

Alcohols as a means to inhibit the formation of precipitates in blends of biodiesel and fossil diesel fuel

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Abstract: The European diesel fuel specification limits the biodiesel content to 7%. It is, however, desirable to increase the amount of renewables in the transport sector; therefore blending with a higher biogenic fuel content is of interest.

Blending of fuels can lead to chemical reactions between fuel components and may result in undesired products. In detail, aged biodiesel from unsaturated FAME and fossil diesel fuels can form oligomers and precipitations with a maximum in the range of B10 to B20. Precursors are oligomers that can be separated from the biodiesel or the blends in an amount of up to 20%. These oligomers seem to have potency for chemical reactions with fuel components or the engine oil.

To prevent tentative problems in the fuel filter, the injecting system and the combustion process itself, the formation of oligomers should be disabled in blends. Alcohols have been proven and tested to dissolve precipitations in the fuel. However, flash point problems occur, in case the alcohols have too low boiling points. In our tests, some alcohols could be identified to reach the demands of the diesel fuel standard EN 590. As acceptable monovalent alcohols, the longer-chained alcohols 1-octanol, 3-methyl-1-butanol (isoamyl alcohol) and 2-hexyldecan-1-ol were found. The blends with these alcohols both showed acceptable flashpoints according to DIN EN 590 and could prevent the occurrence of precipitates when added in a rather low concentration of about 6% to 8%.

Additionally, engine tests were carried out to monitor regulated and non-regulated emissions. The emissions of selected blends (B10+6OctOH, B10+8IsoamylOH, B10+8HexdecOH) were analyzed by using a single cylinder test engine (Farymann Diesel 18W, TIER 4, agricultural 5-mode test). All of these blends showed less NO_x emissions than the pure B10 blend without addition of alcohol. For the CO, HC and PM emissions, no remarkable changes could be found. In the case of non-regulated emissions, no relevant changes were observed in carbonyl and PAH emissions, relative to the B10 blend without addition of alcohol.

In the result, some blends from biodiesel, diesel fuel and alcohols tend to be appropriate to suppress chemical reactions in the fuel and probably in the engine oil. Further research is necessary to explain the chemical interactions that are responsible for the formation of oligomers and their reaction products. Not only chemical but also physical bonds can play important roles and are in the focus of current research.

Keywords: alcohol, biodiesel, emission, oligomer, precipitate, Germany

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1 Introduction

Today, in conformance with the quota of the addition of biogenic components in Germany and Europe, diesel fuel is blended with 7% biodiesel (Deutscher Bundestag, 2006; AGQM, 2010). However, the research on blends

like these shows unexpected precipitates. Terry et al. (2006), Krahl et al. (2008), and Peyton et al. (2008) found oxidative degradation products of the biodiesel as the causer. In detail, aged biodiesel from unsaturated fatty acid methyl ester (FAME) and fossil diesel fuel (DF) can form oligomers and precipitates with a maximum in the range of B10 to B20 (Fang and McCormick, 2006). Precursors are oligomers that can be separated from the biodiesel or the blends in an amount of up to 20%. These

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oligomers are soluble in the fuel, but they seem to have potency for chemical reactions with fuel components or the engine oil (Boffa, 2009; Schumacher, 2010). In order to clear these precipitates in blends the addition of alcohols is helpful. When using low-boiling alcohols as a fuel component for a diesel engine certainly some problems will arise. At first, blending the diesel fuel especially with short-chained alcohols is not possible in the whole temperature and pressure range (Chandra and Kumar, 2007). Furthermore, Brennen (2005) pointed out that the modification of the boiling curve can cause unwanted evaporation and cavitation effects in the fuel system. It is also important to mind the flash point of the blends. If the blends do not meet the diesel fuel standard (> 55 °C required), they must be classified into a higher danger class (Tschöke et al., 2006), which was shown in the case of ethanol by Krahl et al. (2011) and Eilts et al. (2009).

The objective of the project was to find acceptable solvents as efficient blend components. They should ensure the prohibition of the formation or the elimination of precipitates in the fuel and probably the engine oil. Furthermore blends including those components should comply with the diesel standard EN 590 and should show no relevant negative changes relating to the regulated and non-regulated emissions. For this purpose a quantification method of detecting the transmission factor by using a UV-Vis-spectrometer was developed. The emissions of the selected blends were analyzed by using a single cylinder test engine.

2 Results and discussion

2.1 Solution of precipitates

According to Krahl et al. (2009) an analysis of the sediments, which are formed in blends consisting of diesel fuel and aged rapeseed oil methyl ester (RME), showed that oligomers are oxidative degradation products of the biodiesel. This result is supported by an elementary analysis of these oligomers, where an increased oxygen percentage compared to a non-aged biodiesel was

detected. This increased oxygen percentage causes a higher polarity. Therefore in face of the formation of precipitates there are limits compared to the blending with the relative non-polar diesel fuel.

For investigation a B10 blend of 10% biodiesel and diesel fuel was prepared. The properties of fresh and aged RME as well as the fossil diesel fuel are listed in the appendix. The fresh RME was aged by leading a stream of air at 110 °C through the RME for 40 h.

Several solvents with different permittivity were tested to dissolve precipitates in the B10 blend of aged RME and diesel fuel. Therefore, an increasing amount of solvent was added to the B10 blend, and the volume necessary to dissolve the precipitates was determined. If no effect of the solvent was visible, the test was terminated at 5% solvent.

With regard to the efficiency of the solution of precipitates a balanced combination of hydrophilic and lipophilic parts of the molecule is necessary. Table 1 shows the relative permittivity and the amount of solvent that is necessary to suppress clouding. In this case the higher polarity of diols showed a clearly decreased efficiency. Concerning to a higher blend polarity further research is necessary to analyze possible problems with the water content.

Table 1 Efficiency of different selective solvents under specification of the relative permittivity, acc. to the Landolt-Börnstein Database (2011)

Solvent	Relative	Vol. % for
n-Hexane	1.9	-
Xylene	2.3	> 5
Toluene	2.4	8
Biodiesel (RME)	3.4	~ 40
Ethylacetate	6	7
Ethanolamine	6.9	> 5
Tetrahydrofuran	7.6	> 5
2-Hexyldecanol		7
1-Octanol	10	5
1-Hexanol	13.3	6
Cyclohexanol	15	7
3-Methyl-1-butanol	15.6	7
1-Butanol	17.8	~ 5
Ethanol	24.3	4

1,2-Propanediol	32	> 5
Ethane-1,2-diol	37	> 5
Castor oil methyl ester		11
Acetonitrile	37.5	Phased / Clouding
2-Aminoethanol	38.1	Phased / Clouding
Water	80	Phased / Clouding

As acceptable monovalent alcohols ethanol, 1-hexanol, 1-octanol, 3-methyl-1-butanol and 2-hexyl-decan-1-ol

were found. The suppression of clouding with increasing percentage of these alcohols was measured with a UV-Vis spectrometer at the wavelength of 850 nm (Figure 1).

For further investigation B10 blends with three alcohols were prepared. They are called B10+6OctOH (B10 Blend with 6% octanol), B10+8IsoamylOH (B10 Blend with 8% 3-methyl-1-butanol, common name: isoamyl alcohol), and B10+8HexdecOH (B10 Blend with 8% 2-hexyldecan-1-ol), respectively.

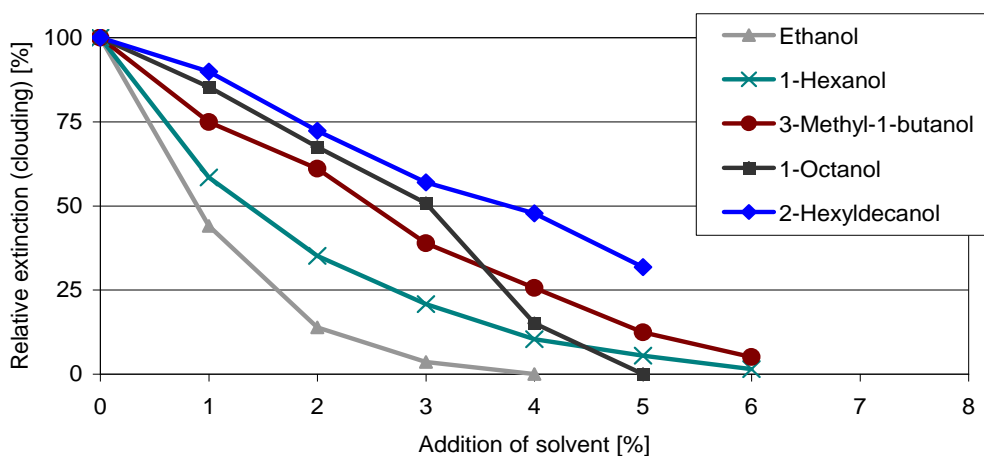


Figure 1 Measurement of the removal of clouding by extinction (Wavelength: 850 nm)

2.2 Compatibility of materials

Especially when new fuel components are used, it has to be checked if compatibility of materials is given in accordance with DIN EN ISO 175. Therefore, over a period of seven days at a temperature of 70 °C sample items for a tensile test of polyamide (PA 66 Ultramid® A3K - 11.2 g) and high density polyethylene (HDPE Lupolen® 4261 - 8.8 g) were stored in the selected fuels. Both materials are classified as biodiesel resistant. For comparison purposes, diesel fuel and RME were included in the test series, too. Furthermore, one test item was storewithout fuel exposure at 22 °C and 45% humidity in a climate chamber. In order to ensure constant temperatures, the fuels were stored in a temperature-controlled water bath. For statistical confirmation, the specimens were weighed three times before and after storage in the selected

fuels. In addition, the modulus of elasticity and tensile strength according to DIN EN ISO 527-2 were tested.

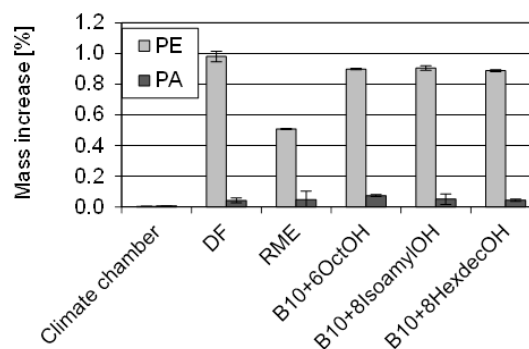


Figure 2 Mass increase during storage of PE and PA in different fuels

In Figure 2, the increase in mass of polyethylene (PE) and polyamide (PA) in selected fuels is shown. The sample from the climate chamber has no statistically significant increase in mass. For PE, the mass increase in DF is almost twice as high as in RME. All the selected blends show a similar behavior. Here, their mass increase

is near the mass increase in DF as expected from the composition of the blends. When PA is used, for all fuels a comparable low level in mass increase was detected.

Figure 3 shows the modules of elasticity from PE and PA stored in the different fuels. Compared to the sample from the climate chamber a decrease of the modules of elasticity was found. This means that the materials were becoming more elastic. In view of the standard deviation, no difference between the fuels was found.

PA exhibited generally a higher tensile strength than PE. For PA no significant changes were detected. PE showed a decrease of the tensile strength when stored in DF and in the selected blends (Figure 4).

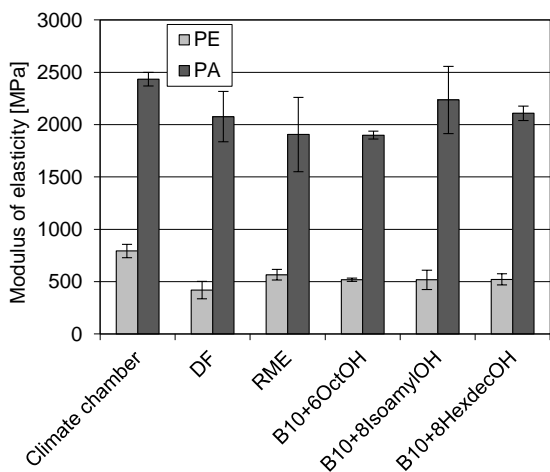


Figure 3 Influence on the modulus of elasticity after storage of PE and PA in different fuels

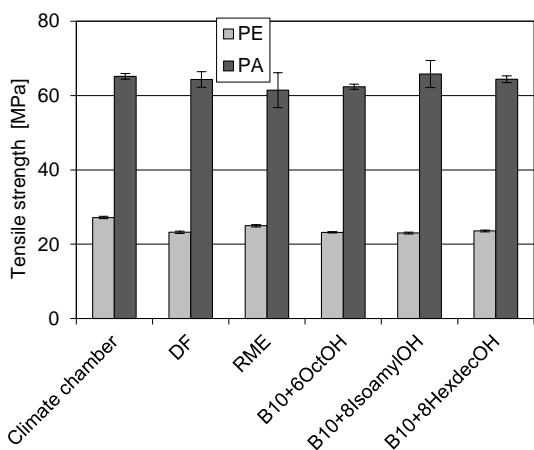


Figure 4 Influence on the tensile strength by storage of PE and PA in different fuels

2.3 Emissions

The emissions of the selected blends (B10+6OctOH, B10+8IsoamylOH, B10+8HexdecOH) were analyzed by

using a single cylinder test engine (Farymann Diesel 18W, TIER 4; Farymann, 2008). The engine was tested in five modes. The single modes of the test are listed in Table 2.

Table 2 Speed, torque and power output of the engine at the selected modes

Mode	Speed,	Torque,	Power,
A	2840	10.1	3.00
B	2650	5.5	1.52
C	1840	4.1	0.79
D	3000	1.7	0.54
E	1060	0.0	0.0

For all fuels same speed and torque were adjusted. In the case of the regulated emissions the blend with 1-octanol shows minor, the other selected ones show higher CO emissions relative to a B10 blend without alcohol addition (Figure 5). A reason for this result could be a changed initial boiling point. In case of 1-octanol it is possible that the consequence is a better mixture of air and fuel in the combustion chamber, which causes a better combustion. All selected blends show minor NO_x emissions relative to a B10 blend without alcohol addition (Figure 6). Obviously a blending with alcohol results in a positive effect to the NO_x emission.

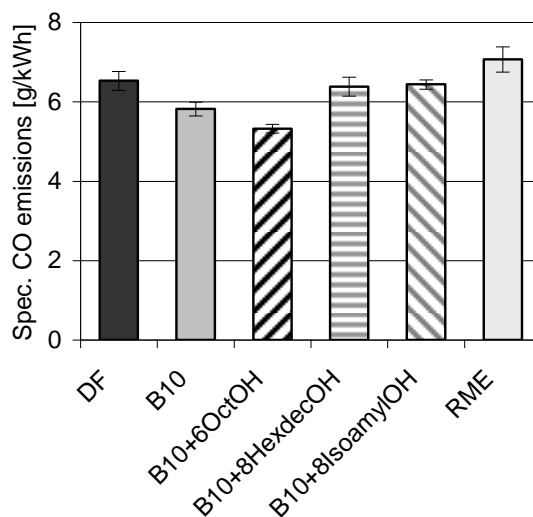


Figure 5 Specific CO emissions of selected blends using a Farymann single cylinder test engine in a 5-mode test

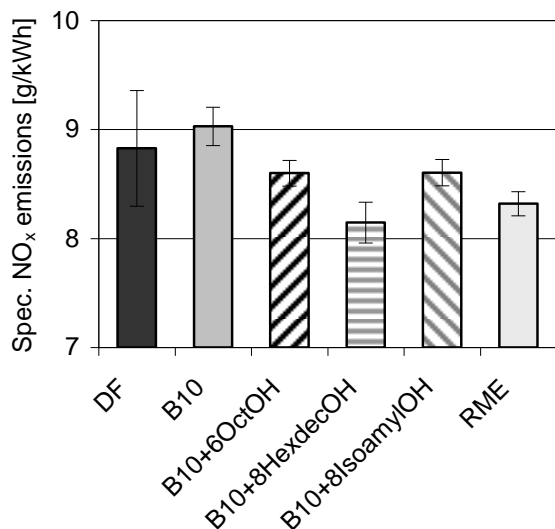


Figure 6 Specific NO_x emissions of selected blends using a Farymann single cylinder test engine in a 5-mode test

Relating to the HC and PM emissions no relevant changes were found relative to a B10 blend without alcohol addition (Figures 7 and 8). The Farymann engine emitted more PM using RME instead of DF. This emissions characteristic is a result of the high amount of unburned fuel in the PM. Due to the high boiling point, biodiesel does not evaporate from the particulate, which is different from diesel fuel.

In the case of the non-regulated emissions there are no relevant changes in carbonyl- (not shown here) and PAH-emissions relative to a B10 blend without alcohol addition (Figures 9 and 10; observe the different scales). According to the EPA, the following 15 PAH were tested: naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbFla), benzo[k]fluoranthene (BkFla), benzo[a]pyrene (BaPyr), dibenz(a,h)anthracene (DBAnt), benzo[ghi]perylene (BPer), indeno (1,2,3-cd) pyrene (IPyr).

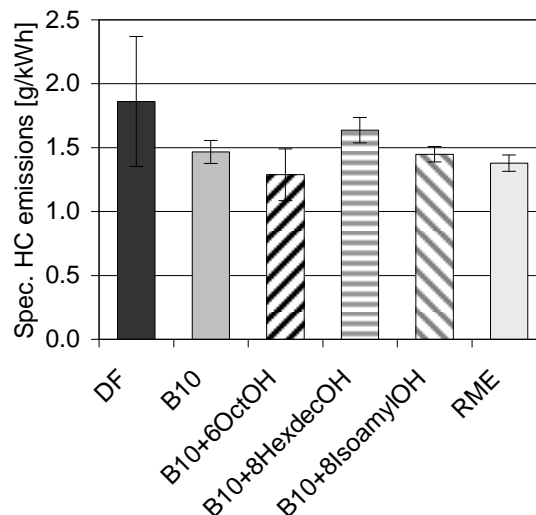


Figure 7 Specific HC emissions of selected blends using a Farymann single cylinder test engine in a 5-mode test

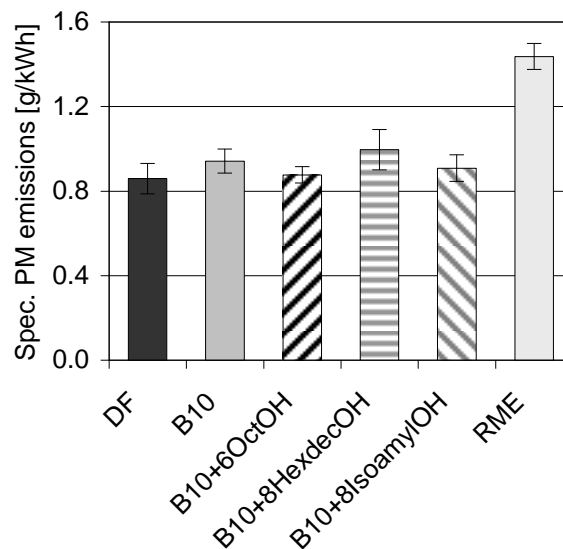


Figure 8 Specific PM emissions of selected blends using a Farymann single cylinder test engine in a 5-mode test

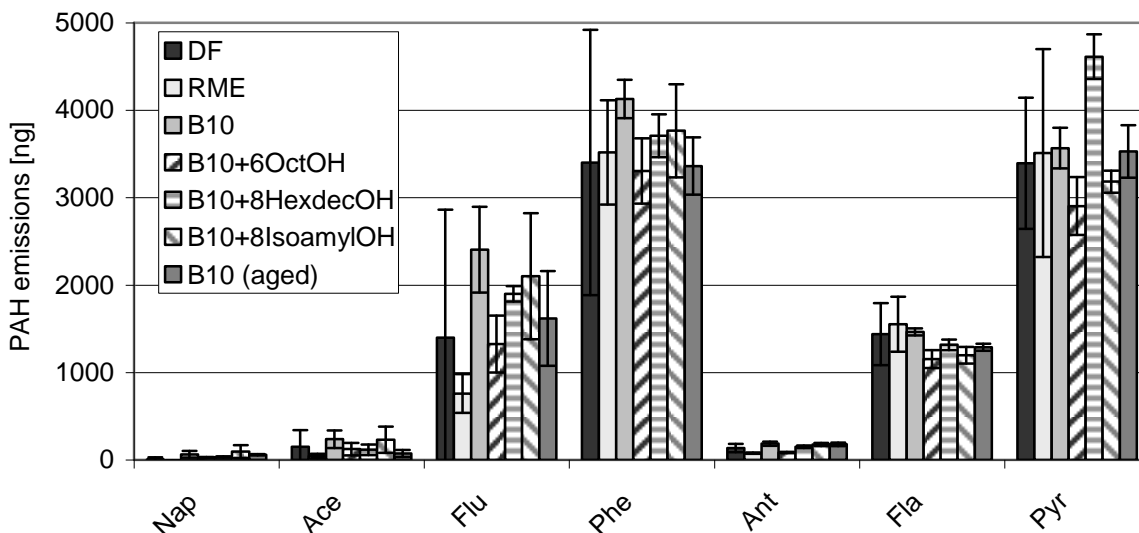


Figure 9 PAH emissions (part 1) of selected blends using a Farymann single cylinder test engine in a 5-mode test

All in all there are no results against the use of the selected alcohols as a blend component. Further re-research is necessary; in particular, also multi-component blends

should be treated and HVO should be considered as a further biogenic component. First results of such research can be found in Schaper et al. (2014).

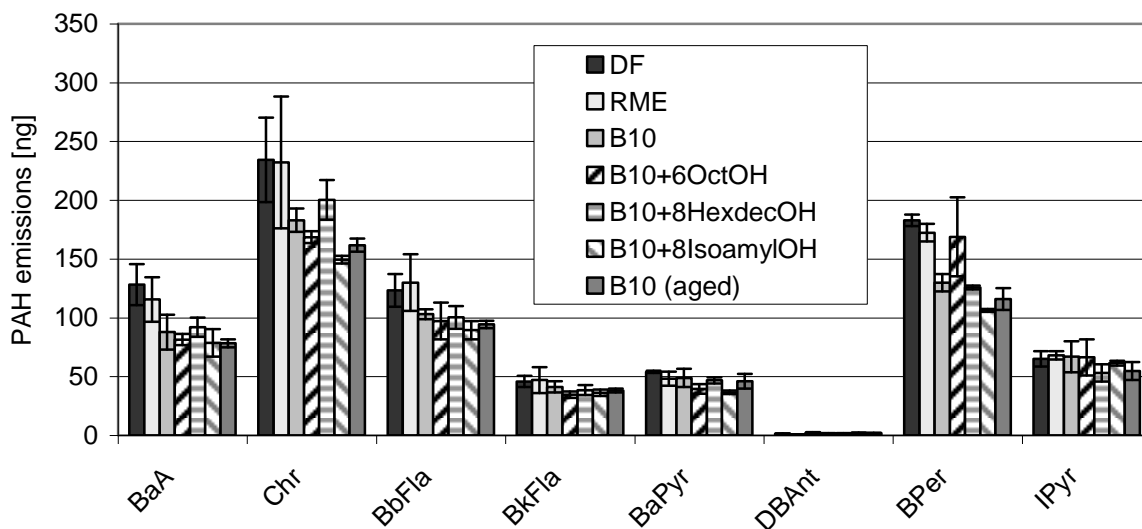


Figure 10 PAH emissions (part 2) of selected blends using a Farymann single cylinder test engine in a 5-mode test

3 Conclusions

To prevent tentative problems in the fuel filter, the injecting system and the combustion process itself, the formation of oligomers should be prevented in blends. Alcohols have been proven and tested to dissolve precipitations in the fuel. In the result, some blends from biodiesel, diesel fuel and alcohols tend to be appropriate

to suppress chemical reactions in the fuel and probably in the engine oil. Some alcohols as a blend component could be identified to meet the demands of the diesel fuel specification. The alcohol compound has no influence on compatibility of materials. Additionally, engine tests showed the applicability of those blends. No relevant negative changes concerning the regulated and non-regulated emissions have been found so far. Further

research is necessary to explain the chemical interactions that are responsible for the formation of oligomers and their reaction products. Not only chemical but also physical bonds can play important roles and are in the focus of current research.

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Abbreviations

Ace	Acenaphthene	Fla	Fluoranthene
Ant	Anthracene	Flu	Fluorene
B10	Blend of 10% biodiesel in DF	HVO	Hydrotreated vegetable oil
BaA	Benz[a]anthracene	IPyr	Indeno(1,2,3-cd)pyrene
BbFla	Benzo[b]fluoranthene	Nap	Naphthalene
BkFla	Benzo[k]fluoranthene	PA	Polyamide
BPer	Benzo[ghi]perylene	PAH	Polycyclic aromatic hydrocarbons
BaPyr	Benzo[a]pyrene	PE	Polyethylene
Chr	Chrysene	Phe	Phenanthrene
DBAnt	Dibenz(a,h)anthracene	Pyr	Pyrene
DF	Diesel fuel	RME	Rapeseed oil methyl ester
FAME	Fatty acid methyl ester	UV-Vis	Ultraviolet-visible light

APPENDIX

Table 3 Properties of fuels

	Test method	EN 14214 limits	RME	RME (aged)	Test method	EN 590 limits	DF
Density (15 °C) [g/L]	EN ISO 12185	875 - 900	883.3	903.1	EN ISO 12185	820 - 845	833.6
Kin. viscosity (40 °C) [mm ² s]	EN ISO 3104	3.5 - 5.0	4.462	6.653	EN ISO 3104	2 - 4.5	2.93
Flashpoint [°C]	EN ISO 3679	> 120	> 151	132	EN 22719	> 55	88
C.F.P.P. [°C]	EN 116	≤ -20	-17	-15	EN 116	≤ -5/-20	-20
Total sulphur [mg/kg]	EN ISO 20884	≤ 10	< 10	7.6	EN ISO 20884	≤ 5	1.6
Carbon residue [w/w %]	EN ISO 10370	≤ 0.30	< 0.3	5.57	EN ISO 10370	≤ 0.30	< 0.01
Ash content [w/w %]	ISO 3987	≤ 0.02	< 0.01	< 0.01	EN ISO 6245	≤ 0.01	0.002
Cetane number [-]	IP 498	≥ 51	52	55.9	EN ISO 5165	≥ 51	52.9
Water content [mg/kg]	EN ISO 12937	≤ 500	250	1539	EN ISO 12937	≤ 200	26
Copper corrosion [-]	EN ISO 2160	≤ 1	1	1	EN ISO 2160	≤ 1	1A
Acid number [mg KOH/g]	EN 10104	≤ 0.5	0.14	3.1	ASTM D974	≤ 0.5	
Lubricity (HFRR, wsd 1.4) [µm]					ISO 12156-1	≤ 460	207
Polycyclic aromatic hydrocarbons [w/w %]					EN 12916	< 8	4.4
FAME content [w/w %]	EN 14103	> 96.5	98.9	82.1	DIN EN 4078	≤ 7	0
Linolenic acid methyl ester [w/w %]	EN 14103	≤ 12	9.7	5.0			
Methanol [w/w %]	EN 14110	≤ 0.2	< 0.05	0.03			
Monoglyceride [w/w %]	EN 14105	≤ 0.8	0.67	0.32			
Diglyceride [w/w %]	EN 14105	≤ 0.2	0.16	0.15			
Triglyceride [w/w %]	EN 14105	≤ 0.2	0.11	0.09			
Free glycerin [w/w %]	EN 14105	≤ 0.02	< 0.005	0.01			
Total glycerin [w/w %]	EN 14105	≤ 0.25	0.21	0.12			
Alkali content (Na, K) [mg/kg]	EN 14538	≤ 5	< 1	< 0.5			
Earth alkali content (Ca, Mg) [mg/kg]	EN 14538	≤ 5	< 1	< 0.5			
Phosphorus content [mg/kg]	EN 14107	≤ 10	< 1	0.8			
Oxidation stability [h]	EN 14112	> 6	> 6	< 0.5			
Iodine number [g iodine/100g]	EN 14111	≤ 120	113	96			