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Behavior of B20 fuels in arctic conditions

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Abstract. Several renewable and sustainable liquid fuel alternatives are needed for different compression-ignition (CI) engine applications to reduce greenhouse gas (GHG) emissions and to ensure proper primary energy sources for the engines. One of the shortcomings of several bio oils and first generation biodiesels has been their cold properties. Still, the need for alternative fuels is also present in arctic areas where the storing of the fuels may become problematic. The main aim of the current study was to determine how the storage related properties of fuel blends change if the fuels first freeze and then melt again. The samples were analyzed three times: as fresh, and after the first and second freezing-melting phase transitions.

The share of renewables within the blends was 20 vol-%. Rapeseed methyl ester (RME) and animal-fat based methyl ester (AFME) were blended with LFO in a ratio of 80 vol-% of LFO and 20-vol% of RME or AFME.

The investigated and compared properties were the FAME content of the neat FAMEs, and kinematic viscosity, density, oxidation stability index, and acid number of the blends. Cold filter plugging point was measured for AFME and its blend. According to the results, the quality of the FAMEs and their blends did not change significantly during the freezing over. The freezing-melting phase transition seems, thus, not to be as big a threat to the fuel quality as the high temperatures are. According to the results of this study, the studied fuels were feasible after the freezing-melting phase transition.

Key words: alternative fuels, fuel blends, storage conditions, arctic conditions, fuel stability, medium-speed engines.

INTRODUCTION

The 2030 EU climate & energy framework sets three key targets. The first one is to cut greenhouse gas emissions at least 40% from the level of 1990. The second target is to have at least a 27% share for renewables in energy consumption by 2030. The third one is to reach at least a 27% improvement in the energy efficiency (European Commission, 2017). All these actions are needed to delay the climate change. In marine industry, the need for cleaner fuels is the most urgent. The emission legislation in maritime is becoming stricter, first the limits of oxides of nitrogen, but now even the sulphur and particulate matter limits. For the EU inland waterways, the pollutant emissions must already be strongly reduced, also including the particulate number emissions. According to Third IMO GHG Study made in 2014, international shipping accounts for approximately 2.6% and 2.4% of $CO_2$and GHGs on a CO_2e basis, respectively (IMO, 2014). Additionally, shipping is one of the most important sources of black carbon in the Arctic sea areas (Quinn et al., 2011).

The development of the emissions legislation directs the transfer from fossil fuels to more sustainable alternative fuels. Many ship operators cannot yet meet the new regulations. The possibilities they have to meet the limitations is installing exhaust after treatment equipment or switching to low-sulphur diesel or residual, or to alternative fuels. Most of the latters are able to reduce engine emissions below the mandated limits. Many of them can be used in engines without engine modification. The commercial choice of the alternative, renewable fuels is, though, at the moment quite narrow. The share of renewables in transport is at present approximately 2.6% worldwide (REN21, 2017). For these reasons, the alternative fuel industry has grown dramatically for both liquid and gaseous fuels (McGill et al., 2013).

For compression-ignition (CI) engine applications, one reasonable solution is to use various blends of renewable and fossil liquid fuels until the availability of renewable fuels reaches the sufficient extent. Biodiesels, FAMEs, have been studied for long time and apparently, despite of the problems they may have, they are still of a great interest. Now, 95% of biodiesels are produced from edible vegetable oils, as RME (rapeseed methyl ester) in this study. The use of edible oils is problematic because it causes environmental problems, increases the edible oil prices and consumes food resources. Waste, recycled and non-edible oils would be much better options as raw materials. Waste animal-fat based biodiesel, AFME, also studied in the present study, forms a more favorable alternative. Nevertheless, the share of non-edible oils is minor, only 2% of total biodiesel production (Sajjadi et al., 2016). Waste animal-fats are still becoming more common feedstock as raw material for biofuel production. Veal and beef tallow, lard, chicken and goose fat have been successfully studied as raw materials for esterification process (Sander et al, 2018). Fur farming is one of the industries which produce animal fat as a residue and waste. The quantity of animal-fat based biodiesel manufactured as a by-product in fur farming is marginal but still it can have a notable regional impact on the energy efficiency and power production.

To be able to promote the transit from conventional fossil fuels to renewable alternatives, a large amount of additional research is required about various alternative fuels and in particular about their blends with conventional fuels. A lot of novel information has to be gathered about the blend properties through several fuel analyses.

Arctic conditions make extra problems in terms of alternative fuels and their handling. The saturated acids in FAMEs, present mainly in animal fat based methyl esters, cause them to solidify at low temperatures (Golimowski et al., 2017). This leads to blockages in filters or makes it even impossible to pump the fuel. For this reason, storing and using of biodiesels, at wintertime in arctic regions may be difficult. Fuel tank or store is usually placed outside. Biodiesels are not recommended to store for long time. The storage stability of fuels is threatened by contact with air, sunlight, metals and high temperature conditions (Agarwal & Khurana, 2013). Apparently, the effect of freezing-melting transitions on the fuel properties is not studied earlier. In case fuels are stored, and they solidify, it is important to know if they still are of good quality.

The main aim of the current study was to determine how the storage related properties of the B20 blends made of LFO and RME or AFME change if the fuels freeze. The samples were analyzed three times: as fresh, and after the first and second freezing-melting phase transitions. The reference sample of each fuel was also analyzed. It was stored at dark at 20°C for 4 weeks.

The investigated and compared properties were the FAME content (for the neat FAMEs), and kinematic viscosity, density, oxidation stability index and acid number of the blends. The cold filter plugging point was measured for the AFME and its blend without reference sample.

MATERIALS AND METHODS

Fuels

Rapeseed methyl ester (RME) was a product of ASG Analytik-Service Gesellschaft mbH, Germany. As antioxidant, it contained 1,000 mg kg^{-1} of butylated hydroxytoluene (BHT) and it was delivered to the University of Vaasa (UV) in January, 2017. RME fulfilled the requirements of Standard EN 14214:2012 (EN 14214, 2012).

Animal-fat based methyl ester (AFME) was Feora Ecofuel, a product of Ab Feora which is located in Uusikaarlepyy, Finland. No antioxidant was added. AFME was delivered to the UV in October 2017.

Light fuel oil (LFO) was a product of Neste, Finland. It was low-sulphur (7.2 mg kg^{-1}) fuel, which fulfilled the requirements of Standard EN590 (EN 590, 2013). LFO was delivered to the UV in April 2017.

Methods

The samples were analyzed as fresh, and after the first and second freezing-melting phase transitions. The reference samples were stored at 20 °C, in dark, and measured after 4 weeks of storage. The temperature of the freezer was -26 °C. The investigated and compared properties were the FAME content for the neat FAMEs, and kinematic viscosity, density, oxidation stability index and acid number of the blends. Below, the analysis methods of the properties are described.

The oxidation stability index was measured by a Biodiesel Rancimat 873 instrument. The method is described in Standards EN 14112 (neat FAMEs) and EN 15751 (FAME blends) (EN 14112, 2003; EN 15751, 2014).

The acid number was analyzed by a titrator Metrohm Titrando 888. The measurement was produced according to Standard EN 14104 (EN 14104, 2003). The acid number was measured for fresh samples and after the first freezing-melting phase transition, as well as for the reference sample.

The kinematic viscosity and density were measured by a Stabinger SVM 3000 rotational viscometer (Anton Paar, 2012).

The ester content was measured by a Perkin Elmer gas chromatograph Clarus 580. The method is described in Standard EN 14103 (EN 14103, 2003).

The cold filter plugging point was measured using the method described in Standard EN116 (EN116, 2015). The cold filter plugging point was measured only for AFME sand its blend and after the first freezing-melting phase transition. The reference sample was not analyzed neither.

The relative standard deviations were the following: ester content < 1%, kinematic viscosity < 1%, oxidation stability 4.5%, acid number 7.9% and density < 1%. The relative standard deviation of CFPP measurement was not known.

RESULTS AND DISCUSSION

During the process, the neat AFME was frozen ice over. The LFO-AFME was frozen stiff but not ice over. The neat RME was also frozen ice over. RME-LFO was frozen stiff and two phases were distinguished.

The results of the properties of neat animal-fat based methyl ester and its blend with LFO are presented in Table 1, Fig. 1 and Fig. 2. The results of the properties of neat rapeseed methyl ester and its blend with LFO are presented in Table 2, Fig. 1 and Fig. 3.

Table 1. Results of the properties of neat animal-fat based methyl ester and its blend with LFO

Sample	Kinematic viscosity, $mm^2\ s^{-1}$ (40 °C)	Density, kg m^{-3} (15 °C)	OSI, h	Acid number, mgKOH g^{-1}	FAME content, % (m m^{-1})	CFPP, °C
AFME-LFO						
Fresh	3.82	843	16	0.08		-4
Frozen (1)	3.83	843	16	0.07		-4
Frozen (2)	3.83	844	17	-		
Reference sample	3.82	844	20	0.08		
AFME						
Fresh	4.44	879	5.4	0.21	96.0	2
Frozen (1)	4.44	879	4.9	0.22	97.9	2
Frozen (2)	4.44	879	4.9	-	94.2	
Reference sample	4.43	879	5.2	0.23	94.7	

The FAME content of AFME, presented in Table 1 and Fig. 1, seemed to increase, from 96.0 m-% to 97.9 m-%, after the first freezing-melting phase transition. This increase is though within the error limits. After the second freezing-melting phase transition the result decreased to 94.2 m-% which is rather close to the result of reference sample, 94.7 m-%. The FAME content of RME, presented in Table 2 and Fig. 1, stayed rather constant during the experiment, for fresh sample it was 97.9 m-% and after both freezing-melting phase transition it was 97.7 m-%. The reference sample showed 98.0 m-%. The FAME content of AFME decreased after the second freezing-melting phase transition but the same was also observed in the reference sample. The trans-esterification reaction is known to be reversible (Fereidooni et al., 2018) and freezing-melting phase transition did not cause the reaction to go backwards.

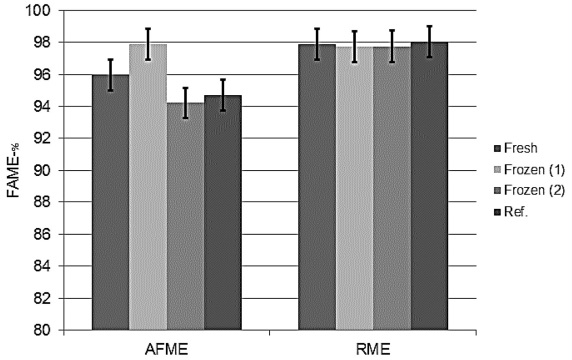

Figure 1. FAME contents of AFME and RME.

The cold filter plugging point was measured only for the AFME and its blends (Table 2). CFPP was recorded as fresh, and after the first freezing-melting phase transition. For the neat AFME and AFME-LFO, the results were the same in both measurements. The result of AFME was 2 °C. AFME-LFO resulted in -4 °C.

Table 2. Results of the properties of neat rapeseed methyl ester and its blend with LFO

Sample	Kinematic viscosity, mm^2 s^{-1} (40 °C)	Density, kg m^{-3} (15 °C)	OSI, h	Acid number, mgKOH g^{-1}	FAME content, % (m m^{-1})
RME-LFO					
Fresh	3.85	844	21	0.13	
Frozen (1)	3.84	844	25	0.13	
Frozen (2)	3.84	844	25	-	
Reference sample	3.84	844	20	0.13	
RME					
Fresh	4.53	883	10	0.51	97.9
Frozen (1)	4.53	883	9.9	0.51	97.7
Frozen (2)	4.54	883	9.7	-	97.7
Reference sample	4.54	883	9.6	0.51	98.0

For fresh RME and RME-LFO, the CFPP had been measured in earlier studies and it was -14 °C and -29 °C, respectively. The difference in fatty acid contents explains the difference of the CFPPs between AFME and RME. High contents of saturated acids (C14:0, C16:0, C18:0) result in higher CFPP values while a high content of unsaturated fatty acids (C18:1, C18:2, C18:3) leads to lower CFPP values (Golimowski et al., 2017). Based on the earlier measurements, the content of saturated acids of AFME (C14:0, C16:0, C18:0, together 27.3%) was much higher than that for RME (6.2%). At the same time, the content of the unsaturated acids of RME (C18:1, C18:2, C18:3, in total 90.2%) was significantly higher than it was for the AFME (58.9%). The CFPP behavior of RME and its B20 blend in freezing-melting phase transition should thus be studied more detailed as it was done for AFME and its blend.

The kinematic viscosity, density and acid number of AFME and its blend stayed nearly constant during the experiment which can be seen in Table 1 and Fig. 2. The kinematic viscosity of AFME remained constant at 4.44 while the viscosity of blend was approximately 3.83 mm^2 s^{-1}. The density of AFME was 879 and of the blend 843 kg m^{-3}. The acid number was measured after the first freezing-melting phase transition but not after the second one. The acid number of AFME was 0.23 mg KOH g^{-1} and the acid number of blend 0.07 mg KOH g^{-1}. The reference samples resulted in slightly higher acid numbers compared to frozen samples. This increase is though within the error limits. The higher acid number of the reference sample may demonstrate that the freezing-melting phase transition did not promote acidification. As the acid number describes the corrosive potential of biodiesel (Xie et al., 2017), the lifetimes of fuel tanks and vehicle engines is reduced by time. According to the results of this study, the corrosive effect was not accelerated by freezing-melting phase transition. All the measured values were within a feasible range for instance for medium-speed engines.

The oxidation stability index (OSI) results of AFME and AFME blend are presented in Table 1 and Fig. 2. OSI was low for neat AFME, approximately 5 h, but for the LFO-AFME blend, it varied from 16 to 17 h. The OSI results for the reference samples were slightly higher than for the fresh samples, being 20 h. The measurements were carried out exactly the same way but there might still be chance for some unexpected issue which has caused the difference as the OSI result should not increase during the storage. Still, freezing over did not reduce the oxidation stability of the blend but. The oxidation stability of neat AFME needs improving for instance by antioxidant addition. Antioxidants butylated hydroxytoluene (BHT) or butylated hydroxyanisole (BHA) are said to be effective in hindering the oxidation process of animal fat based methyl esters (Varatharajan & Pushparani, 2018).

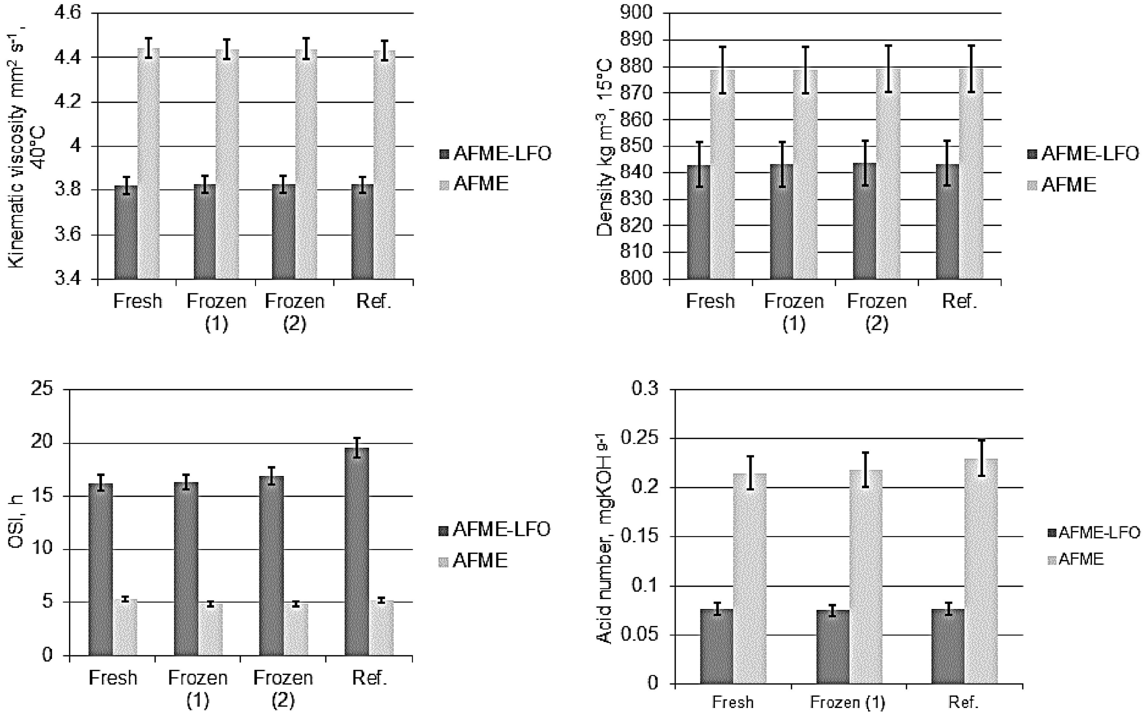

Figure 2. Kinematic viscosities, densities, oxidation stability indexes and acid numbers of AFME and its blend.

The kinematic viscosity, density and acid number of RME and its blend did not vary significantly during the experiment, in other words, freezing over did not reduce the quality of the fuels, which can be seen in Table 2 and Fig. 3. The kinematic viscosity of RME was 4.54 mm^2 s^{-1} and for the blend 3.84 mm^2 s^{-1}. The densities of the samples were 883 kg m^3 for RME and 844 kg m^{-3} for blend. The acid number was measured after the first freezing-melting phase transition but not after the second one. The acid number of RME was 0.51 mg KOH g^{-1} and acid number of RME-LFO blend was 0.13 mg KOH g^{-1}. As for the AFME blend, freezing-melting phase transition did not accelerate the corrosive effect in case of RME and its blend. The acid number of neat RME was though rather high, at its highest 0.51 mg KOH g^{-1}. This might slightly increase the corrosive potential of RME. FAME that is used for fuel blending should fulfill the requirements set in Standard EN 14214. This was not the case for this RME, as according to the mentioned standard, the acid number should not exceed 0.50 mg KOH g^{-1} (EN 14214, 2014).

The OSI results of RME and RME blend are also presented in Table 2 and Fig. 3. OSI of the neat RME remained approximately constant at 10 h. The OSI of RME-LFO blend seemed to increase from 21 h to 25 h after freezing over. The result of the reference sample was only 20 h. Still, similarly to AFME and its blend; freezing over did not reduce the oxidation stability of the RME blend. Altogether, all measured properties of the RME blend were at a proper level and this fuel was still, after freezing-melting transition, feasible for engines. However, the acid number of neat RME was quite high and it may weaken the corrosion tolerance of the tanks and engine parts.

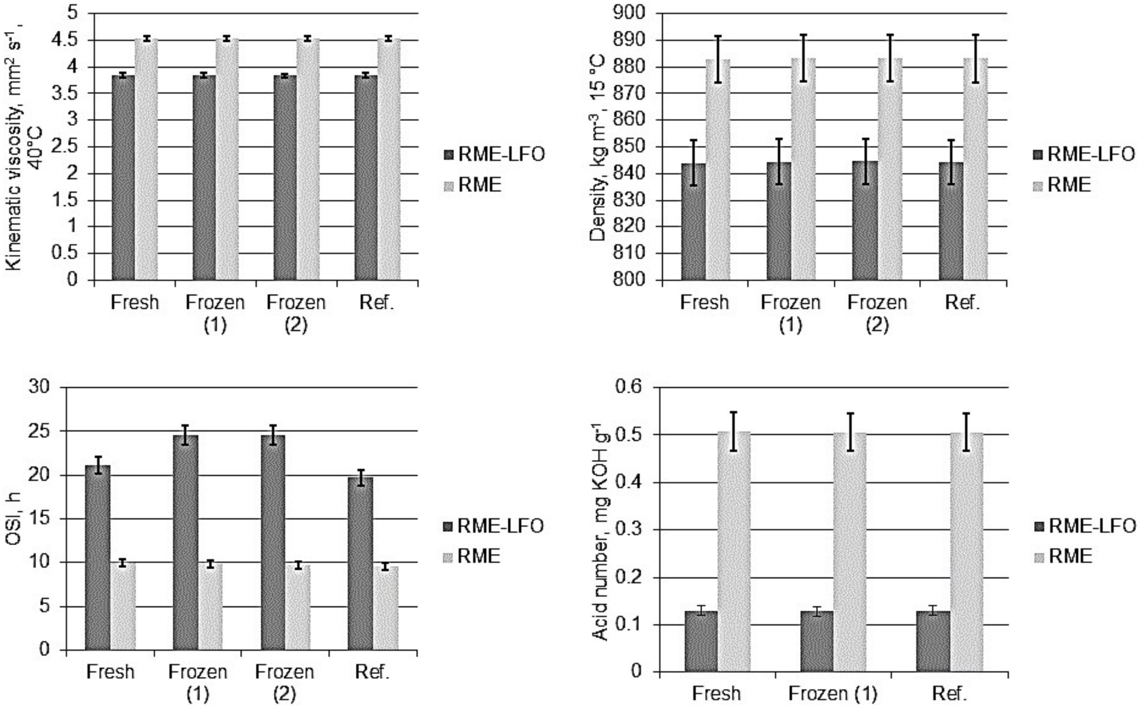

Figure 3. Kinematic viscosities, densities, oxidation stability indexes and acid numbers of RME and its blend.

Dunn (2008) studied the effect of temperature on the oil stability index (h) of biodiesel and found that the higher the temperature, the faster the decrease in oxidation stability (Dunn, 2008). Dwivedi & Sharma (2016) also stated the same, biodiesels are thermally unstable and the temperature increase decreases the oxidation stability (Dwivedi & Sharma, 2016). Compared to the found effects of high temperatures on the fuel stability, it seems that freezing is not as detrimental to the fuel quality as the high temperatures.

CONCLUSIONS

The main aim of the current study was to determine the feasibility and properties of neat RME and AFME and their B20 blends for arctic conditions by analyzing how the properties change if the fuels freeze.

The properties of the samples were analysed three times: as fresh, and after the first and second freezing-melting phase transitions. Rapeseed methyl ester (RME) and animal-fat based methyl ester (AFME) were blended with LFO in a ratio of 80 vol-% of LFO and 20-vol% of RME or AFME. The investigated and compared properties were the FAME content (for the neat FAMEs), and kinematic viscosity, density, oxidation stability index and acid number for the blends. The cold filter plugging point was analysed for AFME and its blend.

According to the results of the study, the following conclusions could be drawn:

- The quality of the FAMEs and their blends did not change significantly during the freezing over. The freezing-melting phase transition seems not to be as detrimental to the fuel quality as the high temperatures are. The studied fuels were feasible after the freezing-melting phase transition.
- The freezing-melting phase transition did not cause the reversible transesterification reaction of FAMEs to go backwards.
- AFME and its blend seemed to be feasible options for medium-speed engines in arctic conditions. The oxidation stability of neat AFME must, however, be improved, e.g., by adding suitable antioxidant.
- RME-LFO blend seemed to be feasible for medium-speed engines even in arctic conditions but the RME should fulfill the requirements set for FAMEs. Neat RME had a slightly high acid number which increases the risk for corrosion.

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