

Improvement of low-temperature characteristics of biodiesel by additivation

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Abstract

In manipulation and utilization of biodiesel and its mixtures, especially in the winter period, one of the most serious problems is relatively poor low-temperature flow properties. Classic methods of transesterification solve this problem, so biodiesel quality can be improved only by additives (cold flow improvers). This research examines the effect of commercial additives on the improvement of low-temperature characteristics of biodiesel. Namely, cold filter plugging point (CFPP), pour point (PP) and cloud point (CP) were tested in accordance with EN 116 and ISO 3015 standards. The influence of additives on different types of biodiesel, its different age and influence on the mixture of 5 % biodiesel and fossil diesel were examined. A better effect of additivation to "fresh" biodiesel (made using rapeseed oil), compared to "aged" biodiesel was noted. Improvement of additivation was achieved by mixing additives with an organic solvent (toluene). It was demonstrated that different types of additives are suitable for different types of biodiesel as well as mixtures of biodiesel and fossil diesel. Additives in which solvent is compatible with the type of biodiesel were found to exhibit better performance.

Keywords: *biodiesel; low temperature properties; additives*

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1. INTRODUCTION

Energy and environmental problems in the use of fossil fuels have prompted research related to alternative fuels that could replace crude derivatives. Biodiesel, that represents fatty acid methyl esters (FAME), has proven to be a suitable alternative. Compared to conventional petroleum diesel, it offers numerous advantages, such as increased biodegradability, reduced toxicity, lower emissions, higher flash point, increased lubrication and derivation from a renewable feedstock [1-4].

A lot of research has been carried out on development of biodiesel technologies and improvement of its technical characteristics, in order to obtain a suitable and economically profitable fuel that can replace diesel oil derived from crude oil [5-8].

Despite all good characteristics of this renewable resource, some significant weaknesses limit its use as a substitute for fuel of fossil origin. Two groups of different problems arise because of inadequate low temperature properties: handling problems and operability problems. Handling, including filtration, refers to storing, installing, and pumping biodiesel in its pure form (B100), or as a mixture of biodiesel with diesel. Operability signifies the use of biodiesel-diesel mixtures as a fuel and problems that may arise during the use in the fuel system or in other equipment of a vehicle.

Several factors can affect low temperature properties (LTP) and functional performance of FAME. Various studies have ascertained that crystallization or thickening of biodiesel at low temperatures causes fuel starvation and

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operability problems as solidified materials clog fuel lines and filters, mainly due to its high amounts of saturated FAME components [9,10].

LTP of FAME vary with composition of fatty acids of the raw material and the number of saturated components, which again depends on the raw material used to produce biodiesel. LTP of biodiesels derived from different raw materials were examined in various studies [11-20]. Typical values of the cloud point (CP), pour point (PP) and the cold filter plugging point (CFPP) of biodiesels (FAMEs) produced from different raw materials are presented in Table 1.

Another factor that influences LTP of FAME is the production process *i.e.* the method of obtaining pure biodiesel (B100). This factor is due to some impurities that can promote formation of deposits. Two major impurities in FAME that can cause handling and functional problems are saturated monoglycerides and sterol glucosides. It is believed that precipitation in the pure biodiesel fuel is associated with the presence of sterol glucosides, while precipitation in diesel mixtures is more often associated with the presence of saturated monoglycerides.

Table 1. Typical low temperature properties (cloud point, CP, pour point, PP, and the cold filter plugging point, CFPP) of biodiesel produced from different raw materials

Biodiesel	CP temperature, °C	CFPP temperature, °C	PP temperature, °C	References
Rapeseed	-5 (-3 to -5)	-9(-8 to -12)	-12	[11,16]
Sunflower	2 (-1 to 3)	-2 (-7 to -2)	-12	[17,19]
Soybean	3 (-7 to 3)	2 (-6 to 2)	-2, -7	[12,16,19]
Coconut	5 (9 to 12)	-3		[13,14]
Palm	18 (13 to 16)	16 (5 to 11)	13	[15,16]
Lard	9 (10 to 20)	9 to 14	6	[18]
Tallow	17	9	15	[20]
Corn	-3	-1, -4	-9, -7	[19,13,14]

Quality of the selected raw material and the impurity content determine whether it must be pre-purified to remove impurities that cannot be removed during the processing, thus impairing low temperature performance of the final product [21,22].

Poor low temperature characteristics of pure biodiesel such as high CP, PP and CFPP make it unsuitable for use in the winter period. In this respect, use of mixtures of biodiesel and diesel of fossil origins is more convenient but still not eliminating the problem. Even if diesel of the fossil origin has better LTP, depending on the quantity of the added biodiesel, these properties of the mixture can be drastically worsened.

There are two basic ways to improve LTP of the biodiesel fuel mixture: by adding additives to improve these properties and by selecting appropriate raw materials for biodiesel production (winterization) before blending it with diesel of fossil origins.

The winterization procedure implies removal of saturated methyl esters, which crystallize at low temperatures. These components having high boiling points are removed by separation and filtering at a reduced temperature. Biodiesel prepared in such a way shows improved low-temperature properties and can be used at winter conditions, either pure or as a component of the mixture. Winterization is unfavorable process due to decreased yield of biodiesel that give out about 25 % after removal of saturated methyl esters [23,24]. For this reason, a common method is additivation.

1. 1. Low temperature properties of biodiesel

Cold flow properties of biodiesel depend mainly on its composition. CP is higher for biodiesel made from feedstock containing higher concentrations of saturated long-chain fatty acids with high-melting point, and this biodiesel tends to exhibit relatively poor cold flow properties. For different saturated FAMEs, CP depends on the chain length, while for unsaturated FAMEs, it depends on the degree of unsaturation and orientation of double bonds [25].

When ambient temperatures decrease below the CP, saturated methyl esters within biodiesel nucleate and form solid crystals. These crystals are primarily composed of methyl octadecanoate. Growth of the crystals depends on the composition of saturated methyl esters other than octadecanoate (*e.g.* hexadecanoate) and morphology is related to the nature of the remaining liquid portion of the mixture [26,27].

With a decrease in temperature, the crystal size continually increases, and a grid is obtained leading to solidification at the pour point (PP). PP is defined as the temperature at which a few crystal agglomerates and gel formation in fuels are observed, consequently preventing the fuel to flow. For practical PP measurements, usually the temperature before materials clog the fuel filter is determined [28].

CP and PP are not acceptable as effective measures for determining possibilities to use a fuel. Fuel at the CP temperature, although exhibits a certain turbidity, can still freely flow so that any problems in mechanical components are not expected to occur. However, fuel at this temperature will not flow through the fuel injection system.

Cold filter plugging point (CFPP) is a reliable low temperature characteristic, which presents the temperature at which the fuel will plug a 45 μm filter (similar mesh opening as in vehicles) under the standard injection pressure.

1. 2. The effect of additives on low-temperature properties

Additives for improving LTP of biodiesel are chemicals that influence the crystal growth, during the decrease in ambient temperature.

It is known that the crystal morphology and/or growth rate are profoundly affected by the presence of impurities in the system. Some impurities suppress the growth while some others stop the crystal growth completely in one or more directions. Several theoretical models have been developed that explain effects of impurities on kinetics of the crystallographic structure development, and the tendency for this structure to form [29]. Additives can be defined as impurities that are added intentionally to produce a well-defined and desired morphological effect on the crystalline structure [28].

Effective concentrations of additives vary depending on the system to which they are added. An important class of additives so-called "intentional" additives are intended for specific interactions with desired parts of a molecular structure in the matter to which they are added. They are designed to contain certain groups of atoms that mimic dissolved molecules and are easily adsorbed at growth sites on the crystal surfaces.

Final shape of a crystal depends on the growth rate of its various surfaces, and its size decreases with the growth rate increase. Certain crystal surfaces will depend on the temperature increase rate and super saturation [31].

Additives for LTP improvement of fossil diesel fuels used since the 1960s are still in use today for FAME [32, 33]. The most common type of the wax crystal modifier used to improve LTP of diesel is based on ethylene vinyl acetate (EVA) copolymer [30]. Due to flexibility of the polymerization process, the molecular weight and acetate ratio may vary in order to obtain the most suitable polymer for a specific fuel.

Performance of an EVA copolymer, as well as other polymers in use such as vinyl acetate-fumarate copolymers, styrene-esters copolymers, diester- α olefin copolymers, malan-styrene esters and polymethacrylates can be enhanced by blending them with a cold flow improver (CFI) additive of different chemistry [30]. Various oil companies have developed specific polymeric additives to improve wax nucleation (to produce many small crystals instead of several large ones) and to slow down the crystal growth.

Reaction between additives and fuel crystals can occur either in solution, on crystal surfaces or, in the case of co-crystallization, in the crystal structure. Based on the macroscopic evidence, it is generally believed that impurities bond preferentially to specific faces on growing crystals, inhibiting therefore the growth along those faces. Recently, a more complex model has been proposed, designated as kinetic growth inhibition. It was found that solidification can occur in the form of macroscopic bands (several hundred micrometers in length) parallel to the front. In this growth model, the front periodically stops growing, allowing a new front to nucleate and spread laterally along the arrested front. These bands are controlled by the process thermodynamics, hence the designation of the effect. As crystallization proceeds, the solute is depleted near the front, and as the sample moves through the gradient, a region ahead of this depletion zone becomes supersaturated, a situation designated as constitutional supercooling. However, if a kinetic inhibitor additive is present, crystals do not grow appreciably [34].

Many studies examined one or more low temperature characteristics of biodiesel and biodiesel blends in which biodiesel of different origins was used, *i.e.* synthesized from different oils [35-41]. As stated in the previous section, there are very few studies dealing with LTP of biodiesel and specifically the effects of additives on these properties. In

the present work, comparative effects of different additives were investigated with respect to improvement of LTP (CP, PP and CFPP) of two pure biodiesel samples and a mixture of biodiesel and diesel fossil fuel.

2. MATERIALS AND METHODS

2.1. Crude properties

Influence of additives on three different biodiesel samples was investigated:

Sample 1: "aged" biodiesel (biodiesel at the start of the experiment was more than 6 months old), derived from a mixture of rapeseed and palm oil, and complicated for additivation.

Sample 2: "fresh" rapeseed biodiesel, additized immediately after production.

Sample 3: mixture of rapeseed biodiesel and a commercial ultra-low sulfur fossil diesel (ULSD), in the volume ratio 5:95.

Characterization of biodiesel samples was performed in an authorized SGS laboratory (Table 2). The ULSD (ultra-low sulfur diesel) was produced in the Pančevo oil refinery (Pančevo, Serbia). The complete analysis of the ULSD is provided in Table S-4 (Supplementary material), which has shown that it fulfills characteristics specified in the EN590 standard.

Table 2. Analysis of biodiesel samples according to EN SRPS 14214

Specification	Standards	Range		Sample 1	Sample 2
		Min.	Max.		
FAME content, % mass	EN 14103	96.5	-	99.6	97.75
Density at 15 °C, g / cm ³	EN ISO 3675, EN ISO 12185	0.86-0.90		0.881	0.884
Viscosity 40°C, mm ² /s (cST)	EN ISO 3104	3.5-5.0		4.499	4.49
Temperature of flash point, °C	EN ISO 2719e, EN ISO 3679	101	-	163.0	184.13
Cetane number	EN ISO 5165	51	-	56	-
Max CU corrosion, 3 ^h /50°C	EN ISO 2160	-	Class 1	1a	-
Oxidation stability [110°C], h	EN 15751, EN 14112	8	-	12.7	8.68
Acid value (max), mgKOH /g	EN 14104	-	0.5	0.14	0.38
Iodine value, g iodine /100 g	EN 14111, EN 16300	-	120	95	114.74
Linol. Acid Methyl Ester, % mass	EN 14103	-	12	7.2	9.77
Polyunsaturated methyl esters content (>4 double bonds), % mass	EN 15779	-	1	<1	-
Methanol content, % mass	EN 14110	-	0.2	0.03	< 0.02
Monoglyceride content, % mass	EN 14105	-	0.7	0.69	0.69
Diglyceride content, % mass	EN 14105	-	0.2	0.07	0.146
Triglyceride content, % mass	EN 14105	-	0.2	<0.1	0.039
Free glycerol content, % mass	EN 14105i, EN 14106	-	0.02	<0.01	0.001
Content of total glycerol	EN 14105	-	0.25	0.166	0.202
Water content, mg/kg	EN ISO 12937	-	500	139	385
Content of total contamination, mg/kg	EN 12662	-	24	20	6.97
Sulfated ash content, % mass	ISO 3987	-	0.02	<0.005	-
Sulfur content, mg/kg	EN ISO 20846, EN ISO 20884, EN ISO 13032	-	10	<3	-
Content of group I metals [Na, K], mg/kg	EN 14108, EN 14109, EN 14538	-	5	<1	<0.1
Content of group II metals [Ca, Mg], mg/kg	EN 14538	-	5	<1	3.55 + 1.4
Phosphorous content, mg/kg	EN 14107, EN 16294	-	4	<4	1.88
Temperature of CFPP, °C	EN 116	-	-	3	-9

Calculated values of molar masses, of the raw material and biodiesel, as well as the iodine number determined based on the gas chromatography (GC) analysis (Supplementary material, Table S-5), for the first sample are: 865.44, 289.82 and 89.65, respectively. These values for the second sample are: 880.61, 294.87 and 106.4 g/mol, respectively.

2.2. Equipment and methods

Physical and chemical characterization of biodiesel samples was performed in compliance with EN 14214. The complete analysis of fatty acids was performed (Table 2), showing compliance with literature values.

Biodiesel samples were analyzed by GC to determine the content of fatty acid esters (according to SRPS EN 14103) (Table S-5, Supplementary material). GC analysis was performed using the gas chromatograph GC-2010 Plus (Shimadzu, Japan), equipped with an autosampler AOC-20i (Shimadzu, Japan), and a capillary column InterCap WAX (Hichrom Limited, UK) (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm). Analysis of the standard mixture of methyl esters (RM-1) was carried out using a reference probe sample of 0.6 μL at split ratio 40:1. The injector and detector temperatures were 260 $^{\circ}\text{C}$, and the analysis was performed under isothermal conditions at 200 $^{\circ}\text{C}$. Helium was applied as a carrier gas at the flow rate of 3 mL/min. Methyl heptadecanoate of a purity >99 % (Fluka Analytical, Germany) was used as an internal standard. Sample of 1 μL was injected into the injector.

CP, PP and CFPP are used to define low-temperature operational limits for diesel fuels. CFPP and PP are determined according to standard methods SRPS EN 116 and SRPS ISO 3015. To eliminate the effect of human error, automatic fuel testing equipment HERZOG MP 852 (Walter Herzog GmbH, Germany) is used as specified in the ISO 3016 for determining CP and PP of mineral oil and petroleum products. A preheated test sample is cooled in steps of 3 $^{\circ}\text{C}/\text{min}$. After each analysis, the testing tube is removed from the cooling bath and bent to 90 $^{\circ}\text{C}$. Movement of the surface of the test substance is observed by a video camera. PP was defined as the temperature at which any movement cannot be observed at the bend angle of 90 $^{\circ}\text{C}$ over a period of 5 seconds. The same automatic device, HERZOG HCP 842, was used to determine CFPP, too. Values of CP, PP and CFPP are given in Supplementary material (Tables S1–S3).

2. 3. Additives used for investigation of low temperature properties

The samples 1-3 were investigated regarding the effects of different commercial additives on LTP. Additive basic compositions are presented in Table S-6 (Supplementary material)

In the first series, effects of five commercial additives (N_1 , N_2 , N_3 , CF and LM) were investigated on the sample 1 ("aged" biodiesel).

In the second and third series, effects of thirteen additives (N_1 - N_3 , CF, LM, V_1 , V_2 , C_1 - C_4 , H_1 and PL1) were investigated on the sample 1 ("fresh" rapeseed biodiesel) and the sample 2 (mixture of rapeseed biodiesel and fossil diesel), respectively. The main characteristics of the additives are given in Table 3.

Table 3. Main characteristics of the additives used

V1	V2	N1
Acrylic copolymers.40.0 - 70.0 %	Acrylic copolymer 60.0 - 100.0 % Rapeseed	Vinyl acetate 0.1 - 1.0 %
Mineral oil 3.0 - 7.0 %	oil 8002-13-9 10.0 - 30.0 % Methyl	Mesitylene 0.1 - 1.0 %
Vaseline oil 1.0 - 5.0 %	methacrylate 80-62-6 0.1 - < 1.0 %	Polymer, reaction product of an olefin anhydride
Solvent kerosene (crude oil), heavy aromatic;		maleic, fatty amine and methacrylic acid ester 1 -
kerosene - without specification 15.0 - 40.0 %		2.5 %
Naphthalene 1.0 - 5.0 %		Hydrocarbons C10, 30-60 % (aromatics >1 %)
1,2,4-trimethylbenzene 0.1 - 1.0 %		Kerosene (petroleum), Hydrodesulfurized 10-20 %
		Naphthalene 1.0 - 5.0 %
N2	N3	CF
Vinyl a0.1 - 1.0 %	Vinyl acetate 0.1 - 1.0 %	Toluene 2 %
Mesitylene 0.1 - 1.0 %	Mesitylene 0.1 - 1.0 %	Diesel fuel 30-60 %
Polymer 1 - 2.5 %, which is product of a-	Polymer 1 - 2.5 %, which is product of a-	
olefin anhydride maleic, fatty amine and	olefin anhydride maleic, fatty amine and	
methacrylic acid ester	methacrylic acid ester	
Hydrocarbons C10, 25-50 %, (aromatics >1 %)	Diesel fuel No.2 30-60 %	
Naphthalene 2.5 - 5.0 %		
1,2,4-trimethylbenzene 1 - 2.5 %		
LM	H1	C1, C2, C3, C4
Hydrocarbons, C10-C13, n-alkanes,	Polyoxyalkylene modified random	Copolymer ester
isoalkanes, cyclics, aromatics 2- 25 %	polyester	Toluene
Solvent naphtha (petroleum),		
heavy arom. 10-<25		
PL1		
Vinyl copolymer in hydrocarbon solvent		
Naphtha		

2. 4. Sampling procedure

The biodiesel sample amount for each experiment of 140 ml was determined based on the available quantity of biodiesel and the required number of experiments.

The biodiesel temperature was determined based on the biodiesel CP, at no less than 5 °C above CP temperature.

The additive should be heated before addition and preliminary recommendations of the producer were the temperature range 45–55 °C. However, due to problems with the viscosity of additives and micro-pipetting, it was necessary to heat additives to higher temperatures and in cooperation with manufacturers, 60 °C was adopted.

The additive was weighted, heated to 60 °C and added to the weighted biodiesel sample 1. However, after reviewing the preliminary results and responses, based on the recommendation of one manufacturer, the additive procedure was further on modified. Namely, for samples 2 and 3 the weighted and heated additive at 60 °C was mixed with an organic solvent (toluene), in the ratio of 1: 9 (additive: solvent), and thereafter added to the weighted biodiesel sample. By this modification, better dispersion of additives in biodiesel was achieved, which resulted in better additivation effects. After blending, all obtained mixtures were tempered at 45–55 °C and mixed until homogenization. Control of the mixture homogenization was performed visually and mixing for all samples lasted 1.45 h. In preliminary experiments, additives were added according to the manufacturer's recommendation (100-1100 ppm). However, a weak response was found, so that the amount of additives was increased to yield concentrations of 2000 ppm and 5000 ppm. Because of the small effect observed at low concentrations of additives, tests with these concentrations have not been performed.

2.5. Sample analysis

Preliminary testing of the first series of samples ("aged" biodiesel), showed that biodiesel drastically degraded in relation to the analysis obtained immediately after its production. (see Table 2). The qualitative sample composition is analytically determined: biodiesel of palm oil and rapeseed, in relation to 40:60 (m/m). The sample degradation can be attributed to the long period of storage (more than 6 months) under inadequate conditions after production. Its degradation is confirmed by low-temperature properties analysis; CFPP increased from initial –3 °C after production to 3 °C for the "aged" biodiesel. Degradation was also confirmed by a decrease in oxidative stability, from 12.7 h, to about 7 h, along with viscosity increase from 4.49 mm²/s (cST) to 4.95 mm²/s (cST)., which precludes the use of this biodiesel as a commercial one since it is no longer in line with EN14214. This has already been evidence of the "aged" biodiesel, while other parameters, such as acid and peroxide number, have not been determined.

Although some literature data indicate that more stable types of FAME can be stored for a year or more, it is generally recommended that the FAME storage time should be limited to a maximum of six months. Basically, diesel blends have a longer shelf life than B100, depending on the type of FAME and added additives. Even in the case of diesel blends, the recommendation for the maximum storage period is also no more than six months. In practice, FAME should not be stored for longer than this time because by its' "aging" in the storage tank, acidity and viscosity increase and different types of deposits (gums, lacquers) are created. In order to monitor the quality of FAME during storage, indicators such as oxidation stability, acid number, viscosity, water and sediment contents must be determined. All these parameters can be used as indicators of whether FAME complies with EN 14214.

The method of comparative testing of additives started with determination of LTP of biodiesel samples in order to establish reference values, in relation to which the effects of additives can be assessed.

In the second series of experiments, a fresh sample of rapeseed biodiesel with CFPP of –9 °C and PP of –11 °C was used. Experiments for the third series contained ULSD and biodiesel obtained from rapeseed oil, in the volume ratio of 95 : 5 , with CFPP of -12 °C and PP of -14 °C.

For the second and third series, only the values of CFPP and PP of pure biodiesel were determined.

3. RESULTS AND DISCUSSION

In the first series ("aged" biodiesel, with palm oil) the effect on CFPP and PP for all additives was small while the improvement in the CP did not show any regularity. The minimum positive effects on the CP, with the addition of additive, are in accordance with the literature [35,36,39]. Generally, additives aimed for LTP improvement are designed

to inhibit agglomeration and growth of wax crystals, while not preventing the initial crystal formation. Since the CP measures the temperature at which crystals of wax appear, the observed lack of additive effect is expected.

The best results regarding the CFPP showed the additive N₁, which at the concentration of 5000 ppm induced the CFPP reduction of 4 °C. N₁ had significant effects even at lower concentrations so that at 900 ppm the reduction of CFPP was 3 °C (Fig. 1). This reduction in CFPP for N₂ and N₃ was achieved at 2000 ppm. The additive N₂ consists of polymer, product of reaction an olefin anhydride maleic, fatty amine and methacrylic acid ester (1–2.5 %), vinyl acetate, hydrocarbons C₁₀, aromatics >1 % (25-50 %), and low content of naphthalene, 1,2,4-trimethylbenzene, and mesitylene (Table 3).

The CF additive had a noticeable effect on the decrease of CFPP at the maximal added concentration, while, on the other hand, the CFPP reduction could not be observed for the LM additive (Fig. 1)

For PP, the best result was achieved with N₂ and CF additives at the concentration of 1100 ppm with a reduction of 2 °C (obtained in the preliminary research), and the same result was achieved with N₁ at 2000 ppm, and N₃ and LM at 5000 ppm (Fig. 2). It is interesting to note that the additive CF does not contain either polymers or copolymers, but only diesel fuel at high concentrations (30–60 %, Table 3). Based on this, its effect can be explained rather by dilution and winterization, and not as an effect of inhibiting crystal growth.

There was almost a negligible effect to the CP, at low concentrations of additives. The best results were obtained by the addition of N₁ at 5000 ppm, which resulted in reduction of CP for 3 °C (Table S-1, Supplementary material). This system has shown also the best response for CFPP (Fig. 1).

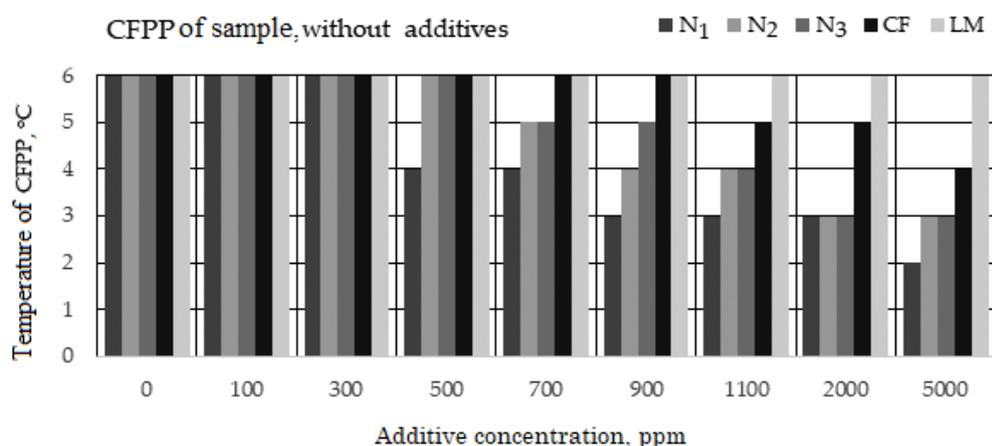


Fig. 1. CFPP vs. concentration of different additives, for "aged" biodiesel with palm oil (sample 1)

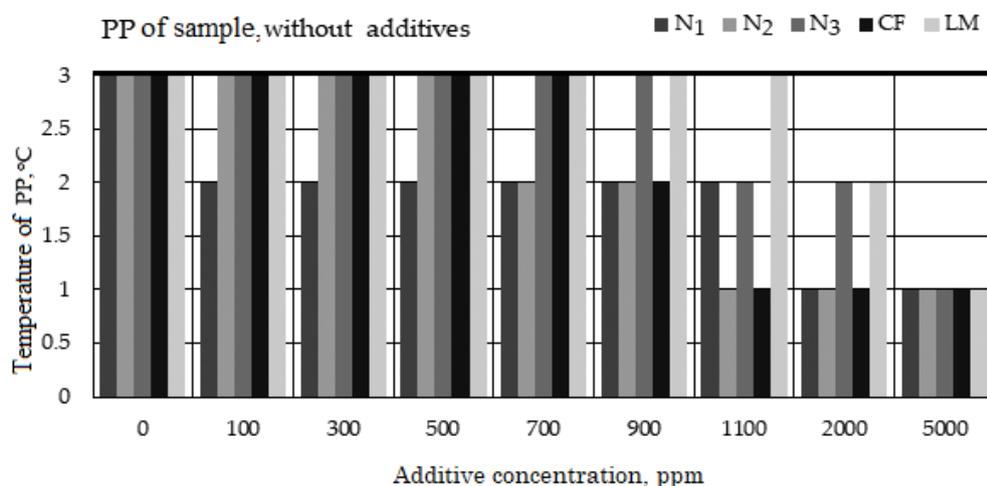


Fig. 2. PP vs. concentration of different additives, for "aged" biodiesel with palm oil (sample 1)

Following this first series with the sample 1 "aged" biodiesel, an alternative method was applied, that is pre-mixing the additive with an organic solvent (see Section 3.1). This method resulted in better effects to CFPP and PP which were improved for 1 °C, and even 3 °C, respectively. The obtained positive results of mixing the additives with an organic solvent, can recommend this procedure as a standard for additivation, and thus this method was applied in the next examinations.

In the second series of experiments ("fresh" rapeseed biodiesel), effects of thirteen additives at only one concentration were investigated (optimal 1000 ppm as determined by the first series of tests). The aim of this series was to determine effects of the additives on a biodiesel from rapeseed oil versus "aged" biodiesel containing biodiesel derived from a mixture of rapeseed and palm oils.

Effects related to CFPP and PP of most additives are noticeably higher in respect to the first series, which confirms the previous conclusion that the "aged" raw material containing palm oil biodiesel is problematic for LTP improvement by additivation.

It is noticeable that the effects of different additives on LTP differ in varying degrees. Some have a pronounced effect on CFPP while some on PP. Also, effectiveness of the additive depends on the type of biodiesel. By comparing changes in CFPP after addition of additives in the organic solvent, it can be deduced that the best results showed additives V₂ (9 °C), and N₁ and V₁ (4 °C) (Fig. 3). These additives contain high concentrations of an acrylic copolymer (60.0–100.0 %, V₂ and V₁) or polymer (N₁; Table 3). There is an interesting difference in the performance of the two additives V₂ and V₁. Although both have almost the same concentration of the acrylic copolymer, the additive V₂ has shown better effectiveness. The difference between these two additives is that V₂ contains rapeseed oil as a solvent, while V₁ kerosene (Table 3).

It can be assumed that compatibility of the solvent contained within the additive and biodiesel (rapeseed oil) improves its function.

Additionally, additives N₂, LM, C₂ and C₄ have shown good results in CFPP reduction (4 °C). According to the standard EN SRPS 116 the reproducibility of the result should be ± 3 °C and the repeatability ± 1 °C, leading to the conclusion that all these additives exhibit beneficial characteristics, with the V₂ additive being undoubtedly the best (Fig. 3).

Additives N₃ and C₁ induced small effects (2 °C) and the additive CF even smaller (1 °C), so that they are not adequate for improvement of CFPP.

For the PP improvement, the best result was achieved with the additive V₂ (25 °C), and good results have shown additives V₁ (13 °C), N₁ (7 °C), CF (7 °C), H₁ (6 °C), C₂ and C₄ (5 °C) (Fig. 4). Small effects have induced additives N₂, LM and C₁, for only 4 °C, which is inadequate to qualify these additives for this purpose. Also, additives C₃ and N₃ have shown very small influences, thus being not suitable for the improvement of PP of the rapeseed biodiesel (Fig. 4).

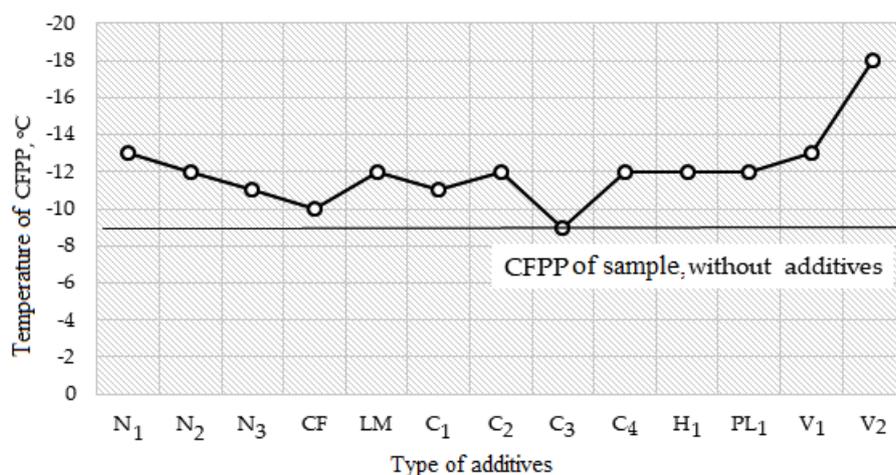


Fig. 3. CFPP as a function of different additives at the concentration of 1000 ppm for "fresh" rapeseed biodiesel (sample 2)

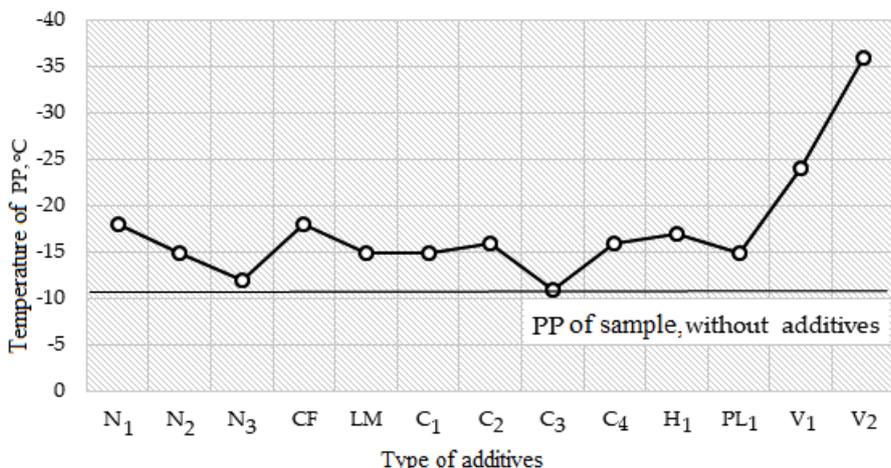


Fig. 4. PP as a function of different additives at the concentration of 1000 ppm for "fresh" rapeseed biodiesel (sample 2)

In the third experimental series, effects of additives at the concentration of 1000 ppm were investigated on the mixture of ULSD with 5 % biodiesel (sample 3) and the results are presented in Figures 5 and 6. Indeed, effects of various additives on CFPP and PP are remarkably different. They are noticeably higher in respect to the first and second series while in some cases, they are drastically lower, which means that the mechanism of action is different and that some additives are suitable for mixtures of biodiesel, and some for pure biodiesel.

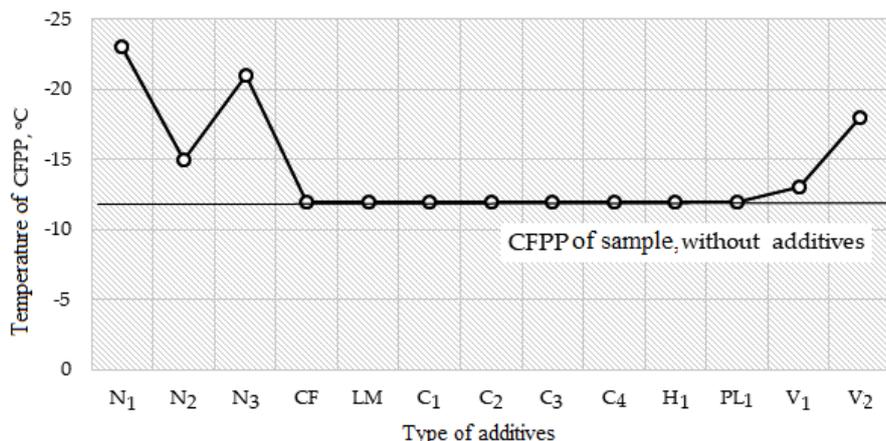


Fig. 5. CFPP as a function of different additives at the concentration of 1000 ppm for the mixture of BD-100 (rapeseed biodiesel) and ULSD (5:95) (sample 3)

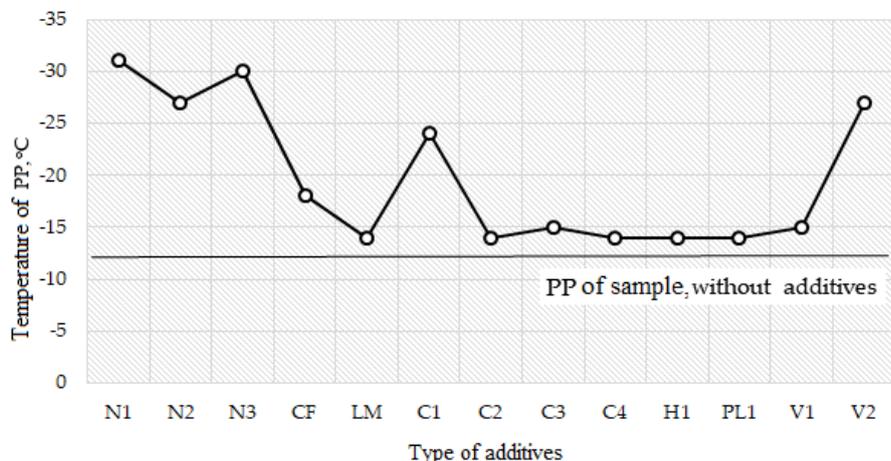


Fig. 6. PP as a function of different additives at the concentration of 1000 ppm for the mixture of BD-100 (rapeseed biodiesel) and ULSD (5:95) (sample 3)



Comparison of the results related to the change of CFPP after additivation revealed that the best results showed additives of the series N: N₁ (11 °C), N₃ (9 °C) and N₂ (3 °C). In addition, a good response had also V₂ (4 °C) (Fig. 5). Effects of all other additives could not be noticed, designating these additives as not suitable for this purpose. The additive N₁, which has shown the best result (11 °C), contains kerosene as the solvent (Table 3). It can be assumed that compatibility of the solvent within the additive and the main fraction in the mixture (95 % ULSD), improves its function.

Analyzes related to PP changes demonstrated similar results. The best additives are from the group N: N₁ (17 °C), N₃ (16 °C), and N₂ (13 °C) including also the additive V₂ (13 °C). In addition, C₁ had a good effect (10 °C). Fair efficiency has also shown the additive CF (3 °C), while the other additives had negligible effects, discarding them as potential additives for this purpose (Fig. 6).

5. CONCLUSION

The primary purpose of modifying low-temperature characteristics of a fuel by using additives is to improve diesel operation under cold weather conditions that is to improve flow properties at low temperatures.

In the present study, we have investigated two different types of fuels: biodiesel, and a mixture of 5 vol. % biodiesel in a fossil diesel. In addition, two biodiesel samples were investigated: the "aged" biodiesel, more than 6 months old and derived from a mixture of rapeseed and palm oils, and a "fresh" biodiesel, made from rapeseed oil.

It is assumed that in "aged" biodiesel, saturated methyl esters nucleate and form solid crystals, which are continually growing in size during aging, inducing deterioration of physical characteristics (viscosity, oxidative stability and low-temperature properties).

Accordingly, in the present study, it was observed that all additives had lower influence on the "aged" biodiesel as compared to the "fresh" one. For example, the additive N₁, which has shown good results in all samples, induced improvement of PP and CFPP in "aged" biodiesel at the concentration of 1100 ppm for 1 °C and 3 °C, respectively, while these values at the concentration of 1000 ppm in the "fresh" biodiesel were 7 °C and 4 °C, respectively. The obtained better effects of additivation of "fresh" biodiesel, compared to the "aged" biodiesel have confirmed the fact that this process has to be done immediately after production.

Mixing of additives with an organic solvent (toluene) and heating have shown improved effects of additives, as a result of better diffusion and distribution of active materials through the biodiesel bulk. This conclusion could be beneficial for additivation in the industrial practice. By adding the organic solvent, CFPP was improved for 1 °C and PP for 3 °C.

For all tested samples, a minimal CP improvement was obtained, which is in line with the literature data. In general, additives for LTP are designed to inhibit agglomeration and the growth of wax crystals and not the initial formation of crystals. Since the CP corresponds to the temperature at which wax crystals appear, the observed lack of additive effects is expected.

Different types of additives are suitable for different types of biodiesel and mixtures of biodiesel and fossil diesel with varying effective concentrations.

Comparison of additivation effects on the biodiesel and biodiesel-fossil diesel mixture has shown that the best additives were V₂ and N₁, respectively.

Comparison of additives with the same wax crystal modifier has revealed better performance of those in which the solvent is compatible with the type of biodiesel. The example is application of additives V₁ and V₂ to biodiesel obtained from rapeseed oil, the latter of which has shown better efficiency. Both additives have almost the same concentration of an acrylic copolymer and the only difference is that V₂ contains rapeseed oil as a solvent while V₁ kerosene.

Some of the additives, *e.g.* CF, do not contain either polymers or copolymers, but only diesel fuel at high concentration (30-60 %). Therefore, effects of these additives can be explained by dilution and winterization rather than the crystal growth inhibition.

Overall, results of the present study have indicated some useful practical guidelines in selecting appropriate additives and the additivation process for different biodiesel fuels.

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САЖЕТАК

Испитивање могућности побољшања ниско-температурних карактеристика биодизела адитивирањем

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(Стручни рад)

У процесу производње биодизела, будући да сировина има највећи удео у цени, преферирају се јефтине сировине - различита термички обрађена отпадна биљна уља (отпадна уља из ресторана) и уља животињског порекла. У манипулацији и у коришћењу биодизела и његових смеша, посебно у зимском периоду, један од најозбиљнијих проблема су нискотемпературна својства. Класичне методе трансестерификације не могу утицати на побољшање нискотемпературних карактеристика, па се квалитет биодизела може побољшати само адитивима (средства за побољшање течења у нискотемпературним условима). Овим истраживањем је испитан утицај комерцијалних адитива на побољшање нискотемпературних карактеристика биодизела. У складу са стандардним методама, које су прописане стандардима „EN 116“ и „ISO 3015“, испитиване су ниско-температурне карактеристике: филтрабилност (енг. cold filter plugging point, CFPP), температура стињавања (енг. pour point, PP) и температура замућења (енг. cloud point, CP). Студијом је испитан утицај адитива на различите врсте биодизела, његову различиту старост и утицај на смесу с доминантним уделом дизела фосилног порекла. Уочен је бољи учинак адитивирања на "свеж" биодизел добијен од уљане репице, у поређењу са "старим" биодизелом. Забележено је побољшање ефикасности адитивирања, мешањем адитива с органским растварачем (толуеном). Утврђено је да су различити типови адитива прикладни за различите врсте биодизела и мешане биодизела са дизелом фосилног порекла. Боље перформансе имају адитиви у којима је растварач компатибилан с врстом биодизела.

Кључне речи: биодизел; ниско-температурна својства; адитиви