

## **Properties of local produced animal-fat based biodiesel and its blend with fossil fuel**

K. Sirviö\*, S. Heikkilä, R. Help, S. Niemi and E. Hiltunen

University of Vaasa, Faculty of Technology, PL 700, FIN-65101 Vaasa, Finland

\*Correspondence: [katriina.sirvio@uva.fi](mailto:katriina.sirvio@uva.fi)

**Abstract.** In the near future, more emphasis must be put on reducing greenhouse gas (GHG) emissions in road transportation, house heating, agricultural activities, marine transport etc. This study concentrated on the use of alternative fuels in engine-driven applications of non-road machineries and decentralized energy production. Today, the engines are mainly designed for crude oil derived fuels and liquid renewable fuels are blended with crude oil based fuels to fulfill the requirements of renewable energy usage. Due to the environmental reasons on one hand and to the agricultural needs, on the other hand, different blends of bio- and fossil fuels are becoming more popular. In Europe, the maximum FAME content in diesel fuel is 7 vol% according to the EN 590:2013 but higher percentages are also available and targeted around the world. For example in the United States, the 20% blend fraction is becoming more common. For these reasons, B20 fuels were chosen to be investigated in this study. Special emphasis was put on improving blending issues since fuel blending may cause some operating risks. The main aim was to research widely the properties of animal-fat based methyl ester (AFME) and B20 fuel blend produced from it. AFME is a waste based fuel and produced in Ostrobothnia region, Finland. The aim was to find out in which engine applications the fuels are feasible and investigate if the fuels fit in the quality of automotive fuel Standards. According to the results, AFME is a feasible option to increase self-sufficient energy production in Ostrobothnia.

**Key words:** Biofuel, blending, FAME, AFME, diesel fuel, B20.

### **INTRODUCTION**

In the near future, more emphasis must be put on reducing greenhouse gas (GHG) emissions in road transportation, house heating, agricultural activities, etc. There is an increasing demand to put alternative fuels into operation for engine usage to replace the conventional fossil fuels. Alternative fuel has to be technologically feasible, economic, ecologically beneficial and easily accessible. For diesel engines, biodiesel, produced from vegetable, animal or waste oils, is one of the alternative fuel sources (Bae & Kim, 2016). Today, the engines are mainly designed for crude oil derived fuels and liquid renewable fuels are blended with crude oil based fuels to fulfill the requirements of renewable energy usage. The amount of renewable energy is then increased but the dependency on crude oil is remained.

Decentralized energy production is one way to decrease the dependence on import energy. It would also have benefits for the environment through reduced transportation. In countryside, there may also be possibilities to utilize own yield of oils and fats as

biodiesel fuel through transesterification and this could be financially beneficial for the farmers. In rural areas, there is an increasing need for cheap, both fossil and renewable, fuels in agricultural engine applications. Due to the environmental reasons on one hand and to the agricultural needs, on the other hand, different blends of bio- and fossil fuels are becoming more popular.

Now, 95% of biodiesels are produced from edible vegetable oils. The use of edible oils is problematic because the use of them 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. Nevertheless, the share of them 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 material for esterification process. Together with feedstock the presence of impurities highly influences the quality of biodiesel. This makes the manufacturing process laborious because the fat needs to be purified before the esterification process (Sander et al., 2018). Further, the esterification processes in animal fat based biodiesel production have not always been successful due to the high free fatty acid contents. It is still possible to optimize the manufacturing process and achieve the ester content above 96.5 m-% which is the lowest limit set in EN 14214 (Encinar et al., 2011). The study of waste based fuels is important because recycling of potential energy raw materials is still one step forward in increasing the suitable and more sustainable options.

Fur farming is one industry which produces 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. Animal fats as well as vegetable oils and residues can also be utilized in production of synthetic, paraffinic diesel, also called as renewable diesel. This kind of fuel is, though, not studied in this paper.

In Europe, the maximum FAME content in diesel fuel is 7 vol% according to the EN 590:2013 (SFS-EN 590:2013, 2013) but higher percentages are also available and targeted around the world. For example in the United States, the 20% blend fraction is becoming more common. B20 and B30 fuels do even have their own Standard, EN 16709, which specifies the quality of those fuels with a high biodiesel content (SFS-EN 16709:2016, 2016). That is why B20 fuels were chosen to be investigated in this study.

Fuel blending may, however, cause operating risks. The fuels need to be stable and compatible with engine and other blended fuels. Several studies have been made to figure out how biodiesels and their blends affect the lifetime of the engines. A review of short run tests reports that biofuels can replace conventional diesel fuel but a long run analysis is needed for assessment of the engine life. Problems that may occur are carbon deposition, lubricating oil dilution, piston ring sticking and injector nozzle choking (Patel et al., 2016).

This study determined the properties of animal-fat based methyl ester (AFME) and B20 fuel produced from it. AFME is a waste based fuel and produced in Ostrobothnia region, Finland. This fuel has earlier been studied in terms of its required antioxidant content (Sirviö et al., 2014). The other properties of AFME have not been studied and published this detailed elsewhere. As the manufacturing process of this AFME is uniquely planned for the certain type of animal fat waste (Feora, 2011), it is well-

grounded to measure the properties of AFME and compare them to fuel Standards. For the FAME type fuels, the bottleneck in the fuel quality has been the cold properties and oxidation and storage stability. If the fuel is not feasible in automotive engine applications, it is possible to utilize it in power generation or as heating oil and still promote the self-sufficient energy production.

The B20 fuel sample was prepared by mixing 20 vol% AFME biodiesel and 80 vol% fossil diesel fuel oil (DFO). The question was, whether the fuels fulfill the requirements set in Standards EN 14214, EN 16709 and EN 590, and if not, what enhancements are needed to improve the fuel quality.

In the current study, the parameters were investigated that correlate with the quality of the fuel blends. The analysed properties were density, kinematic viscosity, oxidation stability, water content, flash point, acid number, Sulphur content, cetane number, distillation curve and cold properties. The aim was to figure out how the fuels fulfill the requirements of the Standards in terms of the measured properties.

## MATERIALS AND METHODS

The AFME was Feora Ecofuel, a product of Ab Feora which is located in Uusikaarlepyy, Finland. The capacity of batch processing line is 2,400 tons per year. The set-up consists of front-end acid esterification for converting free fatty acids (FFAs) into biodiesel with minimal yield loss, and a two-step alkali-transesterification in which triglycerides are turned into biodiesel. After that biodiesel is refined using neutralization (Feora, 2011).

The DFO was a product of Neste, Finland. It was low-sulphuric ( $7.2 \text{ mg kg}^{-1}$ ) fuel, which fulfilled the requirements of Standard EN 590.

All the analyses results, except for distillation, were measured at least twice and the results are presented as arithmetic means of at least two replicate measurements. The distillation curve was measured once for each sample.

### **Acid number**

The acid number of the blends 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).

### **Cetane number**

The cetane number describes the ignition quality of the fuel. The cetane numbers were analysed by the IQT according to Standard EN15195. In this analysis, the ignition delay, ID, is measured. (SFS EN 15195:2014)

### **Cold flow properties**

The cold flow properties were evaluated by three different methods: cloud point (according to ASTM D 7689), pour point (ASTM D 7346), and cold filter plugging point (CFPP) (EN 116), (ASTM D 7689, 2011; ASTM D 7346, 2015; EN 116, 2015).

### **Concentration of elements**

The concentration of elements (S, Na, K, Mg, Ca, P, Cu, Fe, Zn) was measured by a Perkin Elmer ICP OES spectrometer 7000DV. In this method, a weight sample is diluted with kerosene in a weight ratio of 1:1. The solution is injected to spectrometers plasma. Calibration was made by the known concentrations of the standards. The defined standards (emission intensities in known concentrations) and the presence and concentration of the element are evaluated by comparing the intensity of the light to these standards. The analysis is an in-house method carried out according to the standards SFS-EN 14538 and SFS-EN 14107, as well as to the manufacturer's advices. The quality assurance is secured by using an internal standard (SFS-EN 14538, 2007; SFS-EN 14107; 2003).

### **Distillation curve**

The distillation curve was produced according to Standard EN ISO 3405 (EN ISO 3405, 2011).

### **Ester content**

The ester content was measured by a Perkin Elmer gas chromatograph Clarus 580. 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-%.

### **Flash point**

The flash points were measured according to Standard ASTM D93-A (ASTM D93, 2002).

### **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. The 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 and according this Standard the maximum induction period is 48 hours (SFS-EN 15751, 2014).

### **Viscosity and density**

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).

### **Water content**

The water content was measured utilizing a Mettler Toledo C30 Coulometric KF Titrator. The method was coulometric Karl Fischer titration method according to Standard EN ISO 12937. (EN 12937, 2000)

## RESULTS AND DISCUSSION

The analysed results and limitations of fuel Standards are presented in Table 1.

**Table 1.** The analysed properties of AFME and B20 fuel

Property	Method	AFME	B20Unit	EN 590	EN 14214	EN 16709 (B20)
Density @15°C	ASTM D7042	880	843 kg m <sup>-3</sup>	820–845	860–900	820–860
Viscosity @40°C	ASTM D7042	4.46	3.80mm <sup>2</sup> s <sup>-1</sup>	2.00–4.50	3.50–5.00	2.00–4.62
Oxidation stability	EN 14112/EN 15751	2.2	8.9 h	> 20	> 8	> 20
Water content	EN ISO 12937/ manufacturer's device	537	- ppm	< 200	< 500	< 260
Flash point	EN 2719	> 120	84 °C	> 55	> 101	> 55
Sulphur content	EN 14538/ EN 14107/ manufacturer's device	30	10 ppm	< 10	< 10	< 10
Cetane number	EN 15195	64	62	> 51	> 51	> 51
Cloud point	ASTMD7689	5.4	0.3 °C	< -10 (arctic climates)	< -3	
Pour point	ASTMD7346	6	-18 °C			
CFPP	EN116	2	-5 °C	< -20 (arctic climates)	< -10	< -20
Acid number	EN 14104	0.30	0.09 mgKOH g <sup>-1</sup>		< 0.50	
Ester content	EN 14103	94.2	- m-%		> 96.5	
Na+K	EN 14538/ EN 14107/ manufacturer's device	< 2	<2 ppm		< 5	
Ca+Mg	'	< 2	< 2 ppm		< 5	
P	'	< 1	< 1 ppm		< 4	
Cu	'	< 1	< 1 ppm			
Fe	'	< 1	< 1 ppm			
Zn	'	< 1	< 1 ppm			

The relative standard deviations are: density and kinematic viscosity 1%, acid number 7.9%, ester content 1%, flash point 3.0% and OSI 4.5%. These had been determined for the analysis methods earlier.

### Density, kinematic viscosity and oxidation stability

The density of AFME was relatively high, 880 kg m<sup>-3</sup>. Due to AFMEs high density, the density of B20 was also high, 843 kg m<sup>-3</sup> but the result was within the limits of EN 590 and EN 16709 where the maximum values of densities are 845 kg m<sup>-3</sup> and 860 kg m<sup>-3</sup>, respectively. The kinematic viscosities of both fuels, AFME and B20, were within the limits of all Standards. The result of AFME was 4.46 mm<sup>2</sup> s<sup>-1</sup> and of B20, 3.80 mm<sup>2</sup> s<sup>-1</sup>.

The oxidation stability results of both AFME and B20 were poor. Neat AFME showed an OSI result of 2.2 hours. According to the FAME standard, EN14214, the result should be above 8 hours. B20 fuel's oxidation stability was 8.9 hours, which is still far off from the target, the minimum of 20 hours. The fuels studied here were not stabilized by antioxidant addition.

### **Flash point, water and Sulphur contents**

The water content of AFME was 537 ppm (mass based), which is clearly above 200 ppm, the limit of Standard EN590, and 260 ppm, the limit of Standard EN 16709. The water content of B20 was not measured. It can be approximated that when the AFME contained water 537 ppm, B20 contains one fifth of it (108 ppm) plus the content from neat fossil diesel (approx. 100 ppm). The limit of 200 ppm might be exceeded.

The flash point of AFME was high, above 120 °C. The flash point of B20 also fulfilled the requirements set in EN 590 and EN 16709 as the result, 84 °C, was clearly above 55 °C.

The Sulphur content of AFME was relatively high and above the maximum limit of all Standards, being 30 ppm. The fossil diesel used for blending was low sulphuric and the Sulphur content of B20 was 10 ppm, which almost fulfilled the target (< 10 ppm) set in Standards EN 590 and EN 16709.

### **Cold properties**

The allowed cold properties of diesel fuel may vary depending on the season. Here, the results are compared to the arctic limits in the winter time. What needs to be taken account is that the limitation is not as strict in the summer time.

According to Standard EN 590, the CFPP maximum in temperate climates is at its highest +5 °C, but in arctic climates the cloud point must be below -20 °C. Neither B20 nor AFME reached the arctic limitation, the CFPPs being -5 and +2 °C, respectively. The cloud point in arctic areas should be at its highest -10 °C according the EN 590. For AFME, it was 5.4 °C and for B20 0.3 °C. Thus, the requirement set in Standard was not reached for neither of them. No limit is set for the pour point in the Standards. The pour point of AFME was 6° and of B20 -18 °C.

### **Acid number, ester content and concentration of elements**

The acid number of AFME and B20 were 0.30 mg KOH g<sup>-1</sup> and 0.09 mg KOH g<sup>-1</sup>, respectively. The highest Standard limit set for FAMES is 0.50 mg KOH g<sup>-1</sup> and AFME fulfilled the acid number requirement.

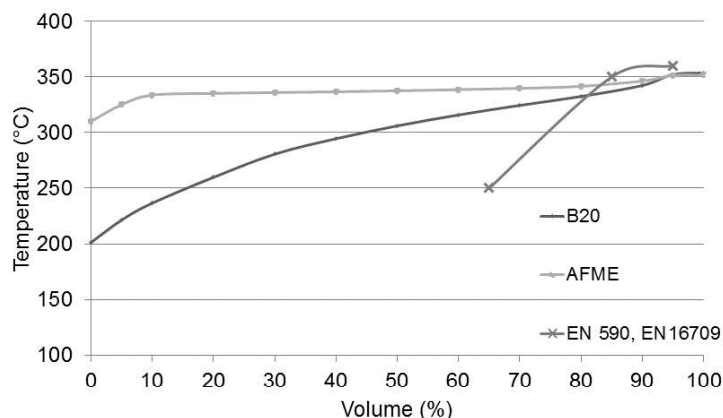
The ester content of AFME was slightly lower (94.2 m-%) than the target set in EN 14214 (min. 96.5 m-%).

No significant amounts of trace elements were found.

### **Distillation**

The shape of the distillation curve of both neat AFME and B20 is rather straight. The shape of fossil diesel fuel's distillation curve is usually 'S' shaped. In Standards EN 590 and EN 16709, the limits are that below 250 °C, no more than 65% is allowed to distillate, at least 85% must be recovered by 350 °C, and at 360 °C, at least 95% has to be distilled. Fig. 1 shows that both neat AFME and B20 fulfilled these requirements. At 250 °C, less than 20% of B20 and 0% of AFME had distilled. At 350 °C, the

recovery percentage of both samples was slightly below 95%. The distillation of both samples was completed at 360 °C.



**Figure 1.** Distillation curves of AFME and B20 compared to the requirements set in Standards EN 90 and EN 16709.

Altogether, the quality of AFME and B20 fuels was fair. Neat AFME does not fulfill all the requirements of an automotive standard but there are other applications for its usage, e.g. power generation. In the Standard EN 16709, it is mentioned that FAME used for blending should fulfill the requirements set in EN 14214. The AFME researched in this study, is therefore not suitable for the EN 16709 blends. Though, the characteristics of the fuels could be enhanced by the following measures and the quality level set in Standards be achieved.

The FAME yield (ester content), being slightly under the target, could probably be increased by optimizing the chemical equilibrium in the manufacturing process.

The oxidation stability of both neat AFME and the blend needs to be enhanced. Several articles have been published related to biodiesel stability and relatively high concentrations of antioxidants were found to be required to fulfil the requirements set for the fuels stability (Das et al., 2009; Yang et al., 2017).

FAMES are likely to bond water molecules. The water content of neat AFME (537 ppm) was above the allowed limit, 500 ppm. The moisture is dried in manufacturing process, but the drying process may be improved for lowering the water content. High water content, together with air exposure, are important factors affecting the degradation of biodiesel (Sorate & Bhale, 2015).

A correlation might exist between the poor oxidation stability and high water content. Karavalakis et al. (2011) have found that the oxidation stability behaviour of biodiesel blends is a very complicated process. The most important factors affecting the blends' oxidation are the biodiesel composition and used antioxidants, in other words stability improving additives. No antioxidants were used in the production of AFME in this study. The effect of suitable antioxidant depends on the raw material used for biodiesel production. As an example, butylated hydroxytoluene (BHT) is said to work well with animal fat based biodiesels (Varatharajan & Pushparani, 2018).

Another weakness was the fuels' cold properties. The cold properties were compared to requirements set for the arctic regions because AFME was produced in Finland. In cold weather, the saturated biodiesel compounds crystallize. In engines, these crystals will clog fuel lines and filters. The higher the amount of saturated compounds is, the higher the cloud and pour points are. Moreover, a fuel suitable for a low ambient temperature must have favorable cold flow properties (Sorate & Bhale, 2015). Generally, neither AFME nor other FAMES, which consist of large fractions of saturated compounds, are suitable for arctic areas without proper improvements.

In arctic conditions, the cold performance of AFME may be challenging but B20 (e.g. CFPP -5 °C) fuel may be feasible in Finland outside of December, January and February. In these months, the average temperatures have been below -5 °C, according to the statistics of 1981–2010. (Finnish Meteorological Institute, 2017, 1) The annual average temperature has though risen 0.2–0.4 °C per decade in last 40 years, though the annual variation is extensive. (Finnish Meteorological Institute, 2017, 2) This may broaden the feasible season range of FAMES at least in blends in Scandinavia in coming decades.

Seames et al. (2010) have proposed a production method, which may lead to improved biodiesel that has better cloud and pour points and better oxidation stability. The suggested thermal batch cracking resulted in the enrichment of the final product by C<sub>7</sub>-C<sub>16</sub> fractions and in converting the unsaturated esters into saturated ones. However, the reaction temperature was quite high being 440 °C. For a waste based fuel, this may be too expensive a way to enhance the quality of the fuel. A more economical way to use the fuel is to confine the usage outside the coldest seasons of the year.

Another option for improving the cold properties are additives (cold flow improvers). In the case of vegetable oil based methyl esters, just blending biodiesel with other fuels than DFO, like kerosene, can sufficiently improve the cold properties (Bhale et al., 2009; Sirviö et al., 2018). However, kerosene is rather expensive and kerosene-FAME blends may not be the most profitable options for the engine applications studied in this paper.

## CONCLUSIONS

In this study, the aim was to research the properties of animal-fat based methyl ester (AFME) and B20 fuel produced from it and fossil diesel fuel. The B20 fuel sample was prepared by mixing 20 vol% biodiesel and 80 vol% fossil diesel. The question was, whether the fuels fulfill the requirements set in Standards EN 14214, EN 16709 and EN 590 and, if not, what are the enhancements needed to improve the fuel quality.

The parameters were investigated that correlate with the quality of the fuel blends. The properties analysed for both the samples were density, kinematic viscosity, oxidation stability, water content, flash point, acid number, Sulphur content, cetane number, distillation curve and cold properties. The aim was to figure out how the fuels fulfill the requirements of the Standards in terms of the measured properties.

Based on the study, the following conclusions could be drawn:

- Neat AFME did not fulfill all the requirements of an automotive standard but there are other applications for its usage, e.g. power generation or heating.



- The restricting quality parameters of AFME were the low ester content, high water content, low oxidation stability and poor cold flow properties. These properties can though be enhanced.
- The high water content and low ester content can be enhanced by optimizing the manufacturing process.
- B20 did not completely fulfill the requirements set for B20 fuel in Standard EN 16709. The restricting parameters were the same as for the neat AFME; low oxidation stability and poor cold flow properties.
- The oxidation stability of AFME and B20 fuel could be enhanced by adding suitable antioxidant straight after manufacturing.
- The cold properties of AFME and B20 fuel could be improved by adding suitable cold flow improver as an additive. Blending AFME with kerosene should also be studied further.

ACKNOWLEDGEMENTS. The authors would like to acknowledge Merchant Gustaf Svanljungs foundation for donation to this study. The authors also wish to thank the companies Feora and Neste for delivering the studied samples.

Funding: This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 634135.

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