

As originally filed**5 Biodiesel fuel mixture comprising polyoxymethylene dialkyl ether**

The present invention relates to a biodiesel fuel mixture comprising polyoxymethylene dialkyl ether.

10

For many years, industry has been making efforts to identify alternative energy sources which are not of fossil origin, and also to make available so-called renewable raw materials. The latter include vegetable oils, i.e. fatty acid esters, typically triglycerides, which can generally be classified as biodegradable and harmless to the environment. Rapeseed oil can
15 be regarded as a prototype of such vegetable oils. In general, such oils comprise the glycerides of a number of acids, the acids being variable with the type and origin of the vegetable oil, and additionally phosphoglycerides if appropriate. Such oils may be obtained by known processes. The vegetable oils can be transesterified to obtain the alkyl esters, for example the methyl esters, of the fatty acids bonded in the glycerides.

20

FR-A 2 492 402 describes a fuel composition comprising one or more fatty acid esters of animal or vegetable origin of the general formula R^1-COOR^2 , in which R^1 is a substantially linear saturated or unsaturated aliphatic radical having from 5 to 23 carbon atoms and R^2 is a linear or branched, saturated or unsaturated aliphatic radical having 1 to 12 carbon atoms.
25 Such fuel compositions are described as being suitable for use in diesel engines since they have a cetane number which corresponds approximately to the cetane number of conventional diesel fuels which are obtained from mineral oils.

30

The main advantage of biodiesel as a renewable fuel is the reduction in the net CO_2 emission. Moreover, the exhaust emissions of sulfur oxides, particles and carbon monoxide are reduced. In contrast, the nitrogen oxide emissions can be slightly increased. Thus, it can be assumed that the amount of CO_2 released when biodiesel is combusted (approx. 2.4 t/t of biodiesel) can be assimilated again by growing plants from which vegetable oils for biodiesel are obtained in turn, so that the net CO_2 output is close to 0. Biodiesel is also
35 virtually sulfur-free (sulfur content between 0 and 0.0024 ppm, compared to up to 350 ppm of sulfur in conventional fossil diesel fuel). Although the NO_x emissions from pure biodiesel are on average 6% above those from diesel of fossil origin, the absence of sulfur enables techniques for NO_x reduction which cannot be employed in conjunction with conventional fossil diesel. The oxygenates present in the biodiesel improve the combustion

and the emission profile, so that about 20% less carbon monoxide is formed compared to fossil diesel fuel. The particle emissions from biodiesel are also significantly lower and are 40% or more below those of conventional fossil diesel. The biodegradability of biodiesel is greatly increased compared to fossil diesel.

5

The energy content of biodiesel is still 92% of that of fossil diesel, so that approx. 1.1 l of biodiesel replace 1 l of fossil diesel fuel.

10

Future European diesel specifications are aiming considerably in the direction of higher cetane numbers, while the content of sulfur and polyaromatic hydrocarbons is to be reduced.

15

It is known that the cetane number of diesel fuels can be increased by admixing linear ethers. In addition, the cold properties of the fuel are improved and the dilution reduces the contents of aromatic hydrocarbons and sulfur. The ethers also have a positive effect on the emissions. The high cetane number leads to lower emission of hydrocarbons and carbon monoxide. The high oxygen content in the ether additionally leads to a reduction of soot particles in the exhaust gas.

20

EP-A 1 070 755 discloses a diesel fuel mixture with a cetane number > 40 composed of a typical diesel oil cut and from 1 to 20% by volume of polyoxymethylene dialkyl ethers. The addition of the polyoxymethylene dialkyl ethers raises the cetane number from 48 to a value between 63 and 100.

25

It is an object of the invention to provide a biodiesel-based diesel fuel mixture with a high cetane number and good emission profile.

The object is achieved by a biodiesel fuel mixture having a cetane number of > 40, comprising

30

- a) from 1 to 100% by weight of biodiesel,
- b) from 0 to 98.9% by weight of diesel oil of fossil origin,
- c) from 0.1 to 20% by weight of polyoxyalkylene dialkyl ether of the formula

35



in which R is an alkyl group having from 1 to 10 carbon atoms and n = from 2 to 10, and

d) from 0 to 5% by weight of further additives.

- 5 As component a), the inventive biodiesel fuel mixture comprises from 1 to 100% by weight, generally from 5 to 90% by weight, preferably from 5 to 50% by weight and more preferably from 10 to 50% by weight, of biodiesel. Biodiesel generally has a viscosity at 40°C of from 1.9 to 6.5 cSt, preferably from 3.5 to 5.0 cSt, a sulfur content of not more than 0.05% by weight, preferably 0.01% by weight, a cetane number of at least 40, preferably at least 49, and an acid number of up to 0.80 mg KOH/g, preferably of up to 0.50 mg KOH/g. Biodiesel consists generally of fatty acid esters of the general formula R^1-COOR^2 in which R^1 is a substantially linear saturated or unsaturated aliphatic radical having from 5 to 23 carbon atoms and R^2 is a linear or branched, saturated or unsaturated aliphatic radical having from 1 to 12 carbon atoms. The fatty acid esters present in the biodiesel preferably
10 derive from linear, saturated or unsaturated fatty acids R^1COOH with from 11 to 23 carbon atoms in the R^1 radical, in particular from saturated fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid and lignoceric acid, monoethylenically unsaturated fatty acids such as lauroleic acid, myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid and erucic acid, and also di- or polyethylenically
15 unsaturated fatty acids such as linoleic acid and linolenic acid. The fatty acids of the fatty acid esters present in the biodiesel are obtained from vegetable or animal fats. Vegetable fats are, for example, rapeseed oil, sunflower oil, copra oil, corn oil, cottonseed oil, soya oil and peanut oil. Suitable fats of animal origin are, for example, pork fat or beef tallow.
- 25 The alcohol component of the ester present in biodiesel is preferably selected from methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, 2-ethylhexanol or dodecanol. The fatty acid esters are preferably obtained from the glycerides present in the natural fats of vegetable or animal origin by transesterification with the alcohol R^2OH .
- 30 As component b), the inventive biodiesel fuel mixture comprises conventional diesel oil of fossil origin. Diesel represents the high boiler fraction of the middle distillates of mineral oil. Typical diesel oil cuts have a boiling point in the range from 150 to 380°C, preferably from 200 to 350°C, and a density of from 0.76 to 0.935 g/ml at 15°C.
- 35 As component c), the inventive biodiesel fuel mixture comprises from 0.1 to 20% by weight, generally from 1 to 20% by weight, preferably from 3 to 11% by weight, more preferably from 4 to 11% by weight, of polyoxymethylene dialkyl ether. Among these,

preference is given to the dimethyl ether and diethyl ether. Preference is further given to polyoxymethylene dialkyl ethers with $n = 3, 4$ or 5 oxymethylene units, and also mixtures thereof. Particular preference is given to polyoxymethylene dimethyl ethers with $3, 4$ or 5 oxymethylene units and mixtures thereof. Particularly preferred are polyoxymethylene dimethyl ethers with $n = 3$ or 4 oxymethylene units and mixtures thereof; especially preferred is tetraoxymethylene dimethyl ether ($n = 4$).

The invention also provides for the use of the polyoxymethylene dialkyl ethers as additives for biodiesel fuel mixtures which comprise at least 1% by weight of biodiesel for increasing the cetane number.

The polyoxymethylene dialkyl ethers c) may, as described in EP-A 1 070 755 be prepared by reacting the appropriate alcohol, preferably methanol, with formaldehyde in the presence of acidic catalysts.

A particularly advantageous process for preparing polyoxymethylene dimethyl ethers which are particularly suitable as biodiesel fuel additives c), in particular the polyoxymethylene dimethyl ethers where $n = 3$ and 4 (trimer, tetramer), starts from methylal ($n = 1$) and trioxane. These are fed into a reactor and reacted in the presence of an acidic catalyst, the amount of water introduced into the reaction mixture by methylal, trioxane and/or the catalyst being $< 1\%$ by weight based on the reaction mixture.

In the reaction of methylal with trioxane to give the polyoxymethylene dimethyl ethers, no water is formed as a by-product. The reaction is carried out generally at a temperature of from 50 to 200°C , preferably from 90 to 150°C , and a pressure of from 1 to 20 bar, preferably from 2 to 10 bar. The molar methylal:trioxane ratio is generally from 0.1 to 10 , preferably from 0.5 to 5 .

The acidic catalyst may be a homogeneous or heterogeneous acidic catalyst. Suitable acidic catalysts are mineral acids such as substantially anhydrous sulfuric acid, sulfonic acids such as trifluoromethanesulfonic acid and para-toluenesulfonic acid, heteropolyacids, acid ion exchange resins, zeolites, aluminosilicates, silicon dioxide, aluminum oxide, titanium dioxide and zirconium dioxide. Oxidic catalysts may, in order to increase their acid strength, be doped with sulfate or phosphate groups, generally in amounts of from 0.05 to 10% by weight. The reaction may be carried out in a stirred tank reactor (CSTR) or a tubular reactor. When a heterogeneous catalyst is used, preference is given to a fixed bed reactor. When a fixed catalyst bed is used, the product mixture can subsequently be contacted with an anion

exchange resin in order to obtain a substantially acid-free product mixture.

5 The amount of water introduced by methylal and trioxane and by the catalyst is in total < 1% by weight, preferably < 0.5% by weight, more preferably < 0.2% by weight and in particular < 0.1% by weight, based on the reaction mixture composed of methylal, trioxane and the catalyst. For this purpose, virtually anhydrous trioxane and methylal are used, and the amount of water introduced by the catalyst, if appropriate, is correspondingly restricted. The hemiacetals (monoethers) or polyoxymethylene glycols formed by hydrolysis in the presence of water from already formed polyoxymethylene dimethyl ether have a comparable
10 boiling point to the polyoxymethylene dimethyl ethers, which complicates removal of the polyoxymethylene dimethyl ethers from these by-products.

In order to obtain polyoxymethylene dimethyl ethers where $n = 3$ and $n = 4$ (trimer, tetramer) in a controlled manner, a fraction comprising the trimer and tetramer is removed
15 from the product mixture of the reaction of methylal with trioxane, and unconverted methylal, trioxane and polyoxymethylene dimethyl ether where $n < 3$ are recycled into the acid-catalyzed reaction. In a further embodiment of the process according to the invention, the polyoxymethylene dimethyl ethers where $n > 4$ are additionally also recycled into the reaction. As a result of the recycling, a particularly large amount of trimer and tetramer is
20 obtained.

In a particularly preferred embodiment, a first fraction comprising methylal, a second fraction comprising the dimer ($n = 2$) and trioxane, a third fraction comprising the trimer and tetramer ($n = 3, 4$) and a fourth fraction comprising the pentamer and higher homologs
25 ($n > 4$) are obtained from the product mixture of the acid-catalyzed reaction of methylal with trioxane. It is especially preferred in this context to carry out the removal of the product mixture of the acid-catalyzed reaction of methylal with trioxane in three distillation columns connected in series, the first fraction being removed from the product mixture of the reaction in one distillation column, the second fraction being removed from the remaining mixture in a second distillation column, and the remaining mixture being
30 separated into the third and the fourth fraction in a third distillation column. In this separation, the first distillation column may be operated, for example, at a pressure of from 0.5 to 1.5 bar, the second distillation column, for example, at a pressure of from 0.05 to 1 bar and the third distillation column, for example, at a pressure of from 0.001 to 0.5 bar.
35 Preference is given to recycling the first and the second fraction, more preferably additionally also the fourth fraction, into the reaction.

When a homogeneous catalyst, for example a mineral acid or a sulfonic acid, is used, it

remains in the fourth fraction and is recycled with it into the acid-catalyzed reaction.

It is common knowledge that acetals, which also include the polyoxymethylene dialkyl ethers used in the present context, are cleaved under acidic conditions. Biodiesel has an acid number of generally at least 0.1 mg KOH/g and up to 0.8 mg KOH/g (according to US standard) or of up to 0.5 mg KOH/g (according to DIN 51606). As a result of an increase in the water content during storage or during consumption, the acid number can rise further as a result of the shift in the chemical equilibrium from fatty acid esters to fatty acids. The acidic properties of the biodiesel lead to the expectation that the polyoxymethylene dialkyl ethers will not be stable in biodiesel and will be cleaved to formaldehyde and methanol. However, it has been found that, surprisingly, this is not the case and polyoxymethylene dimethyl ethers are entirely stable in biodiesel and biodiesel/diesel mixtures in spite of the acidic properties of biodiesel.

- As component d), the inventive biodiesel fuel mixtures may comprise from 0 to 5% by weight, preferably from 0 to 1% by weight, of further additives. Typical further additives are cetane number improvers which may be present in amounts of typically up to 1% by weight.
- The inventive biodiesel fuel mixture has a cetane number of > 40, generally of > 45, preferably of > 50, more preferably of > 52.

A preferred inventive biodiesel mixture comprises

- a) from 5 to 90% by weight of biodiesel
- b) from 6 to 92% by weight of diesel oil of fossil origin
- c) from 3 to 11% by weight of polyoxyalkylene dialkyl ether
- d) from 0 to 1% by weight of cetane number improver.

The invention is illustrated in detail by the example which follows.

Examples

Example 1:

35

150 g of biodiesel (connediesel® CD 99, acid number = 0.12 mg KOH/g) and 20 g of tetraoxymethylene dimethyl ether $\text{H}_3\text{CO}(\text{CH}_2\text{O})_4\text{CH}_3$ were stirred at 25°C. The content of

$\text{H}_3\text{CO}(\text{CH}_2\text{O})_4\text{CH}_3$ was determined by gas chromatography at regular intervals. Over the entire experimental duration of 12 days, no decrease in the $\text{H}_3\text{CO}(\text{CH}_2\text{O})_4\text{CH}_3$ content was detected.

5 Example 2:

150 g of diesel and 20 g of tetraoxymethylene dimethyl ether $\text{H}_3\text{CO}(\text{CH}_2\text{O})_4\text{CH}_3$ were stirred at 25°C. The content of $\text{H}_3\text{CO}(\text{CH}_2\text{O})_4\text{CH}_3$ was determined by gas chromatography at regular intervals. Over the entire experimental duration of 12 days, no decrease in the

10 $\text{H}_3\text{CO}(\text{CH}_2\text{O})_4\text{CH}_3$ content was detected.

What is claimed is:

1. A biodiesel fuel mixture having a cetane number of > 40, comprising

a) from 1 to 100% by weight of biodiesel,

b) from 0 to 98.9% by weight of diesel oil of fossil origin,

c) from 0.1 to 20% by weight of polyoxyalkylene dialkyl ether of the formula



in which R is an alkyl group having from 1 to 10 carbon atoms and n = from 2 to 10, and

d) from 0 to 5% by weight of further additives.

2. The biodiesel fuel mixture according to claim 1, comprising, as component c), polyoxymethylene dialkyl ether with 3, 4 or 5 oxymethylene units or mixtures thereof.

3. The biodiesel fuel mixture according to claim 1 or 2, comprising, as component c), polyoxymethylene dimethyl ether.

4. The biodiesel fuel mixture according to any of claims 1 to 3, comprising

a) from 5 to 90% by weight of biodiesel

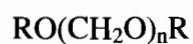
b) from 6 to 92% by weight of diesel oil of fossil origin

c) from 3 to 11% by weight of polyoxyalkylene dialkyl ether

d) from 0 to 1% by weight of cetane number improver.

5. The biodiesel fuel mixture according to any of claims 1 to 4 with a cetane number of > 45.

6. The use of polyoxymethylene dialkyl ethers of the general formula



in which R is an alkyl group having from 1 to 10 carbon atoms and n = from 2 to 10 as an additive in biodiesel fuel mixtures with at least 1% by weight of biodiesel for increasing the cetane number.