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Storage stability of rapeseed methyl ester stored in a sealed barrel for seven years

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Abstract. Storage stability is one of the main quality parameters related to fatty acid methyl esters (FAME) biofuels. The deterioration of biofuels´ properties during storage is a more serious issue than with conventional fuels. In particular, lengthy storage threatens the oxidative stability of FAME fuels because factors such as the presence of air, elevated temperatures or presence of metals promote the oxidation process. Consequently, the acceptable storage time for FAME fuels is generally regarded to be regrettably short, at no more than six to12 months. However, storage conditions play an important role in determining actual storage stability. This study aimed to investigate and evaluate any deterioration in the quality of rapeseed methyl ester (RME) fuel that has been stored for as long as seven years in adequate storage conditions. The fuel was stored in the dark, contained in a sealed steel barrel in an insulated shipping container outdoors. The temperature of the container varied with seasonal fluctuation, but the fuel never froze during storage. The study analysed six key fuel properties of the RME: ester content; water content; density; kinematic viscosity; oxidation stability index; and acid number. The analyses were conducted immediately after opening the barrel, and again after two months of storage in a laboratory. The results were compared to those measured for the fresh fuel, seven years earlier. The comparison of the results indicate that the fuel quality had suffered no serious deterioration during the seven-year period.

Key words: biodiesel, RME, shelf life, storage stability.

INTRODUCTION

Most of energy worldwide is produced from non-renewable sources such as oil, coal and natural gas. These fossil energy sources are depleting and there is an urgent need for new sources of clean and sustainable energy. Increasing the renewable energy share from cleaner sources also helps reduce emissions of toxic pollutants and greenhouse gases. One renewable option is to use sustainably produced biodiesel to replace petroleum diesel as a power source in compression-ignition engines. Not only does biodiesel have the advantage of containing oxygen, but also emissions such as carbon monoxide (CO), hydrocarbons (HC) and particulate matter are lower when combusting biodiesel than when burning petroleum diesel (Ovaska et al., 2019). In Europe, fossil automotive diesel fuel can contain maximum 10 mg kg^{-1} (10 ppm) of sulphur (EN 590:2013, 2013). Generally, biodiesel contains lower levels of sulphur than fossil diesel and only low sulphur oxide (SO_x) emissions are formed when biodiesel is burned. Even though oils and fats can contain significant amounts of sulphur, the sulphur content is reduced when the oils and fats are processed to biodiesel. Most of the biodiesel samples studied by He et al. (2009) contained sulphur at less than 10 ppm.

Biodiesel is composed of methyl esters of long-chain fatty acids. Primary raw materials of biodiesel are waste vegetable oils and animal fats. The production process is based on transesterification of the triglycerides with sodium methoxide or sodium hydroxide and methanol (Varghese et al., 2021).

Despite the advantages of biodiesel, its use is problematic. Biodiesels are prone to oxidation and this may cause major problems in engines´ fuel systems and in fuel storage tanks and pumps. The storage stability of biodiesel also is a matter of concern. The acceptable storage time of FAME fuels currently is reckoned to be only six to 12 months (Bouaid et al., 2007). The tendency to degrade due to oxidation is associated with the chemical composition of biodiesel and so therefore it depends on the fuel´s raw material. FAME made from raw materials with larger amounts of unsaturated fatty acids is considered to be more susceptible to chemical degradation. Vegetable oils usually contain more unsaturated fatty acids than are found in animal fats. The fuel´s degradation becomes more rapid as the storage time lengthens. Other factors that affect the storage stability are humidity, exposure to air and heat (de Siqueira Cavalcanti et al., 2019; de Sousa et al., 2021).

This study set out to investigate any deterioration in the quality of rapeseed methyl ester fuel that had been stored for seven years in adequate, real life storage conditions. The fuel had been purchased for research purposes. One barrel had remained unopened in a fuel storage and this barrel's fuel was investigated in the current study. The fuel was contained in the sealed full steel barrel, stored in the dark in an insulated shipping container outdoors in Vaasa, Finland. The container is a designed fuel storage and contains e.g. catchment basin for the fuels. The temperature inside the container varied due to seasonal fluctuation, but the variation was not followed precisely.

Six properties of the RME were analysed: ester content; water content; density; kinematic viscosity; oxidation stability index; and acid number. The analyses were conducted after opening the barrel and then were repeated after two months of storage in a laboratory. The three-litre fuel sample was stored in the laboratory in a glass bottle inside a fume cupboard. The results from the two sets of analyses were compared to those measured for the fresh fuel seven years earlier. The research question was to establish if the properties of the RME biodiesel had changed during the seven-year storage in a sealed barrel, and whether any further changes would occur if the sample subsequently is exposed to air and light in a laboratory.

MATERIALS AND METHODS

Fuel

The University of Vaasa purchased the RME fuel at the end of 2012. The supplier was Archer Daniels Midland Company (ADM) in the USA. As a fresh fuel, the RME fulfilled the requirements of the prevailing European Standard EN 14214:2012 for FAME biodiesel.

Methods

The RME was stored in a real life fuel storage; in an insulated shipping container outdoors. The temperature inside the container varied due to seasonal fluctuation, but the variation was not followed precisely. The annual average temperature in Vaasa region is +4–+5 °C (Finnish Meteorological Institute, 2021). A radiator ensured that the temperature inside the container remained above 0 °C during the winter. Ambient summer temperatures in Finland are between approximately +10 and +30 °C: the temperature inside the insulated container has been close to that range. The RME barrel had remained sealed until the sample was taken. The sample was taken with a siphon from the middle of the full barrel. Contents were stirred with a rod prior to sampling.

Six key properties of the RME fuel were measured, using the following methods and equipment.

The ester content was measured with a PerkinElmer Clarus 580 gas chromatograph. Methyl heptadecanoate is used as an internal standard for this method. It is suitable for biodiesels containing methyl esters between C14 and C24, and when the ester content is higher than 90 m-%. The ester content, C (m-%), is calculated in compliance with Eq. 1,

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \qquad (1)$$

where $\sum A$ is the total peak area from the methyl ester in C14 to that in C24:1; A_{EI} is the peak area corresponding to methyl heptadecanoate; C_{EI} is the concentration of the methyl heptadecanoate solution (mg mL^{-1}); V_{EI} is the volume of the methyl heptadecanoate solution (mL); and m is the mass of the sample (mg). The method is described in European Standard EN 14103 (EN 14103, 2003).

Water content is measured according to the coulometric Karl Fischer titration method. The in-house procedure used is based on international standard ISO 12937 (ISO 12397, 2000).

Kinematic viscosity and density were measured with a Stabinger SVM 3000 rotational viscometer, which uses torque and speed measurements to determine viscosity. The device calculates the dynamic viscosity, η (mPas), from the rotor speed by applying Eq. 2

$$\eta = \frac{K}{\left(n_2 / n_1 - 1\right)} \qquad (2)$$

where K is constant; n_1 is the speed of the measuring rotor (mm s^{-1}); and n_2 is the speed of the measuring tube (mm s^{-1}).

The viscometer also has a density-measuring cell which utilises the oscillating U-tube principle. The kinematic viscosity, KV (mm^2 s^{-1}), was calculated automatically based on these measurements, according to Eq. 3

$$KV = \frac{\eta}{\rho} \qquad (3)$$

where η is dynamic viscosity (mPas); and ρ is density (g cm^{-3}) (Novotny-Farkas et al., 2010).

The oxidation stability index (OSI) was measured by a Metrohm 873 Biodiesel Rancimat instrument. This uses an accelerated method to determine the oxidation stability of biodiesel, blowing a stream of air through a heated fuel sample. Vaporising compounds from the sample drift with air into water and the consequential change in the water´s conductivity is measured. The end point is achieved when the conductivity increase is at its highest. This method is described in European Standard EN 14112 (EN 14112, 2003).

The acid number was analysed with a Metrohm Titrando 888 titrator, which uses a potentiometric titration method. The sample is diluted with iso-propanol and titrated with potassium hydroxide. The acid number, AN, is reported according to Eq. 4

$$AN = \frac{56.1 \times V \times c}{m} \tag{4}$$

where V is the volume of the standard volumetric potassium hydroxide solution used (mL); c is the exact concentration of the standard volumetric potassium hydroxide solution used (mol L^{-1}); m is the mass of the sample (g); and 56.1 is the molecular mass of potassium hydroxide. Results are expressed as mg KOH g^{-1} (mg of potassium hydroxide per g of sample). The measurement was performed according to European Standard EN 14104 (EN 14104, 2003).

The relative standard deviations for the measurements were: ester content < 1%; kinematic viscosity < 1%; oxidation stability 4.5%; acid number 7.9%; and density < 1%. The relative standard deviation for water content was not measured.

RESULTS AND DISCUSSION

The results are presented in Table 1 and Figs 1–6.

The ester content (Table 1, Fig. 1) of fresh RME was 98.6%. The ester content of the samples stored for seven years and for seven years and two months was 98.3% in both cases, thus remaining compliant with EN 14214, which stipulates a minimum value of 96.5%.

Table 1. Ester content, water content, density, kinematic viscosity, oxidation stability index and acid number

RME sample	Ester content (%)	Water content (mg kg^{-1})	OSI (h)	Density (15 °C) (g cm^{-3})	Kinematic viscosity (40 °C) (mm^2 s^{-1})	Acid number (mg KOH g^{-1})
Fresh	98.6	132	12	0.89	4.5	0.2
Stored for 7 years	98.3	200	12	0.88	4.5	0.2
Stored for 7 years and two months	98.3	170	11	0.88	4.5	0.2
EN 14214	> 96.5	< 500	> 8	0.86–0.90	3.5–5.0	< 0.5

The water content (Table 1, Fig. 2) of the fuel stored for seven years was higher (200 mg kg^{-1}) than it was for the fresh fuel (132 mg kg^{-1}) or the sample stored for seven years and two months (170 mg kg^{-1}). Nevertheless, all three results are comfortably within the EN 14214 maximum limit of 500 mg kg^{-1}. Biodiesels are more prone to degrade when visible water is present or air humidity is high (Yang et al., 2017). In this study, it can be stated that in respect of free water, the storage conditions have been dry and correct.

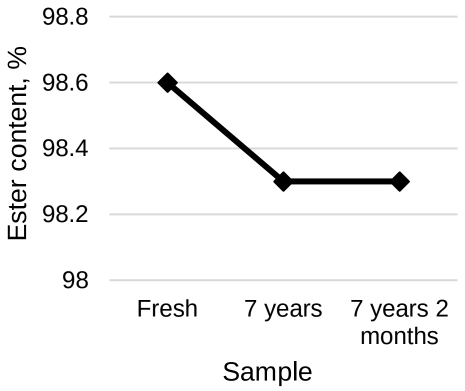

Figure 1. Ester content of the samples.

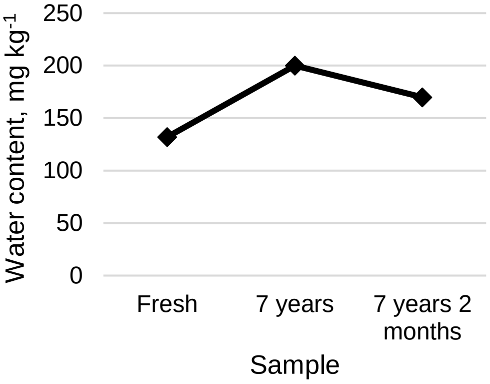

Figure 2. Water content of the samples.

The kinematic viscosity (Table 1, Fig. 3) of all the samples was 4.5 mm^2 s^{-1}. Thus, no change was detected and all three results fall within EN 14214´s acceptable range (3.5–5.0 mm^2 s^{-1}).

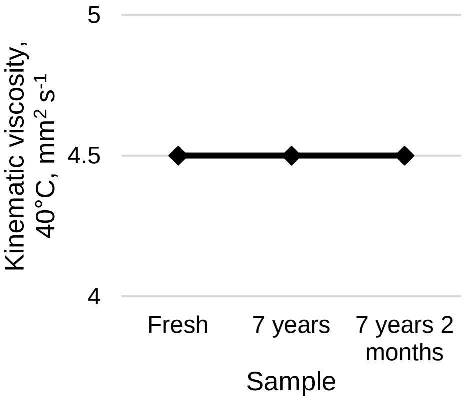

Figure 3. Kinematic viscosity of the samples.

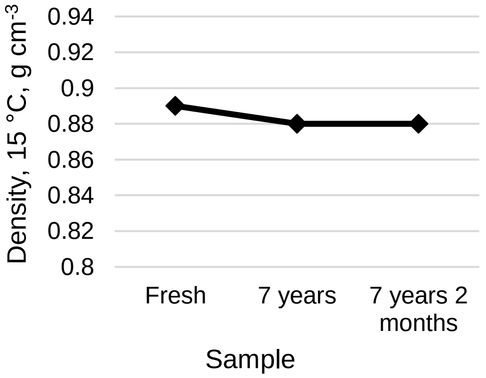

Figure 4. Density of the samples.

The density (Table 1, Fig. 4) for the fresh sample was 0.89 g cm^{-3} and for the samples after seven years and after seven years and two months of storage it was 0.88 g cm^{-3}. The change is very small and all the results are within the limitations of the EN 14214, which sets a minimum of 0.86 and a maximum of 0.90 g cm^{-3}.

The OSI value (Table 1, Fig. 5) of the fresh sample was 12 h, and exactly the same result was obtained for the sample after seven years of storage, so there had been no measurable deterioration in oxidation stability. The OSI value of the sample stored for seven years and two months was 11 h. The minimum limit for OSI in EN 14214 is 8 h, so all three samples comfortably exceeded that requirement. Apparently, the RME contained antioxidant, although the exact quantity was unknown. Antioxidants inhibit the autoxidation process and can be used as additives to extend the storage time of biofuels (Knothe, 2007). Several published articles related to biodiesel antioxidants indicate that relatively high concentrations of antioxidants are needed to meet the requirements set for fuel stability (Yang et al., 2017; Das et al., 2009).

The acid number (Table 1, Fig. 6) of biodiesels must be below 0.5 mg KOH g^{-1} to comply with EN 14214. The acid number for all three samples was 0.2 mg KOH g^{-1} and so the FAME standard limit presented no difficulties.

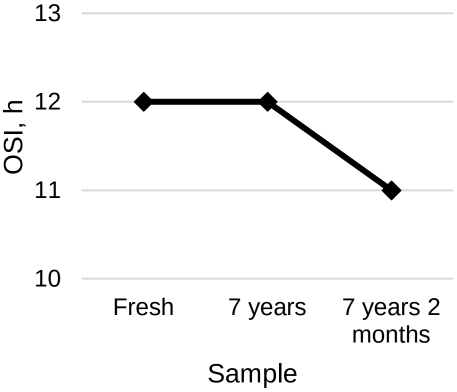

Figure 5. OSI of the samples.

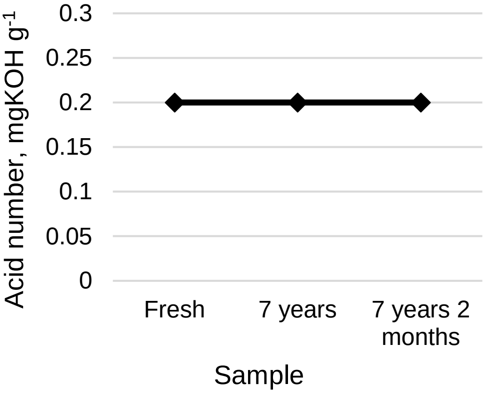

Figure 6. Acid number of the samples.

All the analysed results still fulfilled the requirements set in European Standard EN 14214, indicating that the fuel maintained its quality in a sealed barrel. The exposure to air after opening the barrel did cause an 8% reduction in the fuel´s oxidation stability index. Nevertheless, the fuel quality was still within the specification of EN 14214.

The transesterification process is well known to be reversible (Pullen & Saeed, 2015). No significant reversion occurred in the studied conditions, and nor was there any significant oxidation reaction, i.e., the chemistry of biodiesel seemed to be stable for the studied period. Storage stability in terms of oxidation has been studied widely but there are relatively few recorded results concerning storage stability in relation to ester content.

Thompson et al. (1998) studied RME’s properties for 24 months under various storage conditions. The fuel was in glass and steel containers stored at room temperature at approximately +23 °C, and outdoors at ambient conditions with an annual average temperature of +8.3 °C. The samples were vented to the atmosphere. According to their results, the acid number of all the samples remained below the EN 14214 limit of 0.5 mg KOH g^{-1} for approximately 15 months. Their density rose evenly to reach 0.89 g cm^{-3} at the end of the 24-month storage period. The RME´s viscosity was relatively high even at the beginning of the test, being above 5.5 mm^2 s^{-1}. At the end of the 24-month storage period it was above 7 mm^2 s^{-1} for all the samples. The samples stored indoors degraded slightly faster than the ones stored outdoors. No antioxidants were used. (Thompson et al., 1998).

Mittelbach & Gangl (2001) also studied the storage stability of RME. They stored samples for 170–200 days, at between 20 and 22 °C in polyethylene bottles or tin cans. Some of the samples were exposed to air and daylight. The OSI of their original samples was poor, measured at just 5.6 h at the beginning of the test. The sample exposed to air and daylight had oxidised totally after 170 days and the other samples also lost their oxidative resistance during the storage time. This was shown in the OSI and acid number results. The authors of this study did not mention whether the fuel contained any antioxidants (Mittelbach & Gangl, 2001).

Published studies of biodiesel storage stability have focused on soybean-based fuels far more frequently than on biodiesel made from rapeseed oil. For example, de Siqueira Cavalcanti et al. (2019) studied three commercial Brazilian biodiesels, storing them in carbon steel containers in subtropical conditions. One of the biodiesels was made of soybean oil, one was of beef tallow and the third was a blend of 65% soybean and 35% beef tallow. The samples were initially stored for 60 days in their original storage conditions. The containers were opened after 60 days and the samples were then stored for a further 90 days in conditions where the temperature varied between 24 and 34 °C and the relative air humidity varied from 30 to 80%. De Siqueira Cavalcanti et al. found that biodiesel made solely of soybean oil showed limited shelf life: its water content and oxidation stability results were particularly poor. The two other biodiesels maintained their quality during the storage time.

Storage conditions worldwide differ considerably. The fuel in the present study was much older than in other studies but the storage temperatures were notably lower than in the Brazilian study. The results obtained by de Siqueira Cavalcanti et al. (2019) also indicate that raw material is the key factor in storage stability of biodiesels. The amount of unsaturated fatty acids in soybean methyl ester is much greater than in rapeseed methyl ester.

Additionally, the fuel quality at the beginning of the storage stability research also seems to be important. This is evident by comparing the results from the present study with those obtained by Thompson et al. (1998) and Mittelbach & Gangl (2001). If some of the fuel properties are out of specification at the start, this seems to exacerbate the degradation of biodiesel during storage. Antioxidants are needed for good oxidation stability. Clean, dry and proper storage conditions also play an important role in storage stability, and the biodiesel should be used as soon as possible after the barrel is opened. However, if the barrel remains sealed, the results of this study show that the fuel will maintain its quality for a surprisingly long time.

CONCLUSIONS

The aim of this study was to find out if the quality of rapeseed methyl ester has deteriorated when the fuel has been stored for seven years in adequate storage conditions. The RME was stored in a sealed barrel in a real life fuel storage; in an insulated shipping container outdoors. The temperature inside the container varied due to seasonal fluctuation, but the variation was not followed precisely. A radiator ensured that the temperature inside the container remained above 0 °C during the winter. A fuel sample was taken from the middle of the full barrel after the content had been stirred with a rod.

The properties measured were ester content, water content, kinematic viscosity, density, oxidation stability and acid number. One sample was analysed straight after opening the barrel and another one after two months of storing in the laboratory. The results were promising: after seven years, all the measured properties still fulfilled the requirements for FAME biodiesel set in European Standard EN 14214, being as followed (seven years and two months results in brackets):

- The ester content 98.3% (98.3%)
- The water content 200 mg kg^{-1} (170 mg kg^{-1}.)
- The kinematic viscosity 4.5 mm^2 s^{-1} (4.5 mm^2 s^{-1})
- The density 0.88 g cm^{-3} (0.88 g cm^{-3})
- The OSI value 12 h (11 h).

The exposure to air after opening the barrel did cause an 8% reduction in the fuel´s oxidation stability index. The exposure to air did not cause decrease in the fuel quality in other measured properties.

If biodiesel made of rapeseed oil is of good quality, contains sufficient antioxidant and is stored in dry conditions, without an exposure to air and at temperature above 0 °C and below 30 °C (annual average around +5 °C), the quality of RME seems to remain constant for several years. Nevertheless, the recommendation is to ensure the fuel´s quality before use in engines.

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