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The effect of sulphur content on B20 fuel stability

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Abstract. The aim of this study was to investigate if a high amount of sulphur is favourable for the fuel blends' storage stability. The parameters that correlate with the storage stability of the fuel blends were compared with two B20 fuel samples consisting of 20 vol% biodiesel and 80 vol% fossil diesel. The studied parameters were the oxidation stability (OSI), acid number and kinematic viscosity. The measurements were carried out straight after mixing the blends, and again after 4 and 9 weeks. One of the B20 samples was prepared from rapeseed methyl ester (RME) and fossil diesel fuel containing 6.6 mg kg⁻¹ sulphur and the other from the same RME but the fossil diesel fuel contained 186 mg kg⁻¹ of sulphur. According to the results of this study, the fuel containing less sulphur had slightly better quality during the entire study. Though, the OSI of the fuel containing more sulphur decreased less in percentages than it did for the fuel containing less sulphur. As a conclusion, the study gives a reason to assume that the sulphur may be favourable to fuel blends' storage stability but it should be studied for a longer time to confirm this statement.

Key words: FAME, fuel blends, B20, diesel fuel, storage stability, sulphur.

INTRODUCTION

During the recent decades, the sulphur content of liquid engine fuels has drastically decreased to reduce harmful effects of exhaust sulphur compounds both on the engine components and pollutant emissions. At the same time, the need to increase the use of renewable fuels has grown to also reduce greenhouse gas (GHG) emissions.

Fuel sulphur increases soot and particulate matter emissions in the exhaust of all kind of internal combustion engines, causes corrosion and also has a deleterious effect on advanced after treatment systems used for CO, HC, NO_x and particulate reduction. (Kalghatgi, 2014) The fuel sulphur also causes corrosion inside the engine cylinder. In combustion, it will oxidize to sulphur dioxide. SO₂ will be further oxidized to SO₃ and then again react with water. Formed sulphuric acid, H₂SO₄, will condensate on the metal surfaces and cause corrosion. (Heywood, 1988) This aspect makes the desulphurization important but refining processes which remove the sulphur from the fuel simultaneously reduce fuels lubricity. After processing, the lubricity may be returned by adding certain additives. However, fatty acid methyl esters, i.e. biodiesels, are found to enhance the lubricity when they are mixed together with diesel fuel oil. (Guibet, 1999; Kalghatgi, 2014).

In Europe, the automotive diesel fuel standard, EN 590:2013 allows the fuel to contain a maximum of 10 mg kg⁻¹ sulphur (EN 590: 2013, 2013) but elsewhere in the world the limitations are not as strict. Diesel fuels containing 100–500 mg kg⁻¹ sulphur are commonly in use in many regions outside Europe. E.g. Brazil has two diesel types which are divided by the sulphur content to S10 and S500, whose limits are 10 mg kg⁻¹ for bigger cities and 500 mg kg⁻¹ for rural areas (ANP #50, 2013). Non-road diesel in Brazil has a limit of 300 mg kg⁻¹ (ANP#71, 2011). Though, the levels all over the world have been reduced considerably after the 1990's (Guibet, 1999; Kalghatgi, 2014).

Sulphur emissions, both gaseous and particles, are harmful for human health. An acute exposure can cause trouble in breathing and a long-time exposure for those emissions can cause heart disease, pulmonary illness or even untimely death. In the environment sulphur oxides are reactive and form H₂SO₄ which comes down with the rain and the acid rain again depletes the nature in many ways. Moreover, buildings disintegrate because of the acid rain (Pan, 2011).

When increasing the share of renewable fuels, fuel blends form a realistic and feasible way and therefore, different blends of bio- and fossil fuels are becoming more frequent. In Europe, the maximum fatty acid methyl esters (FAME) content in diesel fuel is 7 vol% according to the: 2013 but higher percentages are also available and targeted around the world. Storage stability is one of the main quality parameters related to biodiesels. The deterioration of the properties of FAMES during storage is more serious than for fossil fuels. Improving oxidation and storage stability is an important issue for commercializing the biodiesel. (Bouaid et al., 2009) Some studies have indicated that higher sulphur contents may affect beneficially the oxidation stability of the fuel blends (McCormick & Westbrook, 2007).

The aim of this study was to investigate if a high amount of sulphur is favourable for the fuel blends' storage stability. The parameters that correlate with the storage stability of the fuel blends were compared in two B20 fuel samples consisting of 20 vol% biodiesel and 80 vol% fossil diesel. One of the samples was mixed with rapeseed methyl ester (RME) and distillate fuel oil (DFO) containing 6.6 mg kg⁻¹ sulphur (later in text: B20 (6.6 mg kg⁻¹ S)) and the other was mixed using the same RME but DFO which contained 186 mg kg⁻¹ sulphur (later in text: B20 (186 mg kg⁻¹ S)). The fuel containing 6.6 mg kg⁻¹ sulphur did not contain any bio component before mixing it with RME. The information about added biodiesel for DFO which contained 186 mg kg⁻¹ sulphur was not available but the supplier assumed that it did not contain any biodiesel before mixing it with RME.

The analyses carried out for these two samples were oxidation stability (OSI), acid number (AN) and kinematic viscosity (KV). The samples were analysed straight after mixing, after 4 weeks and after 9 weeks of storage. The storage conditions were not specified extremely accurately but the samples were similarly placed in a dark cupboard at room temperature (around 20 °C). These mentioned properties (OSI, AN, KV) of RME were measured before mixing it with DFOs. The measured properties of RME fulfilled the requirements set for FAME fuel in Standard EN 14214:2012.

MATERIALS AND METHODS

RME used as the bio component in fuel blends was a product of ecoMotion GmbH, Germany. RME is ISCC EU certified and meets Standard EN14214:2012. Fuel had been produced three years before this study and delivered to the University of Vaasa in 2012. Still the fairly old RME fulfilled the requirements for Standard EN 14214:2012 in terms of the properties measured in this study. The information about added antioxidant was not available.

DFO containing 6.6 mg kg⁻¹ sulphur was a product of Neste and it was produced in Finland. It did not contain any bio component before mixing it with RME. DFO containing 186 mg kg⁻¹ sulphur was Rubilene 813 fuel and it was produced in Brazil. The information about added biodiesel was not available but the supplier assumed that it did not contain any biodiesel before mixing it with RME.

Acid number

The acid number was analysed by a titrator Metrohm Titrando 888. The method is a potentiometric titration method. The sample is diluted with iso-propanol and titrated by potassium hydroxide. The measurement was produced according to Standard EN 14104:2003 (SFS-EN 14104, 2003).

Oxidation stability

The oxidation stability was measured by a Biodiesel Rancimat 873 instrument. The method describes the accelerated oxidation stability of biodiesel. The sample is heated and air flow is conducted through it. Vaporizing compounds of the sample drift with air into water and the conductivity of the water is measured. The end point is achieved when the conductivity increase is at its highest. The method is described in Standard EN 15751:2014 (SFS-EN 15751, 2014).

Viscosity

The viscosities were measured by a Stabinger SVM 3000 rotational viscometer. The measurement is based on torque and speed measurements. The device calculates the dynamic viscosity from the rotor speed. The device also has a density measuring cell that employs an oscillating U-tube principle. The kinematic viscosity is calculated automatically based on these measurements (Anton Paar, 2012).

RESULTS AND DISCUSSION

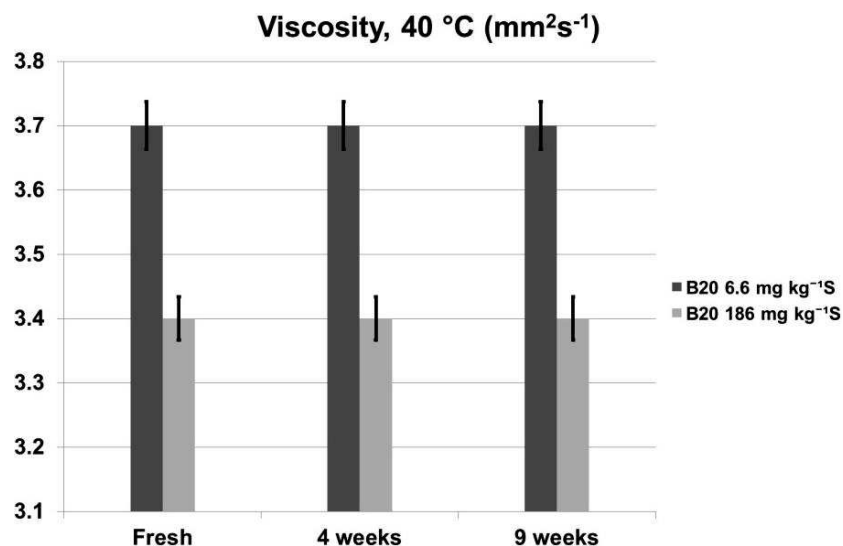
The results of kinematic viscosity, acid number and oxidation stability measurements are presented in Table 1. All the obtained results are arithmetic means of two replicate measurements.

The kinematic viscosity of both samples remained constant during the 9 weeks of time (Fig. 1). During the whole study, the viscosity of the sample B20 (6.6 mg kg⁻¹ S), 3.7 mm² s⁻¹, was higher than it was for B20 (186 mg kg⁻¹ S), 3.4 mm² s⁻¹.

Table 1. The analyses results for B20 fuels

Property	B20 (6.6 mg kg ⁻¹ S)	B20 (186 mg kg ⁻¹ S)	RME
Kinematic viscosity, 40 °C (mm ² s ⁻¹)			
Fresh	3.7	3.4	4.5
4 weeks	3.7	3.4	
9 weeks	3.7	3.4	
Acid number (mgKOH g ⁻¹)			
Fresh	0.07	0.08	0.19
4 weeks	0.06	0.09	
9 weeks	0.07	0.09	
Oxidation stability (h)			
Fresh	36	29	9.5
4 weeks	34	29	
9 weeks	33	28	

The relative standard deviations are: kinematic viscosity 1%, acid value 7.9% and oxidation stability 4.5%. These had been determined for the analysis methods earlier.

**Figure 1.** The results of viscosity measurements.

The acid number of the sample B20 (186 mg kg⁻¹ S) was higher for fresh sample and it increased more than it did for the sample B20 (6.6 mg kg⁻¹ S) (Fig. 2). The result of the sample B20 (186 mg kg⁻¹ S) increased from 0.08 to 0.09 mg KOH g⁻¹. For the B20 (6.6 mg kg⁻¹ S) the result seemed at first to decrease from 0.07 to 0.06 mg KOH g⁻¹ but it increased back to the level of 0.07 mgKOH g⁻¹ after 9 weeks of storage. This phenomenon happened probably due to the measurement precision.

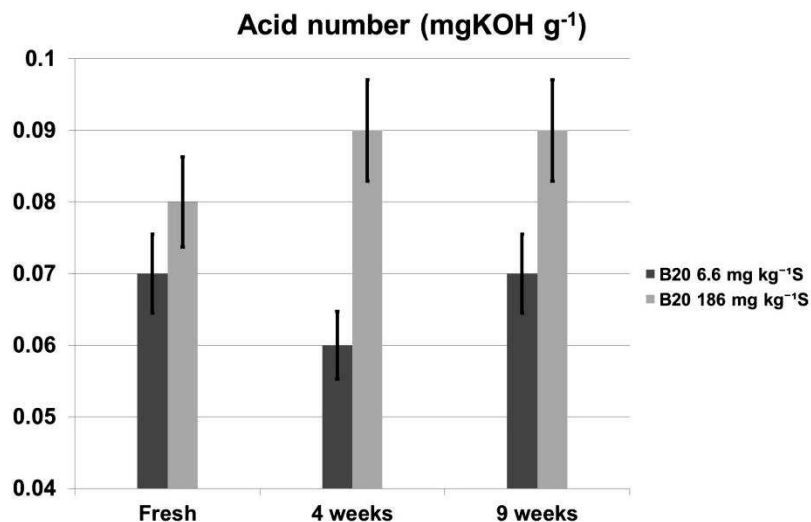


Figure 2. The results of acid number measurements.

Fig. 3 shows that the oxidative stability of the sample B20 (6.6 mg kg⁻¹ S) (36, 34, 33 hours) was higher during the whole study than it was for the sample B20 (186 mg kg⁻¹ S) (29, 29, 28 hours). The decrease in OSI was 8% for the sample B20 (6.6 mg kg⁻¹ S) when it was only 3% for the sample B20 (186 mg kg⁻¹ S).

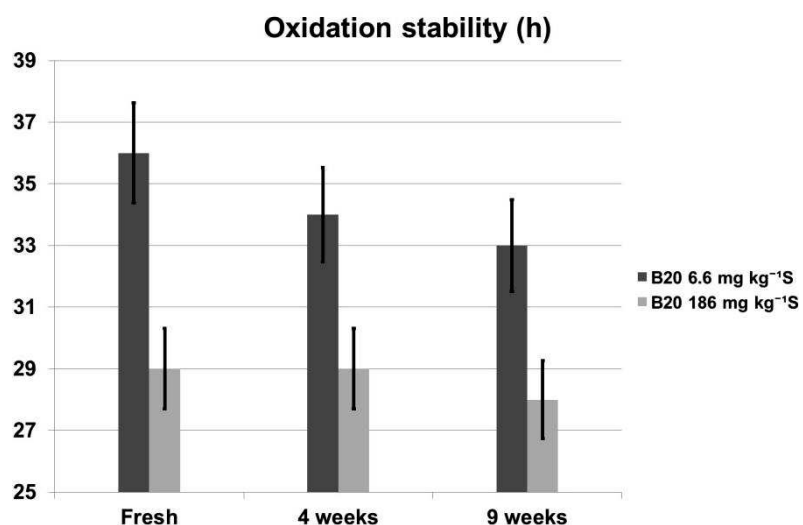


Figure 3. The results of oxidation stability measurements.

Karavalakis et al. (2010) have studied the oxidation stability of biodiesel blends and they have found it a very complicated process. They say that the most important factors affecting the blends' stability are the biodiesel composition and used antioxidants. Also, according to McCormick & Westbrook (2007), the stability of the biodiesel is the most important factor which affects the blends storage stability.

In this study, the biodiesel in both samples was the same and the reason for the difference in OSI of the fresh blend samples was more likely caused by the diesel fuel which also is conceivable according to Karavalakis et al. and McCormick & Westbrook. However, as mentioned, the process is so complex that analyses made in this study are not comprehensive enough to reveal the reason for the quality difference between the diesel fuels. Most probably, the difference is due to oxidative and thermal stability of the diesel fuel (McCormick & Westbrook, 2007). The OSI results of the both DFOs used in this study would have been useful as reference measurements and the OSI analyses of DFOs have necessarily to be included in the future investigations.

McCormick & Westbrook mentioned that sulphur compounds can work as antioxidants and the same conclusion is also supported by the study of Karavalakis et al. (McCormick & Westbrook, 2007; Karavalakis et al., 2010). As mentioned above, here the decrease in OSI was 8% for the sample B20 (6.6 mg kg⁻¹ S) when it was only 3% for the sample B20 (186 mg kg⁻¹ S). This may indicate the antioxidative effect sulphur has. To prove this thesis, also indicated by the current study, a longer follow-up study should, however, be implemented.

Karavalakis et al. (2011) showed in another study, that even 4–6 weeks storage time may cause OSI to decrease under the 20 hours limit due to natural ageing. The 20 hours limit is set in Standard EN 590: 2013 for automotive diesel fuels. In this study, both the samples remained clearly above the 20 hours limit for 9 weeks. The other measured properties were also at a proper level though the adopted RME was produced 3 years before this study.

CONCLUSIONS

As one conclusion, the study gave a reason to assume that the sulphur may be favourable to fuel blends' storage stability. The decrease in OSI was 8% for the sample B20 containing less sulphur when it was only 3% for the sample B20 containing more sulphur. This may indicate the antioxidative effect sulphur has. The phenomenon should, however, be studied for a longer time to confirm this statement.

As another conclusion, it can be stated that even a long time stored RME had a sufficiently good quality to use as a biocomponent in blending. In this study, the OSI of both the B20 samples remained clearly above the 20 hours limit for 9 weeks even though they were prepared using RME which was produced 3 years ago.

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