol/water mixture is carried out in the
10 liquid state to form the fuel according to the invention in a tank. It can also be stored separately and mixed with the alcohol/water mixture to form the fuel according to the invention prior to its injection into the engine, or co-injected to form the fuel according to the invention in a premix chamber of the engine.

The said compound, of the alkyl nitrate type, previously reserved for improving the cetane
15 number of fossil diesel or biodiesel hydrocarbon fuels, is thus used effectively and surprisingly as an additive for improving the ignition of the alcohol in admixture with water.

Brief description of the figures

Figure 1 shows the effect of EHN on the ignition delay of a methanol/water mixture, water
20 making up 5% by weight of the mixture, with a single main injection (circular dots on figure) or a micro-injection followed by a main injection (square dots on figure) into the engine cylinder.

Figure 2 shows the effect of EHN on the ignition delay of a methanol/water mixture, water
25 making up 10% by weight of the mixture, with a single main injection (circular dots on figure) or a micro-injection followed by a main injection (square dots on figure) into the engine cylinder.

Description of the invention

As defined herein, "alcohol" is understood to mean an alcohol having from 1 to 4 carbon atoms. In some embodiments, the alcohol is methanol or ethanol, advantageously
30 methanol.

The present disclosure relates to a fuel for combustion engines of the compression-ignition or spark-ignition type, which comprises about 95.0% to about 99.9% by weight of a

mixture of alcohol and water, water making up 1.0% to 15.0% by weight of the mixture, and about 0.01% to about 5.0% by weight of an alkyl nitrate.

In one embodiment, the fuel comprises about 0.1% to about 3.0% by weight of alkyl nitrate.

- 5 In one embodiment, the fuel of the invention consists of the alcohol/water mixture and of the alkyl nitrate (in which case the amount of alkyl nitrate in the fuel is of at least 0.1% by weight).

In another embodiment, when the sum of the amount of the alcohol/water mixture and the amount of alkyl nitrate is not equal to 100% by weight, the fuel may contain one or more
10 other additives to make the fuel 100% complete, such as additives with preservative, anti-corrosion or detergent functions.

In one embodiment, the fuel according to the invention does not comprise a dimer of an unsaturated fatty acid and/or of an ester of phosphorous acid. In another embodiment, which can be combined with the preceding one, the fuel according to the invention does
15 not comprise a C₈-C₂₀ aliphatic monocarboxylic acid. In another embodiment, which can be combined with the preceding two, the fuel according to the invention does not comprise a mixture of C₄ and/or C₅/C₆ and/or C₅-C₇ hydrocarbons, and does not comprise a mixture of gasoline with at least one of said hydrocarbons.

The alkyl nitrate, which is added to the water/alcohol mixture, is more particularly selected
20 from linear alkyl nitrates having 4 to 36, advantageously 4 to 24 carbon atoms, branched alkyl nitrates having 4 to 36, advantageously 4 to 24 carbon atoms, cyclic alkyl nitrates (or cycloalkyl nitrates) having 5 to 18 carbon atoms, and mixtures thereof. In one embodiment, the said alkyl nitrate is selected from 2-ethylhexyl nitrate, hexyl nitrate, cyclohexyl nitrate, 2-octyl nitrate, n-nonyl nitrate, isononyl nitrate, dodecyl nitrate, 2-propylheptyl nitrate, 2-
25 tetradecyl-1-octadecyl nitrate, a mixture of C₉-C₁₃ branched alkyl nitrates, and mixtures thereof. In one embodiment, the alkyl nitrate is 2-ethylhexyl nitrate alone or in admixture with one or more other alkyl nitrates as defined above, advantageously the alkyl nitrate is 2-ethylhexyl nitrate.

According to one embodiment, the fuel ignition improvement compound, i.e. the alkyl
30 nitrate, is mixed in the liquid state with the alcohol/water mixture in the tank supplying the engine, to obtain the fuel according to the invention.

According to one embodiment, the said alkyl nitrate on the one hand and the alcohol/water mixture on the other hand, are stored separately, and brought together in the liquid state in

an injector, thereby forming the fuel according to the invention before it is fed into the combustion chamber of the engine.

According to one embodiment, the said alkyl nitrate is stored separately from the alcohol/water mixture and is co-injected with the alcohol/water mixture to form the liquid
5 fuel according to the invention in a premix chamber of the engine.

The present disclosure also relates to the use of an alkyl nitrate, in the amounts defined above, as an ignition improver for a fuel based on (consisting of) alcohol and water.

The present disclosure also relates to a method for improving the ignition of a fuel based on (consisting of) a mixture of alcohol and water in an engine (in particular a combustion
10 engine), the method comprising adding an alkyl nitrate(as defined above) to said mixture, in the amounts defined above. In one embodiment, the alkyl nitrate and the alcohol/water mixture are mixed in an injector. In one embodiment, the alkyl nitrate and the alcohol/water mixture are mixed in a premix chamber of the engine.

The present disclosure also relates to an engine (in particular a combustion engine), of a
15 vehicle (such as a car, truck, tractor, etc.), or vessel (such as a tanker, container ship, etc.) containing a fuel as defined above. The present disclosure also relates to a vehicle or vessel comprising an engine as defined above.

The present disclosure is illustrated by the following examples given for information purposes.

20 **Examples**

The performance of the fuel according to the invention compared with a fuel composed solely of methanol and water was measured using an experimental laboratory compression ignition, single-cylinder, 0.499 L direct injection engine, targeting a mean indicated pressure (MIP) of 3 bar at 1500 rpm. After passing 100 cycles (necessary for future
25 calculations to obtain a consistent average of values), the values of the engine's operating parameters were measured. At the same time, it was possible to record 20 pollutant measurement cycles, each 5 seconds apart, to obtain a representative average of emissions from different cycles. From the values recovered above, the following parameters characterizing fuel combustion and engine operation were extracted:

- 30 - dAI auto-ignition delay (ms),
- Mean Indicated Pressure (MIP)
- MIP Covariance (COVMIP),
- CA1 angle,

- CA50 angle,
- combustion time,
- pollutants (NO_x, CO, H₂O, HC),
- heat release rate.

5 The addition of the alkyl nitrate to the methanol/water mixture improved the overall combustion and engine operating parameters, compared with a fuel consisting solely of a methanol/water mixture. The performance of the fuel of the invention could be further improved by controlling fuel injection with multiple injections at each engine cycle, for example with one or more so-called pilot micro-injections followed by a main injection.

10 The ignition delay as a function of the fuel intake temperature is the value resulting from the tests, which is presented below to illustrate the advantages of the invention.

The ignition delay dAI is defined according to the following formula in which P_c is the pressure applied to the injected fuel:

$$dAI = t\left(\frac{dP}{dt}_{max}\right) - t(P_c)$$

15 **Example 1**

This example concerns the improvement, by addition of the compound EHN, of the combustion performance in an engine of a mixture consisting of 95% by weight of methanol and 5% by weight of water.

The ignition delays were determined as a function of the intake temperature (from 313K to 473K – 40°C to 200°C), at a pressure P_c of 300 bar, of a fuel according to the invention
 20 consisting of 99.0 % by weight of a methanol/water mixture, water making up 5.0% by weight of the mixture, and 1.0% by weight of EHN and for a richness of the mixture with air of 0.25. The results are shown in Figure 1 with the ignition delay benchmarks of the methanol/water mixture (95%/5% weight ratio) alone. It can be seen that there is a
 25 significant reduction in fuel ignition delays of the fuel containing EHN, compared to the methanol/water fuel. This reduction in ignition delay compared to that of the methanol/water mixture is all the more important that the temperature is low. For operation with a single main injection, at an intake temperature of 403 K, the ignition delay of the fuel of the invention according to the present example was approximately 3 times less than
 30 that of the reference fuel comprising methanol and water. The fuel of the invention ignited

even at low intake temperatures below 403K, down to 373K with an ignition delay of 2 ms, for which the methanol/water mixture did not ignite.

Under multiple injection conditions comprising a micro-injection (lasting 400 μ s at a crankshaft angle of -25°) followed by a main injection (lasting 1,500 μ s at a crankshaft angle of -15°), an improvement was observed in the combustion characteristics of the methanol/water mixture, which ignited at 373K with an ignition delay of about 1.75 ms. Combustion of the methanol/water mixture under these conditions and at this temperature was close to that of the methanol/water mixture to which 1.0% by weight of EHN was added, but operated with a single main injection. Below 373K, the methanol/water mixture did not ignite. In contrast, the methanol/water mixture containing 1.0% by weight of EHN did ignite at temperatures as low as 313K, with an ignition delay of about 1.2 ms.

Example 2

This example relates to the performance improvement, by addition of EHN, of the engine combustion of a mixture consisting of 90% by weight of methanol and 10% by weight of water.

Ignition delays were determined as a function of the intake temperature (from 313K to 463K), at a pressure P_c of 300 bar, of a fuel according to the invention consisting of 98% by weight of a methanol/water mixture, with water making up 10% by weight of the mixture, and 2% by weight of EHN and for a richness of the mixture with air of 0.25. The results are shown in Figure 2 with the ignition delay reference points for the methanol/water mixture alone. For an addition of 1% by weight of EHN, an improved fuel combustion performance was observed for intake temperatures below 433K. For an intake temperature of 413K, the fuel containing 1% by weight of EHN had an ignition delay approximately 1.5 times lower than that of the methanol/water reference fuel. At an intake temperature of 413K with 2% by weight of EHN, the ignition delay at that temperature was twice lower than that of the methanol/water mixture. At an intake temperature of 403K, the methanol/water mixture did not ignite, whereas fuels containing 1% by weight of EHN and 2% by weight of EHN ignited with a delay of about 4 ms and 2.2 ms, respectively.

Under multiple injection conditions comprising a micro-injection (lasting 400 μ s at a crankshaft angle of -25°) followed by a main injection (lasting 1,500 μ s at a crankshaft angle of -15°), an improvement in the combustion characteristics of the methanol/water mixture was observed, which mixture ignited at 393K with an ignition delay of about 3.5 ms. Below 393K, the methanol/water mixture did not ignite. In contrast, fuel

containing 1% by weight of EHN ignited at temperatures as low as 383K with an ignition delay of about 1.5 ms. Fuel containing 2% by weight of EHN ignited up to 333K with an ignition delay of about 1.75 ms.

The results of Examples 1 and 2 are summarized in Table 1.

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Table 1

Methanol/water (wt%)	EHN (wt%)	Single injection	Micro- injection followed by main injection	Minimum ignition temperature (K)	Ignition delay (ms)
95%/5%	0	X		403	4
	1%	X		373	2
	0		X	373	1.75
	1%		X	313	1.25
90%/10%	0	X		413	3.5
	1%	X		403	4
	2%	X		403	2.2
	0		X	393	3.5
	1%		X	383	1.5
	2%		X	333	1.75

These examples show that the use of alkyl nitrate in a low weight percentage can significantly improve the ignition delay of a fuel based on alcohol and water. More generally, the addition of an alkyl nitrate-type compound to an alcohol/water mixture improves overall fuel performance in a combustion engine, while maintaining limited emissions of nitrogen oxides, up to intake temperatures close to ambient temperature. There was no reason to believe that additives known to increase the cetane number of a diesel or biodiesel hydrocarbon could be used so effectively, in very small amounts, to improve the ignition of an alcohol in admixture with water.

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Claims

1. A fuel for a combustion engine, comprising 95.0% to 99.9% by weight of a mixture of alcohol and water in the liquid state, in which water makes up 1% to 15% by weight of the mixture, and 0.01% to 5.0% by weight of an alkyl nitrate, said alkyl nitrate being a nitrate of a linear alkyl having from 4 to 36 carbon atoms, a nitrate of a branched alkyl having from 4 to 36 carbon atoms, a nitrate of a cyclic alkyl having from 5 to 18 carbon atoms, or a mixture of these nitrates.
2. The fuel of claim 1, comprising 95.0% to 99.9% by weight of alcohol/water mixture, and 0.1% to 3.0% by weight of alkyl nitrate.
3. The fuel of any one of claims 1 to 2, wherein the alkyl nitrate is selected from 2-ethylhexyl nitrate, hexyl nitrate, cyclohexyl nitrate, 2-octyl nitrate, n-nonyl nitrate, isononyl nitrate, dodecyl nitrate, 2-propylheptyl nitrate, 2-tetradecyl-1-octadecyl nitrate, isononyl to isotridecyl nitrate, and mixtures thereof.
4. The fuel of claim 3, wherein the alkyl nitrate is 2-ethylhexyl nitrate.
5. The fuel of any one of claims 1 to 4, wherein the alcohol is methanol or ethanol.
6. The fuel of claim 6, wherein the alcohol is methanol.
7. A process of obtaining a fuel according to any one of claims 1 to 6, which comprises mixing, in a liquid state, of the alkyl nitrate with an alcohol/water mixture.
8. The process of claim 8, wherein the alcohol, water and the alkyl nitrate are mixed in an engine tank.
9. The process of claim 7, wherein the mixture of alcohol and water and the alkyl nitrate are mixed in an injector.

10. The process of claim 7, wherein the mixture of alcohol and water and the alkyl nitrate are mixed in a premix chamber of an engine.

11. Use of an alkyl nitrate in the liquid state, in an amount of 0.01% to 5.0% by weight, in a liquid fuel based on alcohol and water, as agent improving the ignition of said fuel, said alkyl nitrate being a nitrate of a linear alkyl having from 4 to 36 carbon atoms, a nitrate of a branched alkyl having from 4 to 36 carbon atoms, a nitrate of a cyclic alkyl having from 5 to 18 carbon atoms, or a mixture of these nitrates.

12. The use of claim 11, wherein the alcohol is methanol or ethanol, preferably methanol.

13. The use of claim 11 or claim 12, wherein the alkyl nitrate is as defined in any one of claims 3 to 4.

14. A method for improving the ignition, in a combustion engine, of a fuel comprising 95.0% to 99.9% by weight of a mixture of alcohol and water in the liquid state, comprising adding to said mixture an alkyl nitrate in an amount of 0.01% to 5.0% by weight, said alkyl nitrate being a nitrate of a linear alkyl having from 4 to 36 carbon atoms, a nitrate of a branched alkyl having from 4 to 36 carbon atoms, a nitrate of a cyclic alkyl having from 5 to 18 carbon atoms, or a mixture of these nitrates.

15. The method of claim 14, wherein the alkyl nitrate is as defined in any one of claims 3 to 4.

16. The method of claim 14 or claim 15, wherein the alcohol is methanol or ethanol, preferably methanol.

17. A combustion engine containing a fuel as defined in any one of claims 1 to 6.