**Technical paper**

**Testing the possibility of improving the low-temperature characteristics of biodiesel by**

# additivation

Ivan Tasić 1, Milan D. Tomić 2, Aleksandra Lj. Aleksić 3, Nataša Đurišić-Mladenović4,

Ferenc L. Martinović 4, Radoslav D. Mićić 1,\*

1. University of Novi Sad, Technical Faculty “Mihajlo Pupin”, Đure Đakovića b.b., 23000 Zrenjanin;

Serbia

1. University of Novi Sad, Faculty of Agriculture, Trg Dositeja Obradovića 8, 21000 Novi Sad, Serbia
2. NIS a.d. Novi Sad, Narodnog Fronta 12, 21000 Novi Sad, Serbia;
3. University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

**\*Corresponding author**: Prof. Radoslav D. Mićić; micicradoslav@gmail.com; phone: +381-65-506-1024

# Abstract

In the process of biodiesel production, as the raw material has the highest percentage in the price, use of cheap raw materials are favored - various thermally treated used vegetable oils (waste oils from restaurants) and oils of animal origin. In the manipulation and utilization of biodiesel and its mixtures, especially in the winter period, one of the most serious problems are low-temperature properties. Classic methods of transesterification cannot improve low temperature characteristics, 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. Low-temperature properties, namely cold filter plugging point (CFPP), pour point (PP) and cloud point (CP) were tested in accordance with EN 116 and ISO 3015 by standards.

The study has determined the influence of additives on different types of biodiesel, its different age and influence on the mixture with the dominant share of diesel fossil origin.

It was noted a better effect of additivation "fresh" biodiesel from the rapeseed, compared to "aged" biodiesel. Advanced effect of additivation is noted, by mixing additives with organic solvent (toluene).

It has been found that different types of additives are suitable for different types of biodiesel and mixtures of biodiesel and diesel of fossil origin. Better performance has additives in which is the solvent compatible with the type of biodiesel.

**Key words:** Biodiesel; low temperature properties; additives

# 1. INTRODUCTION

An energy and environmental problems in the use of fossil fuels has 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 the development of biodiesel technologies and the 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 a few good characteristics, some significant weaknesses, this renewable resource, limited its use as a substitute for fuel fossil origin. Two groups of different problems arise because of inadequate low temperature properties: handling problems and operability problems. Handling, including filtration, is the ability to store, install, and pump the biodiesel in its pure form (B100), or a mixture of biodiesel with diesel. Operability refers to the use of biodiesel-diesel mixtures as fuel and problems that may arise in the fuel system or on other equipment of the vehicle in their use.

Several factors can affect the low temperature properties and functional performance of FAME. Various studies have been established that crystallization or thickening of biodiesel at low temperatures causes fuel starvation and operability problems as solidified materials clog fuel lines and filters, mainly due to its high amount of saturated FAME components [9, 10].

The low temperature properties of FAME vary with the composition of the fatty acids of the raw material and the number of saturated components, which depends on raw material used to produce biodiesel. In a series of papers, the low temperature properties of biodiesel derived from different raw materials were examined [11-20]. Typical values of cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) of biodiesels (FAMEs) produced from different raw materials are given in Table 1.

Another factor that influences low temperature characteristics of FAME is the process production i.e. the method of for obtaining pure biodiesel (B100). This is because some impurities can promote the 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 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 of biodiesel produced from different raw materials

# Raw

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **material**  | **CP (oC)**  | **CFPP (oC)**  | **PP (oC)**  | **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]

Based on the quality of the selected raw material and the impurity content, it is determined whether it must be pre-purified to remove impurities that cannot be removed by processing, because so remain in the product and impair its low temperature performance [21,22].

Poor low temperature characteristics of pure biodiesel such as high cloud point (CP), a pour point (PP) and a cold filter plugging point (CFPP) make it unsuitable for use, in the winter period. It this period is more convenient, use mixture of biodiesel with diesel of fossil origin. This does not eliminate the problem with low temperature characteristics, because even if diesel fossil origin has better low temperature characteristics, depending on the quantity of added biodiesel, a drastic disturbance of the low temperature characteristics of the mixture can occur.

There are two basic ways to improve the low temperature characteristics of the biodiesel fuel mixture: adding additives to improve low temperature properties and cold flow or selecting raw materials for biodiesel (winterization) before blending with diesel of fossil origin.

The procedure of winterization implies removal of saturated methyl esters, which crystallizes at low temperatures. These components with a high boiling temperature are removed by separation and filtering at reduced temperature. Biodiesel prepared in a such way has improved low-temperature properties and can be used in winter conditions, either pure or as a component of the mixture. The process of sputtering is unfavorable due to a low yield, which can often be only 25% [23, 24]. For this reason, a common method is additivation, not winterization.

##  1.1. A description of the low temperature properties of biodiesel

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

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

With lowering of the temperature, the crystal size continually grows, and a grid is obtained leading to solidification at the pour point. PP is defined as the temperature at which a few crystal agglomerations and gel formation are observed in the fuels, consequently preventing the fuel to flow. For practical measurement of PP, users determine the temperature before materials clog the

fuel filter [28].

The CP and PP are not acceptable as effective measures for determining the fuel's ability to use. Fuel at CP temperatures, although exhibits a certain turbidity, is still able to flow freely and no issues are expected to occur to the mechanical components, however fuel at the temperature will not flow through the fuel injection system.

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

##  1.2. Investigation the effect of additives on low temperature properties

Additives for improving the low temperature properties of biodiesel are chemicals that influence the crystal growth, while reducing ambient temperature.

It is known that the crystal morphology and/or growth rate is profoundly affected by the presence of impurities in the system. Some impurities suppress growth while some others stop growth completely in one or more directions. Some theoretical models have been developed that explain the effect of impurities on the kinetics of crystallographic structure, 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 the 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 surface of crystals.

 The final shape of the crystal depends on the growth rate of its various surfaces, and its size decreases with the rate of growth. Certain crystal surfaces will have their dependence on the rate of increase of temperature and super saturation [31].

Additives for the improvement of LTP fossil diesel fuels used since the 1960s are still used today for FAME [32, 33]. The most common type of wax crystal modifier used to improve LTP diesel is based on ethylene vinyl acetate (EVA) copolymer [30].

In order to obtain a polymer for a specific fuel due to the flexibility of polymerization, it may vary in the molecular weight and acetate ratio

Performance of an EVA copolymer, vinyl acetate-fumarate copolymers, styrene-esters copolymers, diester-alpha olefin copolymers, malan-styrene esters and polymethacrylates can be enhanced by blending with a CFI (cold flow improver) additive of different chemistry [30].

In order to intentionally influence on crystallization, various oil companies have developed specific polymeric additives to improve the wax nucleation (to produce many small crystals than several large ones) and slow down the growth of crystals.

The reaction between additives and fuel crystals can occur either in solution, on the surface or, in the case of co-crystallization in the crystal structure.

Based on macroscopic evidence, it is generally believed that impurities bond preferentially to specific faces on the growing crystals, inhibiting therefore the growth along those faces. Recently, a more complex model has been proposed, designated by kinetic growth inhibition. It was found that the solidification can occur in the form of macroscopic bands (with several hundred micrometers) parallel to the front.

In this growth mode, the front periodically stops growing, allowing a new front to nucleate and spread laterally along the arrested front. These bands are controlled by the thermodynamics of the process, hence the designation of the effect. As the crystallization proceeds, solute is depleted near the front, and as the sample moves though 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, the crystals do not grow appreciably. [34].

Many researchers studied one or more low temperature characteristics of biodiesel and biodiesel blends in which biodiesel of different origin was used, i.e. synthesized from different oils. [35-41]. As stated in the previous section, there are very few papers dealing with the low temperature characteristics of biodiesel and the effect of the additive on low-temperature properties. The paper discusses the comparative effect of additives on the improvement of low temperature properties - CP, PP and CFPP pure biodiesel and a mixture of biodiesel and diesel fossil fuel.

# 3. MATERIALS AND METHODS

##  3.1. Crude properties

The influence of additives on different biodiesel samples was investigated:

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

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

Sample 3: mixture of rapeseed biodiesel and ultra-low fossil diesel (ULSD), 5:95 vol.%

Characterization of commercial biodiesel samples was done in the authorized SGS laboratory (Table 2).

Low sulfur fossil diesel produced in the oil refinery from Pančevo ULSD, (Ultra low sulphur diesel). The complete ULSD analysis is given in Table A-4 (see Appendix) and fully corresponds to the characteristics of the EN590 standard..

 **Table 2.** Analysis of biodiesel used in the tests according to EN SRPS 14214

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Specification**  | **Units**  | **Standards**  | **Range**  | **Sample 1**  | **Sample 2**  |
| FAME content  | % mass  | EN 14103  | 96.5 min  | 99.6  | 97.75  |
| Density 15°C  | g/cm³  | EN ISO 3675, EN ISO 12185  | 0.86-0.90  | 0.8807  | 0.884  |
| Viscosity 40°C  | mm²/s (cST)  | EN ISO 3104  | 3.5-5.0  | 4.499  | 4.49  |
| Flash Point  | °C  | EN ISO 2719e EN ISO 3679  | 101 min  | 163.0  | 184.13  |
| Cetane Number  |   | EN ISO 5165  | 51 min  | 56  | -  |
| Max CU Corrosion  | 3h/50°C  | EN ISO 2160  | Class 1  | 1a  | -  |
| Oxidation Stability [110°C]  | Hours  | EN 15751, EN 14112  | 8 min  | 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 max  | 95  | 114.74  |
| Linol. Acid Methyl Ester  | % mass  | EN 14103  | 12 max  | 7.2  | 9.77  |
| Polyunsaturated Methyl Esters (>4 double bonds)  | % mass  | EN 15779  | 1 max  | < 1  | -  |
| Methanol  | % mass  | EN 14110  | 0.2 max  | 0.03  | < 0.02  |
| Monoglyceride  | % mass  | EN 14105  | 0.7 max  | 0.69  | 0.69  |

 Diglyceride % mass EN 14105 0.2 max 0.07 0.146

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Triglyceride  | % mass  | EN 14105  | 0.2 max  | < 0.1  | 0.039  |
| Free Glycerol  | % mass  | EN 14105i, EN 14106  | 0.02 max  | < 0.01  | 0.001  |
| Total Glycerol  | % mass  | EN 14105  | 0.25 max  | 0.166  | 0.202  |
| Water  | mg/kg  | EN ISO 12937  | 500 max  | 139  | 385  |
| Total Contamination  | mg/kg  | EN 12662  | 24 max  | 20  | 6.97  |
| Sulphated Ash  | % mass  | ISO 3987  | 0.02 max  | < 0.005  |   |
| Sulphur  | mg/kg  | EN ISO 20846, EN ISO 20884, EN ISO 13032  | 10 max  | < 3  |   |
| Group I Metals [Na, K]  | mg/kg  | EN 14108, EN 14109, EN 14538  | 5 max  | < 1  | < 0.1  |
| Group II Metals [Ca, Mg]  | mg/kg  | EN 14538  | 5 max  | < 1  | 3.55 + 1.4  |
| Phosphorous  | mg/kg  | EN 14107, EN 16294  | 4 max  | < 4  | 1.88  |

 CFFP °C EN 116 3 -9

The calculated values, molecular weights, for the raw material, biodiesel, and the iodine number, based on the GC analysis (Appendix, Table A-5), are for the first sample: 865.44 g/mol, 289.82 g/mol and 89.65. These values for the second sample are: 880.61 g/mol, 294.87 g/mol and 106.4

## 3.2. Equipment and methods

The physical and chemical characterization of the biodiesel was performed in compliance with EN 14214. Complete analysis of the fatty acids was performed, and the results are given in Table 2, which is also in compliance with literature values.

Biodiesel samples was analyzed by gas chromatography (GC) to determine the content of fatty acid esters (according to SRPS EN 14103), Table A-5 (see Appendix). GC analysis was performed on the Gas Chromatograph GC-2010 Plus, Shimadzu, equipped with autosampler AOC-20i, Capillary Column InterCap WAX (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 reference probe sample of 0.6 µL at split ratio 40:1. The injector and detector temperatures were 260◦C, and the analysis was performed in isothermal conditions at 200◦C. Helium was applied as carrier gas with flow rate of 3 mL/min. Methyl heptadecanoate (purity >99%) (Fluka Analytical) was used as an internal standard. Sample of 1µl was injected into an injector.

Based on fatty acid composition. obtained by GC analysis, the iodine number (IN) were calculated () and the molecular weight of the biodiesel and the oil from which the biodiesel was obtained, Table A-5 (see Appendix).

CP, PP and CFPP are used to define low-temperature operational limits for diesel fuel. Filtration, CFPP and PP point 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) is used as specified in the ISO 3016 for determining the pour and cloud point of mineral oil and petroleum products. A preheated test sample is cooled in steps of 3oC/min. After each analysis the testing tube is removed from the cooling bath and bent to 90˚. The surface of test substance is observed for movement by video camera. The pour point is the temperature at which no movement can be observed at a bend angle of 90˚C over a period of 5 seconds.

To determine the Cold Filter Plugging Point (CFPP), was used the automatic device, HERZOG HCP 842.

Table values of CP, PP and CFPP are in Appendix 1, 2 and 3.

## 3.3. Additives used for investigation of low temperature properties

The tests were carried out for the two biodiesel samples and one sample of the eurodiesel and biodiesel blend.

In the first series, the effect of five additives was investigated on the "aged" biodiesel which is derived from a mixture of rapeseed and palm oil. Three additives were produced by company N, (N1, N2 and N3), and one additive of CF and LQ company, (Additive trade names and their characteristics are given in Table A-6 (see Appendix).

In the second ("fresh" rapeseed biodiesel) and third series (mixture of rapeseed biodiesel and fossil diesel) , the effect of thirteen additives was investigated: three from company N, (N1, N2 and N3), two from company E (V1, V2), four from company C (C1, C2, C3 and C4), two from CR company (H1 and PL1) and one CF and LQ additive ,(Additive trade names and their characteristics are given in Table A-6 (see Appendix).

## 3.4. Sampling procedure

Sampling procedure: Based on the available amount of biodiesel, and the required number of experiments determined the amount of sample for each experiment. That amount was 140 ml of biodiesel for each experiment.

The biodiesel temperature was determined based on biodiesel CP, at least 5 °C above that temperature.

The additive should be heated before addition. At the preliminary recommendation of the contractor it is necessary to heat it at 45-55 ° C. Due to problems with the viscosity of the additive and the problem with the micro-pipette, it was necessary to heat the additive at a higher temperature. In cooperation with the manufacturer, a higher temperature of about 60 ° C was adopted.

All additives were added to a weighed sample of bio-diesel, with respect to sequence, the additive is added to the biodiesel.

After blending, the mixture of biodiesel and additives was tempered at 45-55 °C and mixed until homogenization. The homogenization control of the mixture was performed visually and mixing for all samples was 1.45 hours. At the beginning of the test, additives were added according to the manufacturer's recommendation (100-1100 ppm). During the laboratory tests for these quantities of additional additives, a weak response was found, so the study was continued by increasing the added amount of additives. In addition to the test, additives were added at concentrations of 2000 ppm and 5000 pp. Because of the small effect observed at low concentrations of additives, tests with these concentrations have not been performed. After reviewing the preliminary results and responses, based on the recommendation of one manufacturer, the additive procedure was modified.

The additive was measured, heated to 60 [deg.] C. and then mixed with an organic solvent (toluene), in the ratio of 1: 9 (additive: solvent), and thereafter added to the biodiesel sample.

This has resulted in better dispersion of additives in biodiesel, which is resulting in better effect additivation.

## 3.5. Description of the samples

Preliminary testing of the first series of samples (mixture of rapeseed and palm oil), showed that it drastically degraded in relation to the analysis obtained immediately after its production. (given in Table 2).

 This can be attributed to the long period of storage in inadequate conditions after production. Biodiesel at the start of the experiment was more than 6 months old. This biodiesel mix is referred to as "aged" biodiesel.

Its degradation is confirmed by low-temperature properties analysis; CFPP is from initial - 3oC, after production, at the time of the study increased to 3oC.

Degradation is also confirmed by a decrease in oxidative stability, starting at 12.7h, at about 7 h, with a growth and viscosity increase of 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, and 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 FAME storage time 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 maximum storage is also no more than six months. In practice, FAME should not be stored for longer than this time because it is "aging" in the storage tank, increasing the acidity, viscosity, and creating different types of deposits (gums, lacquers).In order to monitor the quality of FAME during storage, indicators such as oxidation stability, acid number, viscosity, water and sediment must be determined. All these parameters can be used as indicators of whether FAME complies with EN 14214.

The method of comparative testing of the additive was initiated by determining the low temperature properties of biodiesel in order to establish "O" values, in relation to which a comparative determination of the additive effect can be carried out.

The qualitative composition is analytically determined: biodiesel of palm oil and rapeseed, in relation to 40:60.

In the II series of experiments, was used rapeseed biodiesel with CFPP of -9oC and PP of -11oC. Experiments for the III series contained ULSD and diesel obtained from rapeseed oil, in the ratio of 95: 5%, with CFPP of -12oC and PP of -14oC.

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

# 4. RESULTS AND DISCUSSION

In the 1st series of studies, (for "aged" biodiesel, with palm oil) the effect on CFFP and PP for all additives is small and in improving the CP, after adding additives, it can not notice the regularity.

The minimum positive effects on the CP, with the addition of additive, are in accordance with the literature [35, 36, 39]. In principally, additives for low temperature properties are designed to inhibit agglomeration and the growth of wax crystals, and not the initial formation of crystals. Since the CP measures the temperature at which crystals of wax appear, the observed lack of additive effect is expected.

The best results of CFPP showed additive N1, which at 5000 ppm adding cause CFFP reduction of 4 °C. N1 has a significant effect on the reduction of CFPP and at a much lower level of additivation (900 ppm). At this amount, the additive reduction of CFPP is 3oC (Fig.2).

This reduction in CFPP for other additives of this manufacturer have at 2000 ppm. This additive consists of polymer, reaction product of 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 (Appendix 6).

The CF additive has a noticeable effect to decrease of CFPP at the maximum concentration of the additive, and for the LM additive, the reduction in CFPP can not be observed (Fig.2)

For PP, the best result was achieved with N2 and CF additive at a dosage of 1100 ppm with a reduction of 2oC (obtained in preliminary research), the same result was achieved with N1 at 2000 ppm, and N3 and LM at 5000ppm (Fig.1). It is interesting that the additives CF do not contain either polymers or copolymers, but only diesel fuel in high concentrations (30-60%). Based on this, their effect can be explained rather by dilution and winterization, but as an effect of inhibiting crystal growth (Table A-6 (see Appendix). .

There is almost no effect to the CP, at low concentration of additives. The best results give the addition of N1 additive at 5000 ppm, which results of reduction CP a 3 °C (Table A-1, see Appendix).



**Fig. 1.:** Change of PP with additives concentration, for "aged" biodiesel,

with palm oil.



**Fig. 2.:** Change of CFPP with additives concentration, for "aged" biodiesel,

with palm oil.

Following these tests, an alternative method was applied, pre-setting with an organic solvent (see procedure in part 3.1. Sampling procedure only for a N1 additive that showed the best response for CFPP I for a dosage of 5000 ppm.

The obtained results showed a better effect to the CFPP which is improved for 1oC, and PP for a full 3oC. Positive results, the addition of additives with an organic solvent, can recommend this procedure as a standard for additivation, so this method was applied in the next examinations.

In the second series of experiments ("fresh" rapeseed biodiesel), only one concentration was tested (optimal as determined by the 1st series of tests 1000 ppm). All additives were added according to a procedure determined by the 1st series with the addition of an organic solvent. In the second series of experiments, the effect of the thirteen additives was tested to improve the low temperature performance of rapeseed biodiesel. Pure biodiesel of the rapeseed was chosen as a comparative sample.

The aim of the second series of experiments was to determine the effect of the additive on a biodiesel from rapeseed oil versus "aged" biodiesel containing biodiesel derived from a mixture of rapeseed and palm oil.

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 which is problematic for improving low-temperature properties by additivation.

It is noticeable that different additives differ in varying degrees on low temperature properties. Some have a pronounced effect on CFPP and for some on PP.

There is evident that the effectiveness of the additive is different on the various low temperature properties and the type of biodiesel. Some have a pronounced effect on CFPP and while some on PP. Comparing the results related to the change of CFPP after addition of additives with organic solvents, the best results showed additives V2 (9oC), and N1 and V1 (4oC) (Figure 3).

Additives that exhibit the best results contain high concentrations Acrylic copolymer (60.0 - 100.0 %), V2 and V1, or polymer N1 (Table A-6, see Appendix). There is an interesting difference in the performance of two additives of the same manufacturer V2 and V1. Although both have almost the same concentration of Acrylic copolymer, the additive V2 having a better effectiveness in relation to additive V1. The difference between these two additives is that V2 has rapeseed oil, as a solvent, and V1 kerosene (Table A-6, see Appendix).

It can be assumed that the compatibility of the solvent in the composition of additives and biodiesel (rape oil), improves its function.

Additionally, additives N2, LM, C2 and C4 (4oC) showed good results. Since according to EN SRPS 116, the reproducibility of the result is ± 3oC and the repeatability is ± 1oC, it can be concluded that all these additives have good characteristics, but it should be emphasized that, however, the V2 additive has the best characteristics (Fig.3).

N3 and C1 have small effect (2oC), CF (1oC), while for CF additive haven’t effect on the improvement of CFFP of biofuel from the rapeseed and that they are not adequate for this purpose.

For PP the best result is achieved with V2 (25oC), and good results have V1 (13oC). N1 (7oC), CF (7oC), H1 (6oC), C2 and C4 (5oC) (Fig.4). Small effect has N2, LM and C1, only 4oC, and it is inadequate to qualify it for this purpose. Additives C3 and N3 show very small influence and are not suitable for the improvement of PP rapeseed biodiesel (Fig.4).



**Fig. 3.:** Change in CFPP with additives concentration for "fresh" rapeseed biodiesel.



**Fig. 4.:** Change in PP with additives concentration for "fresh" rapeseed biodiesel.

When testing the effect of the additive on the mixture of biodiesel ULSD, with 5% biodiesel (third series of tests), the following results were obtained (Figures 5 and 6)

Indeed, the effect of various additives on CFFP and PP is remarkably different.. They are noticeably higher in respect to the first and second series and 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 clean biodiesel.



**Fig. 5.:** Change in CFPP of additives for BD-100 (rapeseed biodiesel)

+EURODIESEL (5:95), mixture

 

**Fig. 6.:** Change in PP with additives concentration for BD-100 (rapeseed biodiesel)

+EURODIESEL (5:95), mixture

Comparing the results related to the change of CFFP after additivation, the best results showed additives of the series N: N1 (11oC), N3 (9oC) and N2 (3oC). In addition, a good response also has V2 (4oC) (Fig.5). All other additives haven’t any effect, which means that these additives are not suitable for this purpose. The best results of CFPP showed additive N1 (11oC), which have kerosene solvent It can be assumed that the compatibility of the solvent (kerosene) in the composition of additives and main fraction in mixture (95% ULSD), affects the improvement of improves its function. (Table A-6, Appendix)

Analyzes related to PP demonstrated similar results. The best additives are from samples N: N1 (17oC), N3 (16oC), N2 (13oC) and V2 (13oC). In addition, C1 (10oC) had a good effect. Good efficiency also shows CF (3oC), while other additives have negligible response, which means that these additives are not suitable for this purpose (Figure 6).

# 5. CONCLUSION

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

So far, these studies have included two different types of fuels: biodiesel, and a mixture of 5% biodiesel in diesel of fossil origin.

One of biodiesel was more than 6 months old, and it is derived from a mixture of rapeseed and palm oil, and other was “fresh” rapeseed biodiesel.

It is assumed that in “old” biodiesel, saturated methyl esters within biodiesel nucleate and form solid crystals, and the crystal size continually grows during standing, confirming the deteriorated physical characteristics in relation to the characteristics obtained immediately after the synthesis (viscosity, oxidative stability and initial low-temperature properties).

It has been observed that all additives have worse influence on “old” biodiesel. It has been also observed that all applied additives had less efficiency to improve low temperature characteristics. It proves that the best improvement of PP and CFPP was obtained with "old" biodiesel at a concentration of 1100 ppm of the best additive (N1) for 1oC and 3oC and for the "fresh" one 7oC and 4oC.

A better effect of additivation "fresh" biodiesel from the rapeseed, compared to "aged" biodiesel has confirmed the fact that additives need to be done immediately after production.

Advanced effect of additivation by mixing additives with organic solvent (toluene) and heating has shown that the effect of the additive can be improved, as a result of better diffusion and distribution of active materials through the volume of biodiesel. This conclusion can help with possible additives in industrial conditions. By adding organic solvent CFPP improved for 1oC and PP for a full 3oC.

In all the tested samples, the minimum CP improvement was obtained, which is in line with the literature data [35, 36, 39]. In principle, additives for low temperature properties are designed to inhibit agglomeration and the growth of wax crystals and not the initial formation of crystals. Since the CP measures the temperature at which crystals of wax appear the observed lack of additive effect is expected.

It has been found that different types of additives are suitable for different types of biodiesel and mixtures of biodiesel and diesel of fossil origin. Effective concentrations of additives vary depending on the system they are added to.

Comparing the effect of the additivation biodiesel and biodiesel-fossil diesel mixture N1 additive shows better efficiency with the fossil fuel mixture, and V2 additive for rapeseed biodiesel.

By adding additives to the same wax crystal modifier, it was noted that they have had better performance with additives in which the solvent is compatible with the type of biodiesel that is being additivated (rapeseed biodiesel).

This difference is expressed in the application additives of the same manufacturers, V2 and V1. These additives have almost the same concentration of acrylic copolymer. Additive V2 has a better efficiency compared to V1 additive. Only, the difference between these two additives is that V2 has rapeseed oil as a solvent and V1 kerosene V1 (Table A-6, see Appendix).

Some of the additives (CF) do not contain either polymers or copolymers, but only diesel fuel at high concentrations does (30-60%). Based on this, their effect can be explained by dilution and winterization rather than because of crystal growth inhibition (Table A-6 (see Appendix).

# 6. LITERATURE

1. Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technol.* 2005; 86**:** 1059-70.
2. Agarwal, A. K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progr Energy Combust Sci.* 2007; 33: 233−271.
3. Lapuerta, M., Armas, O. and Rodríguez-Fernández, J. Effect of biodiesel fuels on diesel engine emissions. *Progr. Energy. Combust. Sci*. 2008; 34: 198−223.
4. Monyem, A. and Gerpen, J. H. The effect of biodiesel oxidation on engine performance and emission. *Biomass Energy.* 2001; 20: 317−325.
5. Ali Y, Hanna MA. Alternative diesel fuels from vegetable oils. *Bioresource Technol.* 1994; 50: 153-163.
6. Agarwal AK, Das LM. Biodiesel development and characterization for use as a fuel in compression ignition engines. *Transactions of the ASME, Journal of Engineering for Gas Turbines and Power.* 2001; 123: 440-447.
7. Demirbas A. Progress and recent trends in biofuels*. Progress in Energy and Combustion Science.* 2007; 33: 1-18
8. Demirbas A. Diesel fuel from vegetable oil via transesterification and soap pyrolysis. *Energy Sources.* 2002; 24: 835-841.
9. Rushang MJ, Michael JP. Flow properties of biodiesel fuel blends at low temperatures. *Fuel.* 2007; 86: 143-151.
10. Kerschbaum S, Rinke G. Measurement of the temperature dependent viscosity of biodiesel fuels. *Fuel.* 2003; 83: 287-291.
11. Rashid, U. & Anwar, F. Production of biodiesel through optimized alkaline catalyzed transesterification of rapeseed oil. *Fuel,* 2008; 87: 265–273.
12. Dunn, R. O. Bagby, M. O. Low-temperature properties of triglyceride-based diesel fuels: Transesterified methyl esters and petroleum middle distillate/ester blends*. J. Am. Oil Chem. Soc.* 1995; 72: 895-904.
13. Chiou, B.S.; El-Mashad, H. M., Avena-Bustillos, R. J., Dunn, R. O., Bechtel, P. J., McHugh, T. H., Imam, S. H., Glenn, G. M., Ortz, W. J. & Zhang, R. Biodiesel from waste salmon oil. *Trans. ASABE.* 2008; 51: 797-802.
14. Serdari A.; Fragioudakis, K., Kalligeros, S., Stournas, S.,Lois, E. Impact of using biodiesels of different origin and additives on performance of a stationary diesel engine. *J. Eng. Gas Turbines Power (Trans. ASME).* 2000; 122: 624–631.
15. Sarin, R.; Sharma, M., Sinharay, S., Malhotra, R. K. Jatropha-palm biodiesel blends: An optimum mix for Asia. *Fuel.* 2007; 86: 1365-1371.
16. Pengmei Lv, Yufeng Cheng, Lingmei Yang, Zhenhong Yuan , Huiwen Li , Wen Luo Improving the low temperature flow properties of palm oil biodiesel: Addition of cold flow improver, *Fuel Processing Technology.* 2013; 110: 61–64.
17. Antolin G., Tinaut F.V., Briceno Y., Castano V., Perez C., Ramırez A.I., Optimisation of biodiesel production by sunflower oil transesterification, *Bioresource Technology*. 2002; 83: 111–114
18. Chinyere B. E., Callistus N. U., Okechukwu D. O., Optimization of the methanolysis of lard oil in the production of biodiesel with response surface methodology, *Egyptian Journal of Petroleum*. 2017; 26: 1001–1011
19. Li H.,Shen, B. X. Yu P. H., The Cold Temperature Fluidities of Biodiesel Prepared from Vegetable Oil, *Energy Sources,* 2010; Part A, 32: 1195–1200.
20. Foglia TA, Nelson LA, Dunn RO, Marmer WN. Low-temperature properties of alkyl esters of tallow and grease. J Am Oil Chem Soc. 1997; 74: 951–955.
21. Tremblay A., Montpetit Al. The in-process removal of sterol glycosides by ultrafiltration in biodiesel production. *Biofuel Research Journal*.2017;13: 559-564
22. Songtawee S., Ratanawilai S.,.Tongurai Ch. Effect of Sterol Glucosides in Biodiesel Production. *IJACEBS.* 2014;Vol. 1, Issue 1: 119-122
23. Dunn, R. O., Shockley, M. W. and Bagby, M. O., Improving the Low-Temperature Properties of Alternative Diesel Fuels: Vegetable Oil-Derived Methyl Esters, *Journal of the American Oil Chemists’ Society.* 1996; 73(12): () 1719-1728,
24. Lee, I, Johnson, L. A. and Hammond, E. G., Reducing the Crystallization Temperature of Biodiesel by Winterizing Methyl Soyate, *Journal of the American Oil Chemists’ Society*, 1996; 73(5): 631-636.
25. Parag Saxena, Mevada S. V., Joshipura M. H., Prediction of cold flow properties of Biodiesel, Nirma University, *Journal of Engineering and technology,* 2016; Vol. 5, No. 1, Jan-Jun
26. Chandler, J.E., Horneck F.G., Brown G.I., in SAE Technical Paper Series Paper No. 922186, *Society of Automotive Engineers*, Warrendale, 1992: October.
27. Lewtas, K., R.D. Tack, D.H.M. Beiny, J.W. Mullin, Advances in Industrial Crystallization, edited by J. Garside, R.J. Davey and A.G. Jones, Butterworth-Heineman, Oxford;1991: pp. 166
28. .Monirul I. M., Masjuki H. H.,. Kalam M. A,. Zulkifli N. W. M, Rashedul H. K.,. Rashed M. M, Imdadul H. K., Mosarof M. H., A comprehensive review on biodiesel cold flow properties and oxidation stability along with their improvement processes, *RSC Adv. 5* ;2015: 86631–86655
29. Kubota, N., Effect of Impurities on the Growth Kinetics of Crystals. Department of Chemical Engineering, Iwate University ; 2001: 749-769.
30. Lopes PM, Muller D, Harrison R, Bordado JC. Effect of additives to improve the performance of biodiesel at low temperatures. Arizona Chemical/Instituto Superior Tecnico.;2007: 1–7. PMid: 17224990.
31. Hatakka, H. Effect of Impurities and Additives on Crystal Growth. Lappeeranta University of Technology; 2006.
32. Brown, G. Enhancing Diesel Fuel Low Temperature Operability - Additive Developments . Wissenschaft & Technik; 1990.
33. Lopes, P. Biodiesel - Overview of Solutions to Improve the Performance at Low Temperatures. Technology Forum. Almere, The Netherlands: Arizona Chemical; 2005.
34. Alkane Crystalization Theory. Retrieved June 2007, from www.physics.uwo.ca
35. Dunn, R. O. and Bagby, M. O., “Low-temperature properties of triglyceride-based diesel fuels. Transesterified methyl esters and petroleum middle distillate/ester blends*”, Journal of the American Oil Chemists’ Society*, 1995; 72(8): 895-903,
36. Dunn, R. O. and Bagby, M. O., Low-Temperature Filterability Properties of Alternative Diesel Fuels from Vegetable Oils; in Proceedings of the Third Liquid Fuel Conference: Liquid Fuel and Industrial Products from Renewable Resources, edited by J.S. Cundiff, E.E. Gavett, C. Hansen, C.
37. Peterson, M.A. Sanderson, H. Shapouri, and D.L. Van Dyke*, American Society of Agricultural Engineers*, St. Joseph, MI, 1996; 95–103.
38. Dunn, R. O., Shockley, M. W. and Bagby, M. O., Improving the Low-Temperature Properties of Alternative Diesel Fuels: Vegetable Oil-Derived Methyl Esters, *Journal of the American Oil Chemists’ Society,* 1996; 73(12): 1719-1728.
39. Chiu, C.-W., Schumacher, L. G. and Suppes, G. J., Impact of cold flow improvers on soybean biodiesel blend, *Biomass and Bioenergy,* 2004; 27(5): 485-491.
40. Conley, S. P. and Tao, B., “Biodiesel Quality: Is All Biodiesel Created Equal?”, *Purdue Extension BioEnergy Series Report*, ID-338, (December, 2006, [http://www.ces.purdue.edu/ extmedia/ ID/ ID- 338.pdf)](http://www.ces.purdue.edu/%20extmedia/%20ID/%20ID-%20338.pdf).
41. Joshi, R. M. and Pegg, M. J., Flow properties of biodiesel fuel blends at low temperatures, *Fuel;* 2007;86:143-151.
42. Shrestha, D. S., Van Gerpen, J. and Thompson, J., Effectiveness of Cold Flow Additives on Various Biodiesels, Diesel, and Their Blends, *Transactions of the American Society of Agricultural and Biological Engineers*, 2008; 51(4): 1365-1370

**ИЗВОД**

**Испитивање могућности побољшања ниско-температурних карактеристика биодизела**

**адитивирањем**

Иван Тасић 1, Милан Д. Томић 2, Александра Љ. Алексић 3 , Наташа Ђуришић-Младеновић4, Ференц Л. Мартиновић 4, Радослав Д. Мићић 1

1Универзитет у Новом Саду, Технички факултет „Михајло Пупин“, Ђуре Ђаковића б.б., 23000

Зрењанин; Србија

2 Универзитет у Новом Саду, Пољопривредни факултет, Трг Доситеја Обрадовића 8, 21000

Нови Сад, Србија

3НИС а.д. Нови Сад, Народног Фронта 12, 21000 Нови Сад, Србија;

4 Универзитет у Новом Саду, Технолошки факултет Нови Сад, Булевар цара Лазара 1, 21000 Нови Сад, Србија

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 се испитује 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 (CFPP), температура стињавања (PP) и температура замућења (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 с "старим" биодизелом. Забележена је побољшање ефикасности адитивирања, мешањем адитива с органским растварачем (толуеном).

Утврђено је да су различити типови адитива прикладни за различите врсте биодизела и смеше биодизела са дизелом фосилног порекла. Боље перформансе имају адитиви у којима је растварач компатибилан с врстом биодизела.

**Кључне речи:** биодизел; нискотемпературна својства; адитиви