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Effects of storage on the properties of rapeseed oil and alcohol blends

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Abstract. Kinematic viscosity and density are important fuel properties because they influence fuel atomisation during injection into the engine cylinder. The viscosity and density of neat vegetable oils usually are too high to allow optimal use of these oils in compression ignition engines. Blending vegetable oils with alcohols can improve these properties, but it is not known whether the blend properties remain stable during storage. This study measured kinematic viscosity (at 40 °C), density (at 15 °C) and surface tension of rapeseed oil-alcohol blends that had been stored in closed borosilicate glass bottles at room temperature in the dark for 49 weeks. The values were compared with those of the fresh blends. Further measurements of oxidation stability for the rapeseed oil and the blends were taken after 72 weeks of storage. The blends consisted of rapeseed oil with ethanol at 5 vol–%, and rapeseed oil with 1–butanol at 5 vol–%, 10 vol–%, 20 vol–% and 30 vol–%. All in all, the observed changes during storage were small. Density values deviated by less than 1%, surface tension by no more than 3% and kinematic viscosity differed from the fresh blends' values by 1% to 8%. Surface tension had increased in some blends and decreased in others. Kinematic viscosity rose in all blends, with the smallest increase measured for the rapeseed oil–butanol 30 vol–% blend. This blend also showed the best oxidation stability, which was close to six hours.

Key words: blending, butanol, ethanol, stability, vegetable oil.

INTRODUCTION

Research into renewable fuels has been conducted for some time to find solutions that help mitigate climate change and balance depletion of fossil oil resources. In the Renewable Energy Directive II of the European Union, the member states have agreed that renewable energy should account for at least 32% of their total energy consumption by 2030, with the sub-target for renewables providing at least 14% of the energy consumed in road and rail transport (Directive (EU), 2018). Using fuels produced from biomass can contribute to reaching these goals. The Directive encourages member states to limit the amount of biofuels and bioliquids that are produced from cereal and oil crops, for example, but it does not restrict the possible use of such biofuels and bioliquids (Directive (EU), 2018). Obviously, the use of as sustainable feedstock as possible is highly desirable and recommended.

Alternative renewable fuels must have properties suitable for combustion in existing technologies and they also need to be stable. Viscosity, density and surface tension are all important fuel characteristics because they affect fuel injection, drop formation and atomisation (Guibet, 1999). Vegetable oils are a renewable source and have been used as neat material or in blends with fossil diesel in compression ignition engines (D'Alessandro et al., 2016; Čedik et al., 2018; Mat et al., 2018). Two of the critical properties for use of vegetable oils in combustion engines are density and viscosity: both usually are too high in neat vegetable oils to work optimally. Transesterification of oil triglycerides into fatty methyl esters can profoundly reduce viscosity of oils or fats (Kralova & Sjöblom, 2010). Blending vegetable oil with alcohols can also reduce viscosity and density of vegetable oil (Laza & Bereczky, 2011).

Another challenge with vegetable oils is their propensity to degrade when in contact with oxygen. All vegetable oils, animal fats and biodiesels are susceptible to oxidative degradation and this is related to the occurrence and the amount of unsaturated fatty acids in the material (Dunn, 2005). In turn, oxidative degradation of biodiesel can lead to an increase in viscosity due to the formation of high molecular weight molecules (Pölczmann et al., 2014).

When developing and testing new fuels or fuel blends, it is important to study properties over time to evaluate fuel stability. One way of investigation is to store fuels for an appropriate time under defined conditions.

This study investigates some selected fuel properties of rapeseed oil-alcohol blends after having stored the blends in closed borosilicate glass bottles in the dark at room temperature for almost one year. Kinematic viscosity, density and surface tension were measured and compared with results reported for the fresh blends before storage. Data from the initial measurements of fresh rapeseed oil and rapeseed oil-alcohol blends were presented in Nuortila et al. (2020). The current study also used a Rancimat test to measure oxidation stability of the neat rapeseed oil and its blends with ethanol and butanol after storage for over one year. This study presents results from investigating the stability of rapeseed oil-alcohol blends as a contribution to exploring potential alternative renewable fuels for compression ignition technology.

MATERIALS AND METHODS

Blends of rapeseed oil and ethanol at 5 vol–% and rapeseed oil and 1–butanol at 5, 10, 20, and 30 vol–% were prepared to a final volume of 200 mL. The blending ratios and abbreviations used for the blends are shown in Table 1. In pre-tests, the blends had proven to be stable at these blending ratios for a couple of weeks prior to the initial measurements. The blend components were commercial products: ethanol (denatured, 91.2% Etax A12) from Altia, Finland; *butanol (1–Butanol ≥ 98.5%, GPR RECTAPUR®) from VWR International, France; and rapeseed oil (100% rapeseed oil) containing vitamin E from Avena Kantvik Oy, Finland.

Table 1. Blending ratios and abbreviations of rapeseed oil and alcohol blends

	Blending ratio (v–v%)	
Blend abbreviation	Rapeseed oil	Alcohol
RSO	100%	no alcohol
BU5–RSO	95%	1–Butanol 5%
BU10–RSO	90%	1–Butanol 10%
BU20–RSO	80%	1–Butanol 20%
BU30–RSO	70%	1–Butanol 30%
E5–RSO	95%	Ethanol 5%

The kinematic viscosity at 40 °C, density at 15 °C and surface tension at room temperature were measured for the fresh blends and the original rapeseed oil. The blends and the rapeseed oil (RSO) were then stored in closed borosilicate glass bottles in a dark chemical safety cabinet in the laboratory at room temperature. After 49 weeks, kinematic viscosity at 40 °C, density at 15 °C and surface tension of the blends and the rapeseed oil were measured again. In addition, oxidation stability was measured after 72 weeks of storage. A visual inspection of the blends and the RSO was made after storage before mixing the batches prior to analyses.

Kinematic viscosity and density

Kinematic viscosity and density were measured with a Stabinger SVM 3000 rotational viscometer (Anton Paar GmbH, Austria). The measurements follow standard EN ISO 3104 for kinematic viscosity at 40 °C and EN ISO 12185 for density at 15 °C.

Surface tension

Surface tension was measured with a Lauda tensiometer TD 2 (Lauda Dr. R. Wobser GmbH & CO.KG). Measurements were made according to the manufacturer's instructions (Tensiometer TD 2 Operating Instructions).

Oxidation stability

In order to evaluate the blends' susceptibility to oxidation, samples were investigated in an accelerated aging test. Samples of three grams of each were measured at 110 °C in a Biodiesel Rancimat 873 (Metrohm AG, Herisau, Switzerland). The method is used for measurement of biodiesels and is based on change of conductivity in ionised water when degradation products are vented from the heated sample into the water. The induction time is recorded, i.e. the time that passes until secondary reaction products are formed. This analysis had not been done with the fresh blends.

Two replicate measurements were made to determine kinematic viscosity, density and oxidation stability for each blend and the rapeseed oil. The results are shown as the arithmetic mean of the two measurements. Single measurements were made to determine surface tension of the samples.

The analysis methods had been previously validated in the laboratory using validation samples. The relative standard deviation (RSD) for both kinematic viscosity and density was < 1%; RSD for oxidation stability was 2.10% (validated for bio–oils). The RSD was not measured for surface tension.

RESULTS AND DISCUSSION

There was no phase separation in any of the rapeseed oil-butanol blends. In the BU20–RSO and BU30-RSO blends there was some slight deposit at the bottom of the bottles. The E5-RSO blend had separated into three phases of which the lowermost and biggest phase was slightly turbid. A clear phase had formed about 5 mm thick beneath the surface, and a third phase was distinguished just at the surface, slightly oscillating in colour. Phases disappeared after mixing the blend batch.

Rapeseed oil-alcohol blends showed only relatively small changes in kinematic viscosity and surface tension during storage. Essentially, there were no changes in density when compared to the values for the fresh blends and rapeseed oil. All of the

changes were about one unit or less for any of the measured properties in the RSO-butanol blends, and at most two units in the RSO-ethanol blend.

The kinematic viscosity at 40 °C decreased with increasing vol–% of butanol in the rapeseed oil–butanol blends, from 35.9 $mm^2 s^{-1}$ for RSO to 11.4 $mm^2 s^{-1}$ for BU30–RSO (Fig. 1). The relationship of kinematic viscosity to butanol vol–% could be described with a reciprocal exponential equation. The kinematic viscosity increased in the rapeseed oil and all the blends by between 1% to 8% compared to the values measured for the fresh material (Fig. 2). The biggest change was seen in the E5-RSO blend, and the smallest change in the BU30-RSO blend. Also, kinematic viscosity of the rapeseed oil and the 30 vol–% blend underwent a similar degree of change during storage.

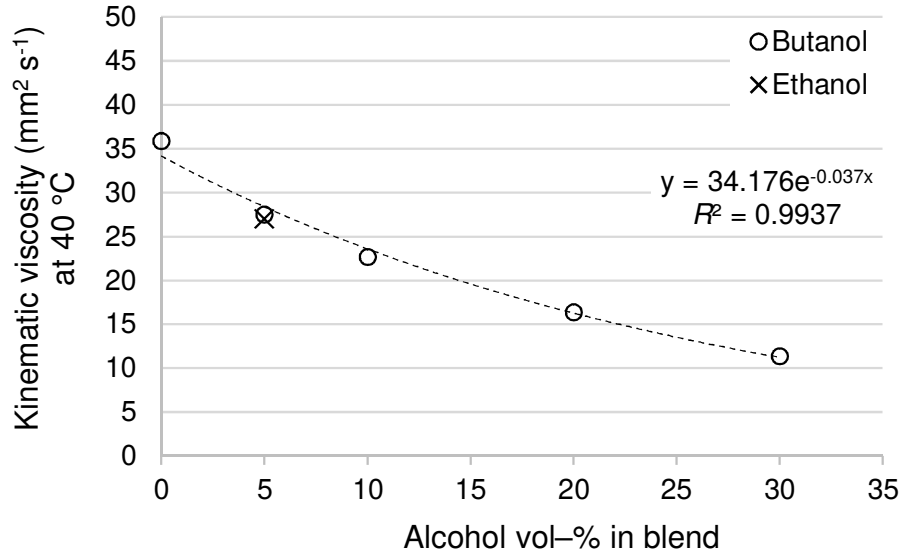

Figure 1. Kinematic viscosity of rapeseed oil-alcohol blends after 49 weeks of storage. The trendline and equation is given for the rapeseed oil–butanol blends only.

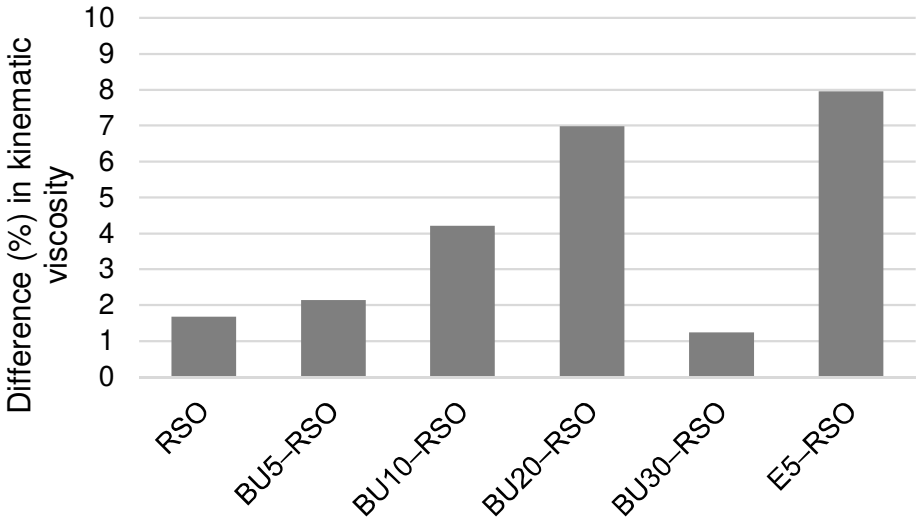

Figure 2. Difference (as a percentage) in kinematic viscosity at blend age 49 weeks as compared to the fresh blends and rapeseed oil.

Density at 15 °C decreased with increasing vol–% of butanol in the blends, from 920 g cm^{-3} for RSO to 888 g cm^{-3} for BU30-RSO (Fig. 3). The relationship was linear between density and the increasing vol–% of butanol in the blends. The density of the E5-RSO blend was 914 g cm^{-3}, the same as the BU5-RSO blend. Over the storage time of almost one year, the density of the RSO and all the rapeseed oil-alcohol blends changed only minimally, by less than 0.2% (Fig. 4).

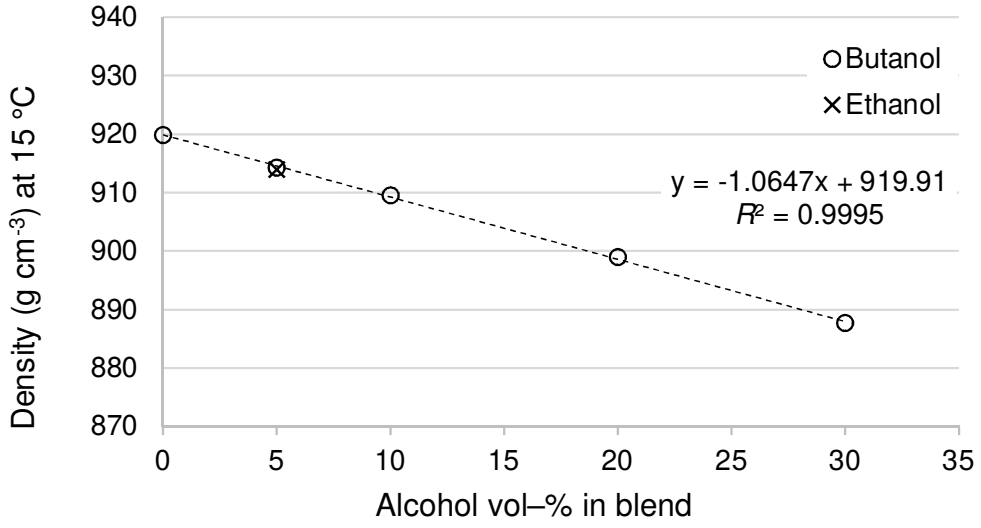

Figure 3. Density of rapeseed oil-alcohol blends after 49 weeks of storage. The trendline and equation is given for the rapeseed oil-butanol blends only. Note the y-axis scale starts at 870 g cm^{-3}.

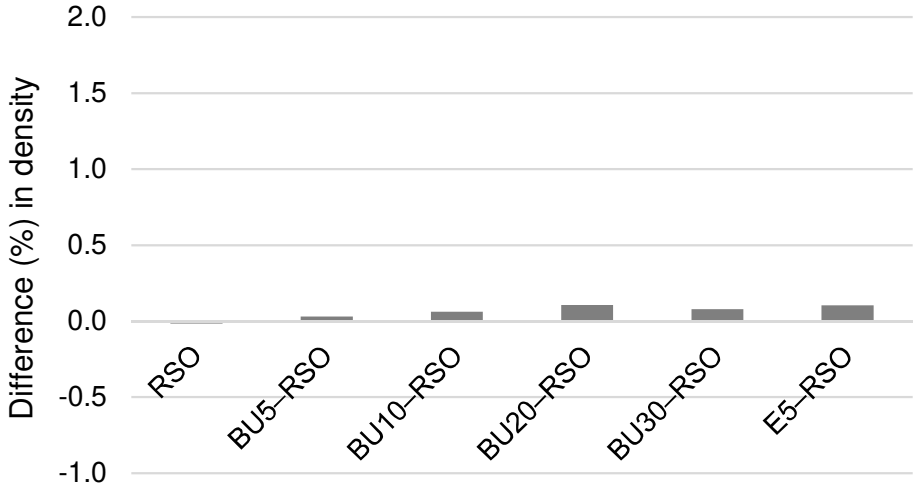

Figure 4. Difference (as a percentage) in density at 15 °C at blend age 49 weeks as compared to the fresh blends and rapeseed oil.

The surface tension decreased with increasing vol–% of butanol in the blends, from 33 mN m^{-1} for RSO to 26 mN m^{-1} for BU30-RSO (Fig. 5). The relationship could be described with a linear equation. The surface tension was 28 mN m^{-1} for E5-RSO, almost identical to the value for BU20-RSO. Surface tension had changed by between 1% and 3% during storage (Fig. 6). While kinematic viscosity had slightly increased, surface

tension was either almost the same as in the fresh material or had decreased during storage.

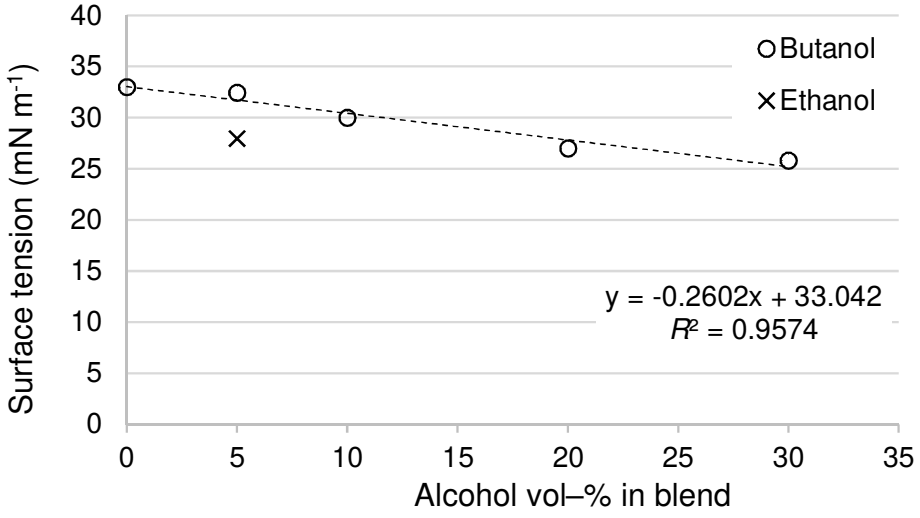

Figure 5. Surface tension of rapeseed oil-alcohol blends after 49 weeks of storage. The trendline and equation is given for the rapeseed oil-butanol blends only.

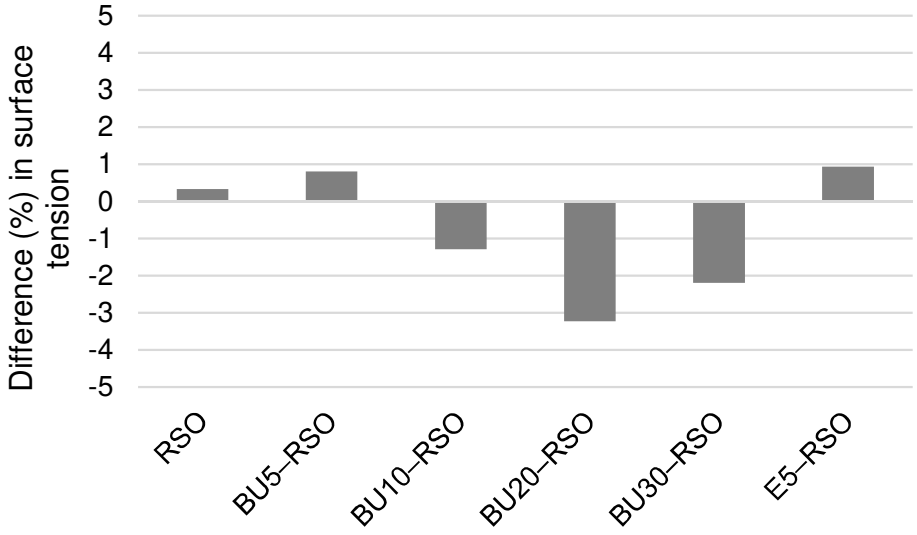

Figure 6. Difference (as a percentage) in surface tension at blend age 49 weeks as compared to the fresh blends and rapeseed oil.

Differences in oxidation stability emerged when the batches were older than one year. The oxidation stability for BU20-RSO was almost twice, and for BU30-RSO almost three times, the value for neat rapeseed oil. The Rancimat measurement results for RSO, BU5-RSO and BU10-RSO blends were between 2.1 h and 2.4 h (Fig. 7). But the result for BU20-RSO was 3.8 h, and for BU30-RSO it was 5.7 h. The oxidation stability of the E5-RSO blend was 3.2 h. At 5 vol–%, the ethanol-RSO blend showed better oxidation stability than the butanol-RSO blend. Oxidation stability was rather poor in all the samples.

At present, there is no information available in the scientific literature reporting effects of storage on vegetable oil-alcohol blends. Therefore, the results from this study will be compared to results from storage studies with vegetable oils and biodiesel.

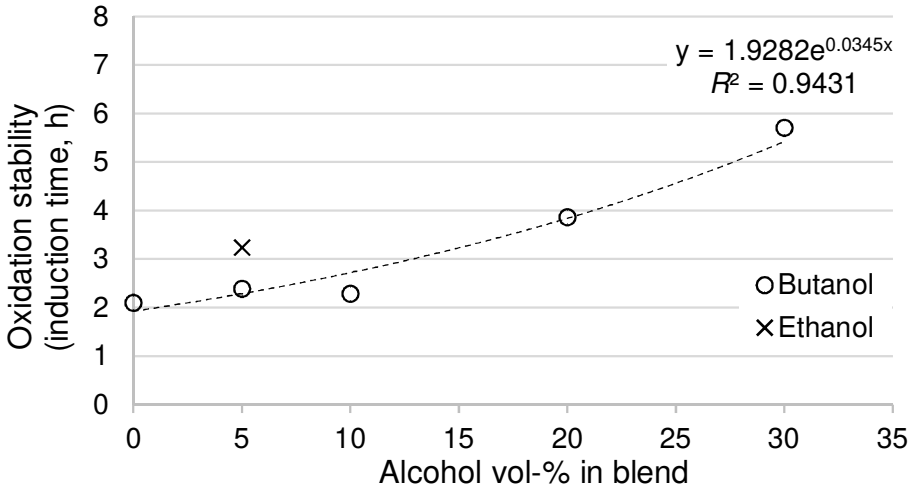

Figure 7. Oxidation stability measured as induction time in a Rancimat for rapeseed oil-alcohol blends after 72 weeks of storage. The trendline and equation is given for the rapeseed oil-butanol blends only.

Kreivaitis et al. (2013) reported an increase of approximately 5% in kinematic viscosity of rapeseed oil after 70 days of storage at 70 °C. Bezergianni & Chrysikou (2012) investigated oxidative stability of waste cooking oil and white diesel stored in air–tight bottles in the dark at room temperature for a year. They reported that density of the waste cooking oil did not change noticeably, but viscosity increased slightly by approximately 2%. In a study by Pattamaprom et al. (2012), kinematic viscosity of palm stearin and palm olein biodiesel did not increase during six months of storage in dark and closed containers at room temperature, but density increased by 5–6%. The authors noticed that viscosities dropped slightly and argued that this was possibly caused by chain scission of biodiesel into smaller molecules. Palm-oil diesel without antioxidants showed an increase in kinematic viscosity, from approximately 6 cSt to approximately 7 cSt (i.e. approximately 6 $mm^2 s^{-1}$ to 7 $mm^2 s^{-1}$, equalling a change of about 16%) when stored at 20 °C for 125 days (Lin & Chiu, 2009). Bouaid et al. (2009) reported an increase in viscosity from 5.1 to 6.9 $mm^2 s^{-1}$ (equalling an increase of 35%) for biodiesel made from *Brassica carinata* and ethanol after 12 months storage. The samples had been stored under argon in a closed glass bottle at room temperature and exposed to daylight. These literature results indicate that kinematic viscosity of oils and biodiesel can vary in response to different materials and storage conditions.

Biodiesels vary also in oxidation stability depending on their constituent materials (reviewed in Jain & Sharma, 2010). A neat animal fat methyl ester without antioxidant showed an oxidation stability of only 2.2 h (Sirviö et al., 2018). The oxidation stability of biodiesel made from rapeseed oil and used cooking oil decreased from 5–6 h to approximately 1 h over the course of 136 weeks (Pölczmann et al., 2014). Laza & Bereczky (2011) measured oxidation stability of rapeseed oil and propanol, and of rapeseed oil and butanol blends with alcohol volume percentages from 5% to 20% at

80 °C in a Rancimat. The authors found that oxidation stability was about 4.3 h for the RSO and its various blends. The study did not investigate blend properties in relation to storage. So far, oxidation stabilities reported in the current study are comparable to literature values.

The Rancimat test, routinely used for biodiesel, is designed to measure oxidation stability of oils and fats (Läubli & Bruttel, 1986), not vegetable oil-alcohol blends. The measurements made in this study therefore should be treated with caution and the results should be verified with additional measurements and with other methods. For instance, adjusting the operation temperature might be necessary to achieve adequate time to ensure reliable results (Dunn & Knothe, 2003).

The results from the initial measurements of fresh rapeseed oil-alcohol blends already had been compared with standards for automotive fuels, biodiesel and marine fuels (Nuortila et al., 2020). That earlier study had concluded that the blends were suitable for use in power plants and marine engines, but not for use in on-road vehicles. The same conclusion holds for the results after storing the blends for almost one year.

CONCLUSIONS

Storage of the neat rapeseed oil and the blends for one year did not cause noteworthy changes in their kinematic viscosity, density and surface tension. Density showed almost no changes at all, while kinematic viscosity showed an increase of between 1% and 8% compared to the initial results from the fresh blends. Nevertheless, values of the measured parameters changed by only one to two units. The blends and the neat rapeseed oil remained relatively stable under their storage conditions of tightly closed glass bottles in the dark, at room temperature. This observation encourages further investigation of vegetable oil-alcohol blends.

As a preliminary conclusion, oxidation stability in rapeseed oil with ethanol at 5 vol–% or butanol at 20 vol–% or 30 vol–% was better than that of the neat rapeseed oil. The results indicate that blending rapeseed oil with higher-chain alcohol not only improves kinematic viscosity and density, but also oxidation stability. However, additional research is needed to confirm the observations. Experiments could focus on properties of blends with higher volume ratios of butanol.

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