Fuel blends behavior in freezing-melting phase transition

Author(s): Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Help, Riikka; Vauhkonen, Ville; Hiltunen, Erkki

Title: Fuel blends behavior in freezing-melting phase transition

Year: 2019

Version: final draft

Please cite the original version:

Sirviö, K., Niemi, S., Heikkilä, S., Help, R., Vauhkonen, V., & Hiltunen, E., (2019). Fuel blends behavior in freezing-melting phase transition. In: *Fuels : conventional and future energy for automobiles: 12th International Colloquium Fuels - Conventional and Future Energy for Automobiles (2019), Ostfildern, Deutschland, 25.06.2019–26.06.2019*. Technische Akademie Esslingen.

Fuel blends behavior in freezing-melting phase transition

Katriina Sirviö
University of Vaasa, Finland

Seppo Niemi
University of Vaasa, Finland

Sonja Heikkilä
University of Vaasa, Finland

Riikka Help
University of Vaasa, Finland

Ville Vauhkonen
UPM-Kymmene Oyj, Lappeenranta, Finland

Erkki Hiltunen
University of Vaasa, Finland

Summary

Several renewable and sustainable liquid fuel alternatives are needed for different compression-ignition (CI) engine applications to reduce greenhouse gas (GHG) emissions. Biodiesels, FAMEs, have been studied for long time and apparently, despite of the problems they may have, they are still of great interest. Other options of different alternative fuels are residues and also fuels originating from circular economy. Fuel blending may be problematic, as the new mixtures may not always be miscible to each other. Due to incompatibility, such fuels can occasionally tend to be unstable when mixed. The aim of this study was to investigate if the fuels will be stable and feasible after the freezing-melting transitions. To evaluate the feasibility several storage related properties were analyzed. The mixed fuels were rapeseed methyl ester (RME) and animal-fat based methyl ester (AFME) blended with renewable naphtha and marine gas oil (MGO). Naphtha was produced from residues and MGO from used lubricants. According to the results, the freezing-melting phase transition was not a threat to the fuel quality.

1. Introduction

For compression-ignition (CI) engine applications, one reasonable solution to increase the amount of renewable energy is to use various blends of renewable and fossil liquid fuels until the availability of renewable fuels reaches the sufficient extent. There are plenty of alternative liquid fuels which can be utilized 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 [1]. For these reasons, the alternative fuel industry has grown dramatically for both liquid and gaseous fuels [2]. The development of the emissions legislation directs the transfer from fossil fuels to more sustainable alternative fuels.

Biodiesels, FAMEs, have been studied for long time and apparently, despite of the problems they may have, they are still of 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 [3]. 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. [4] 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.

Another option of different alternative fuels is residues. In the present study, renewable naphtha was a residue of the manufacturing process for renewable diesel based on wood and forest residues namely tall oil.

In addition to special renewable fuels, fuel options originating from circular economy can be blended with other fuels. In this study, MGO (marine gas oil) was the light fraction from the hydrotreaters of the process for regeneration of used lubricant oils. The main products of the process are base oils derived from used lubricant oils. Recycled fuels are not necessarily renewable, but recycling of potential energy raw materials is still one step forward in increasing of the suitable and more sustainable options. In the latest years, more attention has been paid to this fuel category. It has been proposed that the EU member countries would collect 100% of the waste oils by 2025 [5].

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. 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 [6]. 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 [7]. 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 blends 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 samples for each studied blend were stored at 20°C, in dark, and measured after 4 weeks of storage. The share of renewables within these six blends varied from 80 vol-% to 100 vol-%: Rapeseed methyl ester (RME) and animal-fat based methyl ester (AFME) were blended with

- renewable naphtha in a ratio of 80 vol-% of RME or AFME and 20 vol-% of naphtha
- MGO in a ratio of 80 vol-% of RME or AFME and 20 vol-% of MGO.

The suitability of the fuels for was evaluated based on the possible change of properties.

2. Materials and methods

2.1 Fuels

Rapeseed methyl ester (RME) was a product of ASG Analytik-Service Gesellschaft mbH, Germany. As antioxidant, it contained 1000 mg/kg 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 [8].

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.

Naphtha was a product of UPM, Finland. It is a residue of the manufacturing process for renewable diesel based on wood and forest residues via tall oil. Naphtha was delivered to the UV in February 2017.

Marine gas oil (MGO) was a product of STR Tecoil, Finland. It was the light fraction from the hydrotreaters of process for regeneration of used lubricant oils. MGO was delivered to the UV in September 2016.

Table 1 shows the studied fuel blends and their blending ratios. The share of renewables within these six blends varied from 20 vol-% to 100 vol-%. The neat AFME and RME were also analyzed.

Table 1. Fuel blends and blending ratios.

Sample	AFME (V-%)	RME (V-%)	MGO (V-%)	Naphtha (V-%)
AFME-MGO	80		20	
AFME-Naphtha	80			20
RME-MGO		80	20	
RME-Naphtha		80		20

2.2 Methods

The samples were analyzed as fresh, and after the first and second freezing-melting phase transitions. The reference samples for each studied blend 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, kinematic viscosity, density, oxidation stability index and acid number. 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). [9, 10]

The acid number was analyzed by a titrator Metrohm Titrando 888. The measurement was produced according to Standard EN 14104 [11].

The kinematic viscosity and density were measured by a Stabinger SVM 3000 rotational viscometer [12].

The ester content was measured by a Perkin Elmer gas chromatograph Clarus 580. The method is described in Standard EN 14103 [13].

The relative standard deviations were the following: ester content <1%, kinematic viscosity <1%, oxidation stability 4.5%, acid number 7.9% and density <1%.

3. Results and discussion

All the samples were stored in a freezer at -26°C. The samples were let to freeze. The neat FAMEs, both AFME and RME were frozen ice over, and so were the AFME-naphtha and AFME-MGO blends which both contained 80 V-% of AFME. RME-MGO was almost totally frozen over but a liquid layer could be seen on the top surface. RME-naphtha was frozen stiff.
The results of the analyses are presented in Tables 2 and 3 and Figures 1-3.

Table 2. Results of the properties of neat animal-fat based methyl ester and its blends.

Sample	Kin. viscosity, mm^2/s (40°C)	Density, kg/m^3 (15°C)	OSI, h	Acid number, mgKOH/g	FAME content, % (m/m)
AFME-NAPH-THA					
Fresh	2.83	847	6.0	0.18	
Frozen (1)	2.77	847	5.4	0.19	
Frozen (2)	2.73	848	5.5	-	
Reference sample	2.71	848	6.6	0.19	
AFME-MGO					
Fresh	4.78	872	7.0	0.18	
Frozen (1)	4.78	872	6.5	0.18	
Frozen (2)	4.79	872	7.1	-	
Reference sample	4.78	872	8.2	0.20	
AFME					
Fresh	4.44	879	5.4	0.21	96.0
Frozen (1)	4.44	879	4.9	0.22	97.9
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 (Table 2, 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 (Table 3, 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 shown for the reference sample. The trans-esterification reaction is known to be reversible [14] and freezing-melting phase transition did not cause the reaction to go backwards.

Table 3. Results of the properties of neat rapeseed methyl ester and its blends.

Sample	Kin. viscosity, mm^2/s (40°C)	Density, kg/m^3 (15°C)	OSI, h	Acid number, mgKOH/g	FAME content, % (m/m)
RME-NAPH-THA					
Fresh	2.87	851	9.6	0.43	
Frozen (1)	2.76	851	9.6	0.43	
Frozen (2)	2.77	851	9.6	-	
Reference sample	2.82	851	9.2	0.43	
RME-MGO					
Fresh	4.87	875	11	0.42	
Frozen (1)	4.87	876	11	0.42	
Frozen (2)	4.87	875	11	-	
Reference sample	4.88	875	11	0.42	
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

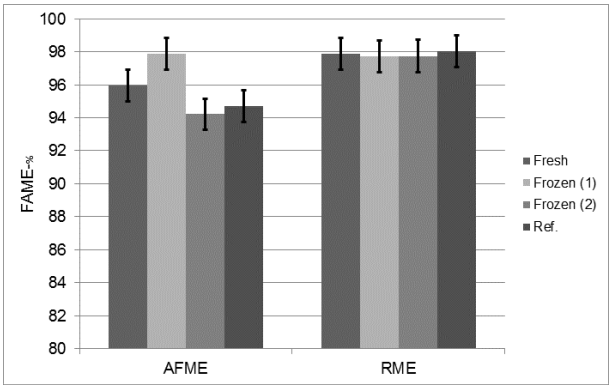

Figure 1. FAME contents of AFME and RME.

The kinematic viscosity and density of AFME and its blends stayed nearly constant during the experiment. The acid number of all the samples seemed to increase slightly. All these values were though within a feasible range for instance for medium-speed engines. This can be seen from Table 2 and Figure 2. The reference samples resulted in slightly higher acid numbers compared to other samples. This increase is though within the error limits. Higher acid numbers of the reference samples may also demonstrate that the freezing-melting phase transition was not promoting the acidification. As the acid number describes the corrosive potential of biodiesel [15], the lifetimes of fuel tanks and vehicle engines are reduced by time. According to the current results, the corrosive effect was not accelerated by freezing-melting phase transition.

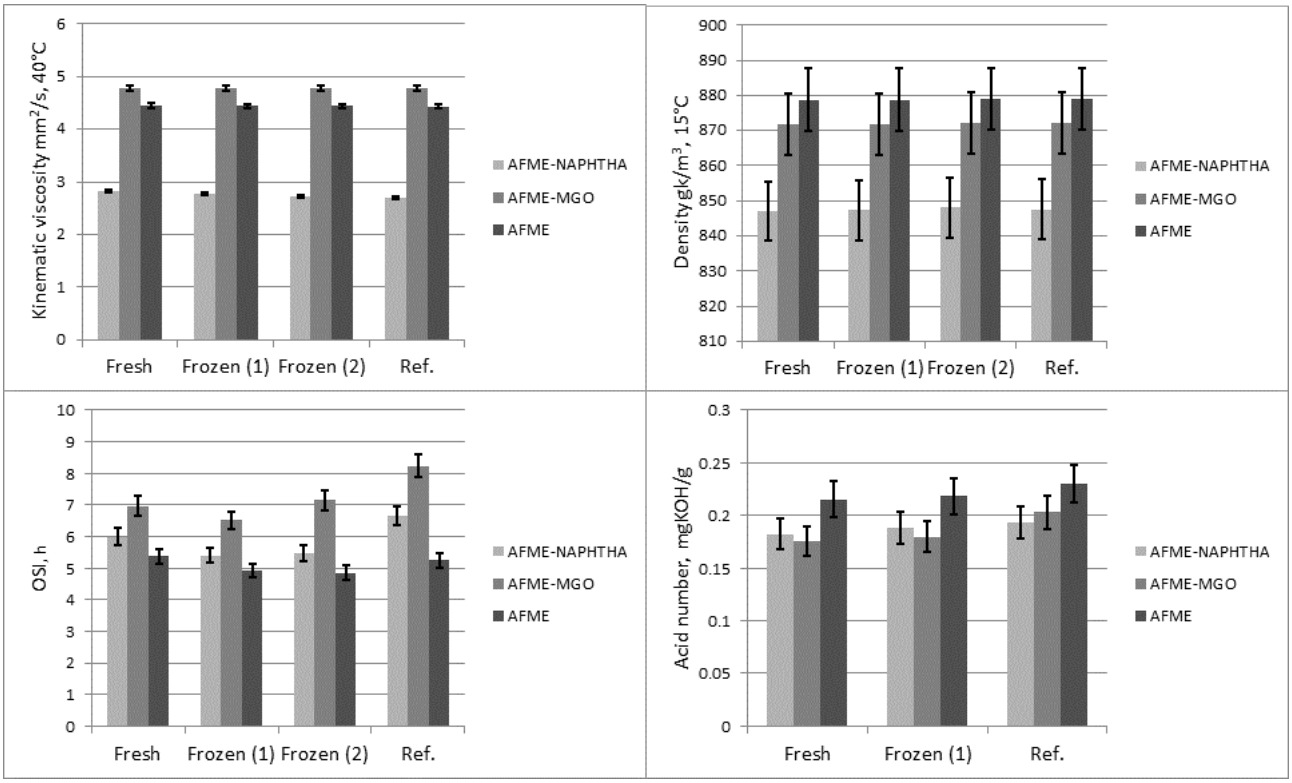

Figure 2. Kinematic viscosities, densities, oxidation stability indexes and acid numbers of AFME and its blend.

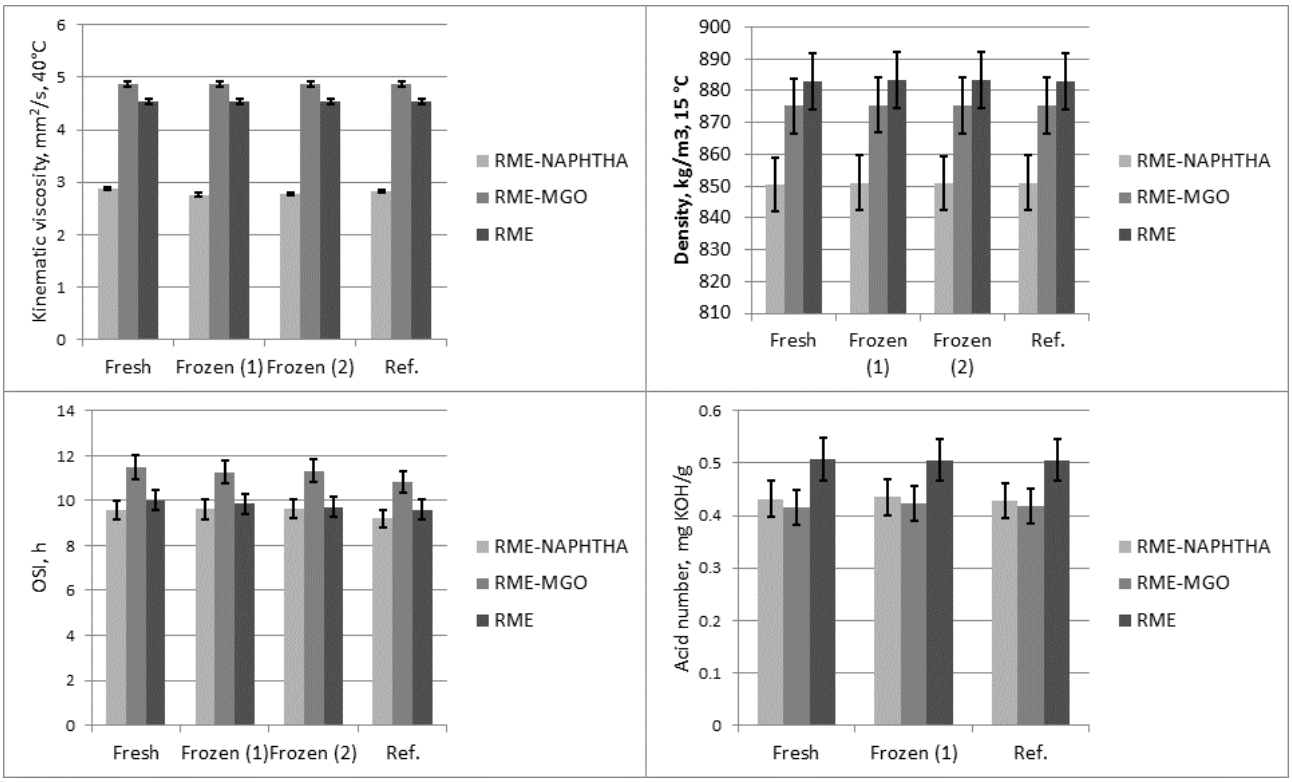

Figure 3. Kinematic viscosities, densities, oxidation stability indexes and acid numbers of RME and its blends.

The oxidation stability indexes were the lowest for the neat AFMEs, approximately 5 h. Naphtha is a mixture of light hydrocarbons and due to its chemical structure, the lightest hydrocarbons most likely evaporate easily. This was though not shown in the naphtha-AFME results by reducing its oxidation stability index. As a whole, the oxidation stability index did not vary much but the results for the reference samples were slightly higher than for the fresh samples. The measurements were carried out exactly the same way but there might still be chance for some unexpected issue which has caused the difference. Still, freezing over did not reduce the oxidation stability of the samples significantly. The quality of all the samples was fair and with the exception of the oxidation stability, AFME and its blends are feasible for medium-speed engines. The oxidation stability of all the AFME samples was restrictive and 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 [16]. The kinematic viscosities of all the samples varied between 2.71-4.79 mm^2/s. The densities of the samples were 847-879 kg/m^3. The acid numbers fluctuated from 0.18 to 0.23 mgKOH/g. The OSI of all the samples varied between 5.2-8.2 h.

The kinematic viscosity, density and acid number of RME and its blends did not either vary significantly during the experiment, in other words, freezing over did not reduce the quality of the fuels. This can be seen from Table 3 and Figure 3. As in terms of the AFME samples, the corrosive effect was not accelerated by freezing-melting phase transition in case of RME and its blends. The acid number of neat RME was though rather high, being at its highest 0.51 mgKOH/g, and may slightly increase the corrosive potential of RME.

The oxidation stability indexes were the lowest for the neat RME and RME-naphtha blend, approximately 10 h. Still, similarly to AFME and its blends, freezing over did not reduce the oxidation stability of RME and its samples. The light naphtha components may have weakened the OSI result of RME-naphtha blend. The OSI results of this blend were the lowest of all the measured RME samples. Altogether, all measured properties of the RME blends were at a proper level and these fuels were still, after freezing-melting transition, feasible for engines. The acid number of neat RME was, however, quite high and it may weaken the corrosion tolerance of the tanks and engine parts.

The kinematic viscosities of all the samples varied approximately between 2.76-4.54 mm^2/s. The densities of the samples were 851-883 kg/m^3. The kinematic viscosities and densities were at feasible range for medium-speed engines. The acid numbers fluctuated from 0.42 to 0.51 mgKOH/g. The OSI results varied between 9.2-11 h.

Dunn (2008) [17] 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. Dwivedi & Sharma also stated the same, biodiesels are thermally unstable and the temperature increase decreases the oxidation stability [18]. Compared to the storage studies investigating the effect of high temperatures on the stability of fuels, it seems that freezing is not as significant threat to the fuel quality as the high temperatures.

For both AFME and RME, adding naphtha to FAMEs decreased slightly the kinematic viscosity and density of FAMEs. For AFME blends, the OSI results were not significantly lower when adding naphtha but for RME blends, the naphtha addition seemed to decrease the OSI result. This may occur due to the light, easily evaporating hydrocarbons of naphtha. Adding MGO, instead, increased the kinematic viscosity but decreased the density of the blends. For both AFME and RME, the added MGO had a positive effect on the OSI results.

4. Conclusions

The main aim of the current study was to determine how the properties of new renewable fuel blends change if the fuels freeze and melt. The suitability of the fuels for was evaluated based on the possible change of properties.

The properties of the samples were analysed three times: as fresh, and after the first and second freezing-melting phase transitions. The share of renewables within these six blends varied from 80 vol-% to 100 vol-%. Rapeseed methyl ester (RME) and animal-fat based methyl ester (AFME) were blended with

- renewable naphtha in a ratio of 80 vol-% of RME or AFME and 20 vol-% of naphtha, and
- with MGO in a ratio of 80 vol-% of RME or AFME and 20 vol-% of MGO.

The investigated and compared properties were the FAME content (for the neat FAMEs), kinematic viscosity, density, oxidation stability index and acid number. According to the results of the study, the following conclusions could be drawn:

- The quality of the FAME's and their blends did not change significantly during the freezing over. The freezing-melting phase transition seems not to be as big a threat to the fuel quality as the high temperatures are.
- AFME and its blends seemed to also be feasible options for medium-speed engines. The oxidation stability of all the AFME blends must, however, be improved e.g. by adding suitable antioxidant.
- RME blends also appeared feasible for medium-speed engines. Neat RME had a slightly high acid number which may increase the risk for corrosion.

- Adding renewable naphtha to FAMEs decreased slightly the kinematic viscosity and density of FAMEs.
- Adding MGO to FAMEs increased the kinematic viscosity but decreased the density of the blends.

Acknowledgements

The authors wish to thank STR Tecoil for delivering MGO, Feora for delivering AFME and UPM for delivering naphtha for research purposes. This study was implemented within the EU Hercules-2 project.
Funding: This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 634135.

References

[1] REN21. Renewables 2017 Global Status Report. 2017 Available: http://www.ren21.net/wp-content/uploads/2017/06/17-8399_GSR_2017_Full_Report_0621_Opt.pdf, accessed 18.2.2019

[2] R. McGill, W. Remley, K. Winther. Alternative Fuels for Marine Applications. Annex 41. A Report from the IEA Advanced Motor Fuels Implementing Agreement. 2013

[3] Sajjadi, B., Raman, A.A.A., Arandiyan, H.: A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. Renewable and Sustainable Energy Reviews, 63 (2016), 62–92

[4] Sander, A. Košćak, M.A., Kosir, D., Milosavljević, N., Vuković, J. P., Magić, L.: The influence of animal fat type and purification conditions on biodiesel quality. Renewable Energy, 118 (2018), 752–760

[5] GEIR. Waste Framework Directive revision: European waste oil re-refining industry position. 2016 Available: http://www.geir-rerefing.org/documents/GEIRpositionpaperWFD_2016_FINAL.pdf, accessed 11.1.2018

[6] Golimowski, W., Berger, W.A., Pasyniuk, P., Rzeznik, Czechlowski, M., Koniuszy, A.: Biofuel parameter dependence on waste fats' fatty acids profile. Fuel, 197 (2017), 482–487

[7] Agarwal, A.K., Khurana, D.: Long-term storage oxidation stability of Karanja biodiesel with the use of antioxidants. Fuel Processing Technology, 106 (2013), 447–452

[8] EN 14214:2012+A1:2014 Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test method. Finnish Petroleum and Biofuels Association 2014

[9] EN 14112 Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of oxidation stability (accelerated oxidation test). Finnish Standards Association 2003

[10] EN 15751:2014 Automotive fuels. Fatty acid methyl ester (FAME) fuel and blends with diesel fuel. Determination of oxidation stability by accelerated oxidation method. Finnish Petroleum Federation 2014

[11] EN 14104:2003 Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of acid value. Finnish Standards Association 2003

[12] ASTM D7042-16e3 Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity). ASTM International 2016

[13] EN 14103:2003 Fat and oil derivatives. Fatty Acid Methyl Esters (FAME). Determination of ester and linolenic acid methyl ester contents. Finnish Standards Association 2003

[14] Fereidooni, L., Tahvildari, K., Mehrpooya, M.: Trans-esterification of waste cooking oil with methanol by electrolysis process using KOH. Renewable Energy, 116:A (2018), 183–193

[15] Xie, W.-Q., Gong, Y.-X., Yu, K.-X.: A rapid method for the quantitative analysis of total acid number in biodiesel based on headspace GC technique. Fuel, 201 (2017) 236–240

[16] Varatharajan, K. & Pushparani, D.S.: Screening of antioxidant additives for biodiesel fuels. Renewable and sustainable energy reviews, 82 (2018) 3, 2017–2028

[17] Dunn, R.O.: Effect of temperature on the oil stability index (OSI) of biodiesel. Energy Fuels, 22 (2008) 1, 657–662

[18] Dwivedi, G. & Sharma, M.P.: Investigation of Oxidation stability of Pongamia Biodiesel and its blends with diesel. Egyptian Journal of Petroleum, 25 (2016) 1, 15–20