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INFULENCE OF BIODIESEL ON THE OXIDATION STABILITY OF ENGINE OILS

Abstract
In order to replace the fossil fuels in developed Western countries are performing significant researches on the introduction of renewable fuels. Today, the highest usage have biodiesel and bioethanol. The most commonly used are mono-alkyl esters of different fatty acids, which are obtained from different types of natural oils and fats. Application of biodiesel have already reached significant level. The most of technical problems associated with his application have already been solved. However, in biodiesel application, there remain a number of failures. One of the main technical problem that appears when using biodiesel is his tendency to oxidation which results in a formation of acid products, products of polymerization, insoluble residues and sediments which leads to filter clogging and poorer lubrication. In addition, during operation, the small amount of fuel reaches in the sump and considering that biodiesel compared to conventional diesel has a significant higher boiling point, it comes to his accumulation, which leads to accelerated degradation of oil, with potential impact on engine durability. In this paper is investigated the impact of biodiesel on the oxidative stability of motor oils. For evaluation of oxidative stability of oil caused by the presence of biodiesel are used two test methods IP 48 and ASTM D 2272. The results of using these methods showed a negative influence of biodiesel on oxidative stability of selected motor oils.
Keywords: biodiesel, oxidation stability, motor oil

1. Introduction

To minimize dependence on fossil fuels, a growing number of countries introduce alternative fuels, of which the most frequently used are biodiesel and bioethanol. Compared to diesel, biodiesel provides environmental protection, primarily reduces greenhouse gas emission, emission of sulfur oxides, particulate matters and carbon monoxide. By using biodiesel are being replaced significant amounts of diesel, since biodiesel has properties very similar to diesel. It is usually blended with diesel at a concentrations that does not exceed 20%. The striving of all developed countries is to use larger quantities of biodiesel and to reduce dependence on crude oil.

Biodiesel is a renewable fuel obtained by esterification process of different types of fats and methanol. As a raw material are usually used vegetable oils, animal fats and waste greases. Compared to diesel, biodiesel shows a number of disadvantages that limit its application [1]. The main disadvantages of biodiesel are poor oxidative stability, high boiling point and its adverse impact on seals. During the engine operation a certain amount of fuel reaches the engine oil. Conventional diesel fuel, due to its lower boiling point evaporates, while biodiesel accumulates in the engine oil. Therefore, biodiesel in engine oil changes the most important characteristics of oils reflecting negatively on basic functions of lubricants [2]. In addition, the presence of biodiesel in oil contributes to its rapid chemical changes and shorten the oil change interval. However, today's engine oils contain oxidation inhibitors to prevent a negative impact on the oxidative stability of biodiesel.

This paper presents test results of the effects of biodiesel on some important physical and chemical properties of the oil, as well as on the oxidation stability of engine oils. For testing were used IP 48 and ASTM D 2272 test methods [3,4].

2. Experimental part

2.1. Methods and materials

Oxidation stability tests were performed with two different engine oils and biodiesel with a concentrations of 5%, 10% and 20%.

Table 1: Engine oils characteristics

	MU-1	MU-2
Quality level	API SF/CD	ACEA A3/B4; API SL/CF; MB 229.1 VW 500 00/502 00/505 00
Viscosity gradation	SAE 15W-40	SAE 10W-40
Viscosity at 100 ^oC, [mm^2/s]	14.7	14.5
Viscosity Index	130	145
Density at 15 ^oC, [kg/m^3]	860	855
Flash point, [^oC]	225	230
Pour point, [^oC]	-24	-30

Table 2: The main parametars of test methods IP 48 and modified ASTM D 2272

Test conditions	IP 48	Modified method ASTM D 2272*
Temperature, °C	150	150
Duration, h	48	-
Air flow	15L/h	-
O_2 , pressure	-	620 kPa
Catalyst	-	copper wire

* without water

For testing of oxidation stability were used following methods: method IP 48 and modified method ASTM D 2272. The aims of this paper were to examine the effect of biodiesel on oxidation stability of engine oils and to evaluate the possibility of using these methods for the evaluation of oxidative stability. Table 2 shows the main parameters of these methods.

Examination of physical and chemical properties was conducted according to standard test methods. The evaluation of oxidative stability was based on changes in viscosity, total acid and base number, as well as on changes in absorption at 1710 cm^{-1} by using FT-IR spectroscopy. The main physical and chemical properties of biodiesel are given in Table 3.

Table 3: The main characteristics of biodiesel

Characteristics	Units	Biodiesel	Methods
Viscosity at 40 °C	mm^2/s	4.57	BAS ISO 3104
Flash point	°C	173	ISO 2592
Sulfur content	mg/kg	68.9	ASTM D4294
Coke	% m/m	0.008	BAS ISO 6615
Cetane index (CI)	-	57.1	ASTM D4737

3. Results and disccusion

The samples of engine oils MU-1 and MU-2 were blended with 5, 10 and 20 wt. % of biodiesel. Physical and chemical properties of oils are shown in Table 4 and on Figures 1, 2 and 3.

Table 4. The main characteristics of fresh samples

Characteristics		Viscosity at 100 ºC, [mm^2/s]	TAN [mg KOH/g]	TBN [mg KOH/g]
Motor oil	Metods	BAS ISO 3104	ASTM D 664	BAS ISO 3771
MU-1		14.7	1.73	5.74
MU-1+ 5% biodiesel		12.98	1.72	5.40
MU-1+10% biodiesel		11.51	1.59	5.14
MU-1+20% biodiesel		8.94	1.52	4.45
MU- 2		14.5	2.35	8.47
MU-2+5% biodiesel		12.79	2.26	8.10
MU-2+10% biodiesel		11.38	2.02	7.67
MU-2+20% biodiesel		9.0	1.77	6.94

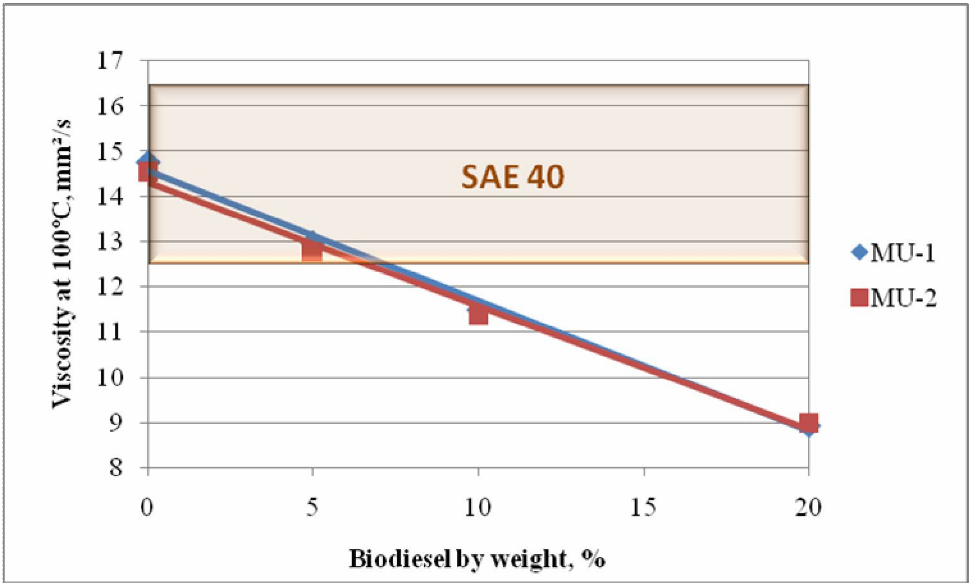

Figure 1: Oil dillution with biodiesel

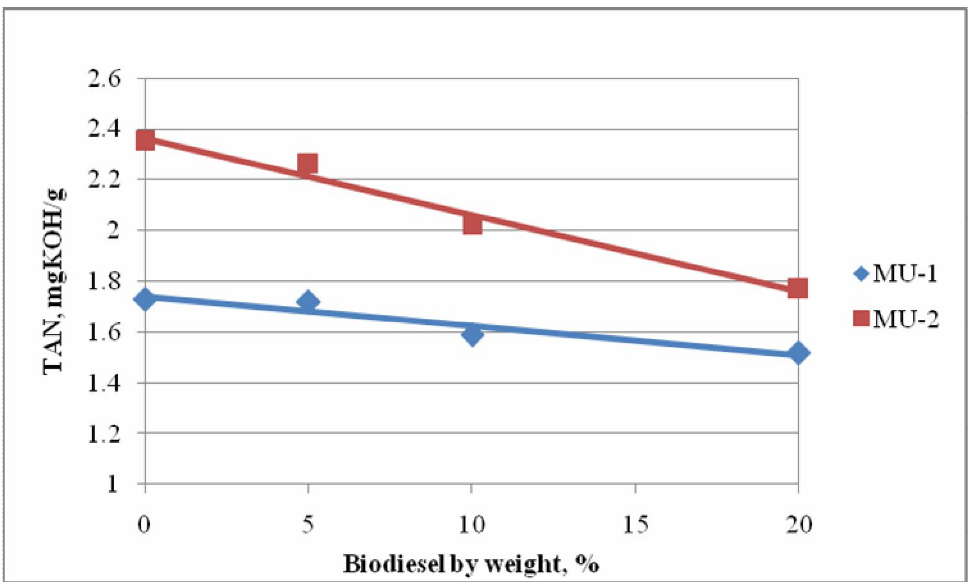

Figure 2: Change of TAN number with biodiesel addition

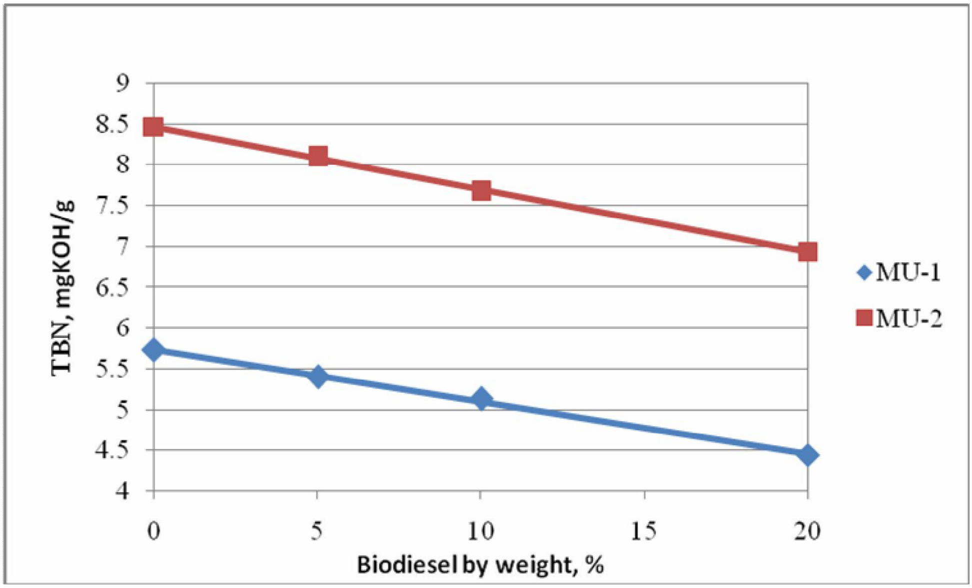

Figure 3: Change of TBN number with biodiesel addition

Oil dilution reduces total performance potential of engine oils. However, due to lower viscosity of biodiesel, there is a significant reduction in viscosity. With 10% of biodiesel, engine oil passes into lower viscous gradation, which can lead to inadequate lubrication of vital engine components, increased wear and consequently to reduce life of the engine.

Prepared samples of oils were subjected to oxidation according to the standard test IP 48. The test results are shown in Tables 5 and 6 and on Figures from 4 to 7.

Table 5: Amount of carbonyl compounds in oils after oxidation test IP 48

Motor oil	Oxidation (1710 Abs/cm)
MU- 1	7.206
MU-1+ 5% biodiesel	14.690
MU-1 +10% biodiesel	24.750
MU-1+20% biodiesel	52.721
MU- 2	2.153
MU-2+ 5% biodiesel	6.274
MU-2+10% biodiesel	9.552
MU-2+ 20% biodiesel	19.339

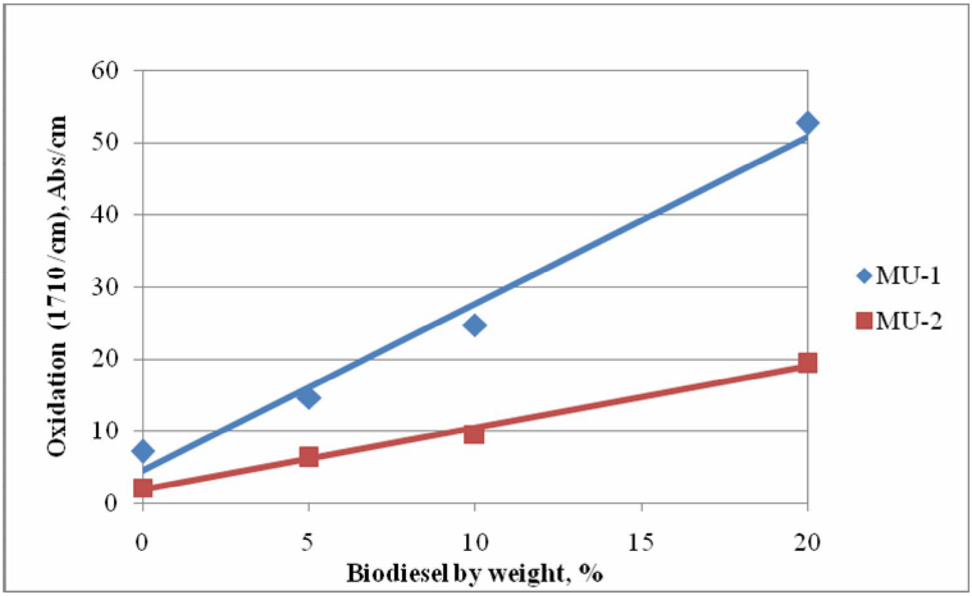

Figure 4: Dependence of carbonyl compounds content in engine oil on biodiesel content

Table 6: The main charcteristics of samples after test IP 48

Characteristics	Viscosity at 100 °C, [mm²/s]	TAN [mg KOH/g]	TBN [mg KOH/g]
Motor oil / Methods	BAS ISO 3104	ASTM D 664	BAS ISO 3771
MU-1	13.5	2.78	3.21
MU-1+ 5% biodiesel	12.13	3.91	2.95
MU-1+10% biodiesel	11.51	4.96	2.18
MU-1+20% biodiesel	11.35	7.3	0.13
MU- 2	14.14	2.17	6.04
MU-2+5% biodiesel	13.59	4.39	5.70
MU-2+10% biodiesel	12.43	5.47	4.60
MU-2+20% biodiesel	10.73	6.46	2.43

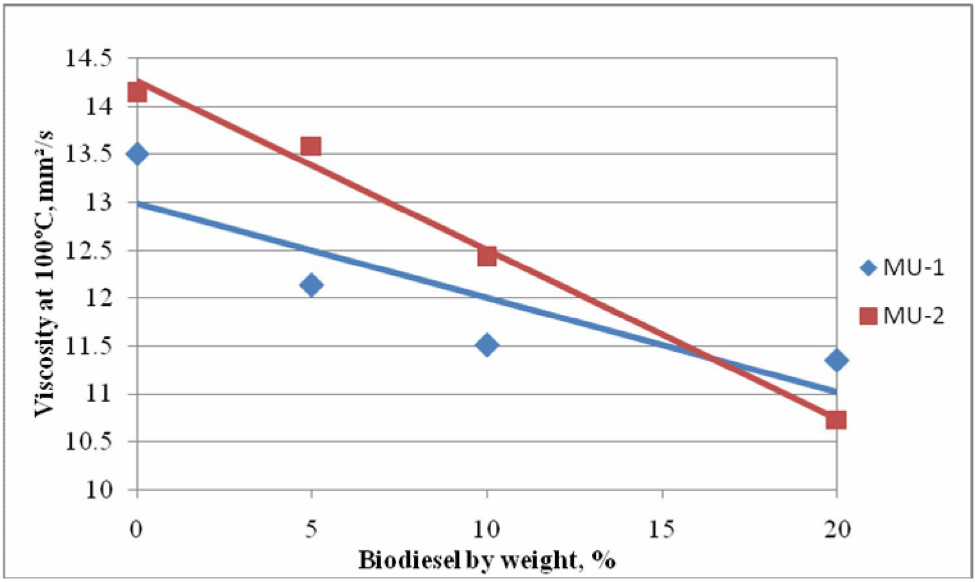

Figure 5: Depencence of viscosity on biodiesel content after the test IP 48

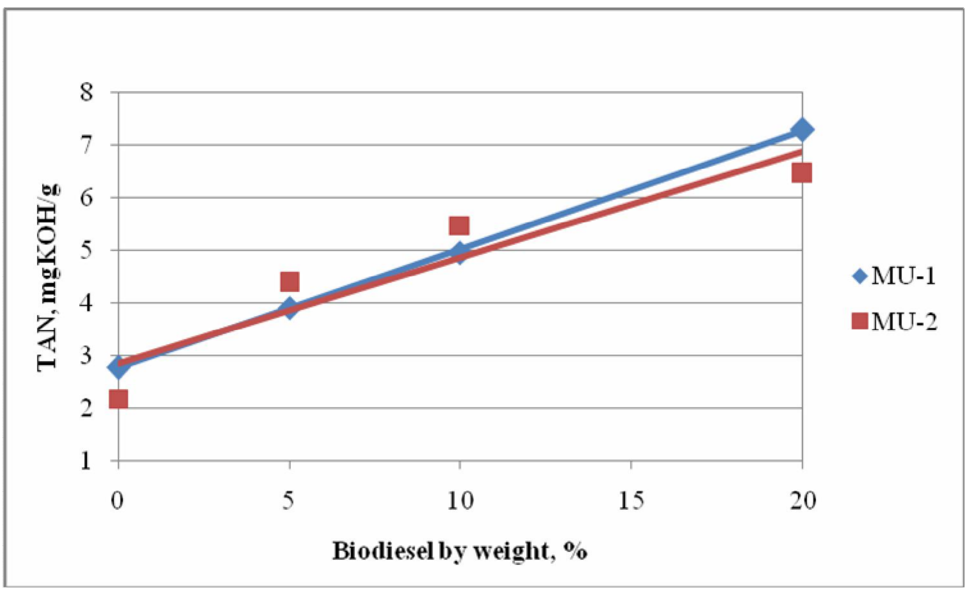

Figure 6: Dependence of total acid number on biodiesel content after the test IP 48

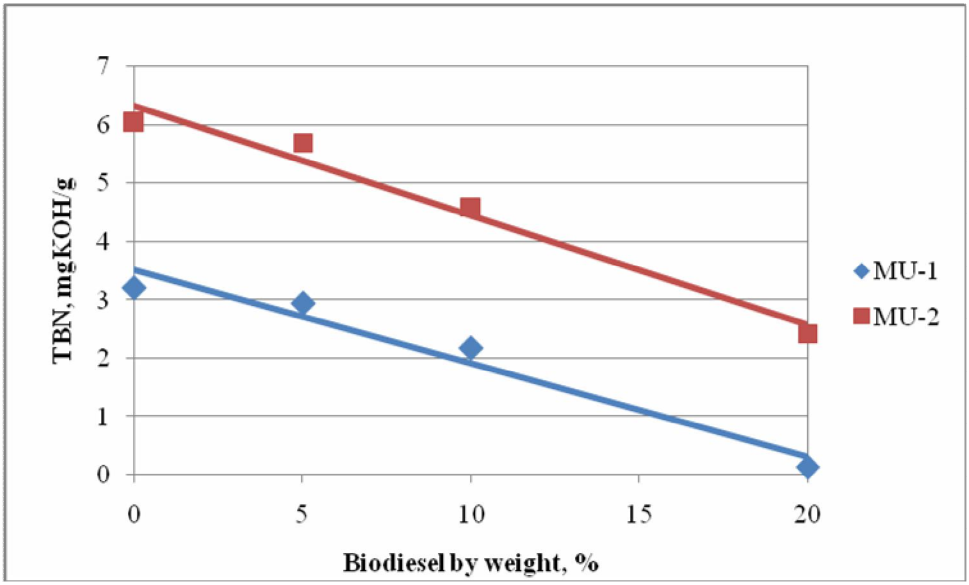

Figure 7: Dependence of total base number on biodiesel content after the test IP48

Based on these results it can be concluded:

• With increasing content of biodiesel, absorption at 1710 cm^{-1} is being increased, it indicates that in oil happened significant oxidative changes.
• With increasing content of biodiesel the value of TAN is being increased - increased amount of acid products.
• The results show decreasing of TBN as a consequence of neutralization of acid products.
• Compared to fresh oils, after oxidation, viscosity values are much higher and it can be concluded that there was a thickening of oil by oxidation and polymerization products.
• In case of MU-2 engine oil, all the changes are expressed in a lower degree due to the more efficient oxidation inhibitors.

In the second part of experimental work the results obtained by the test method ASTM D 2272 are shown. The test results are given in Table 7 and shown in Figures from 8 to 11.

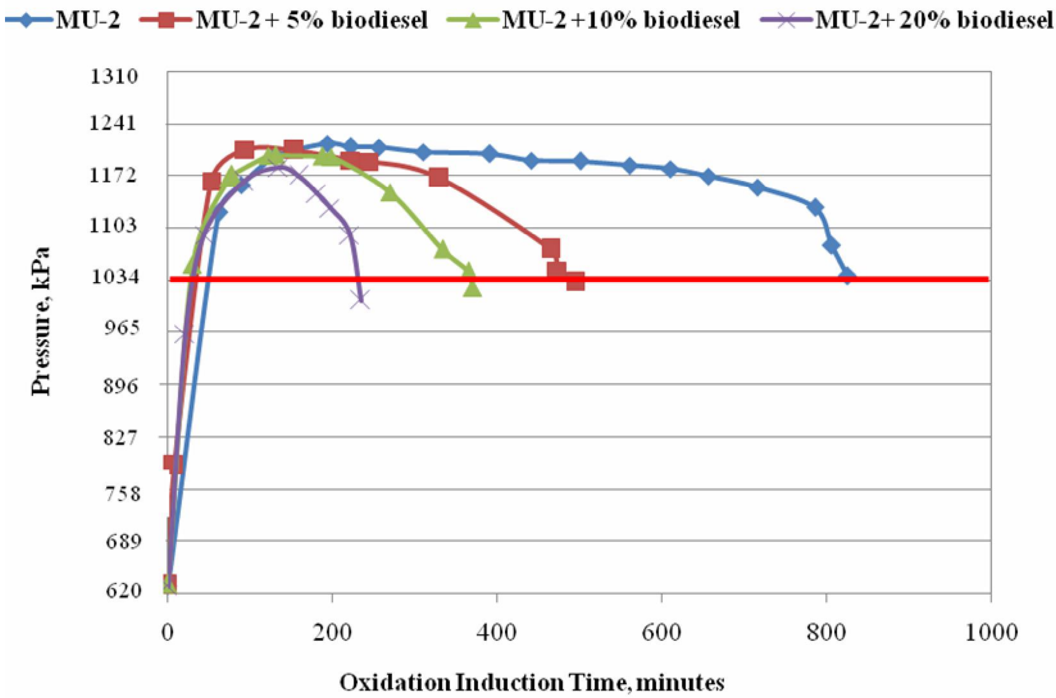

Figure 8: Oxidative curves of MU-2 engine oil with the different biodiesel content

Table 7: The results obtained by the method ASTM D 2272

Characteristics	Units	MU-2 + % biodiesel				Methods
		0	5	10	20	
TAN	mg KOH/g	5.5	5.7	6.0	6.5	ASTM D 664
TBN	mg KOH/g	3.7	2.5	1.8	0.6	BAS ISO 3771
Oxidations at 1710/cm	Abs/cm	7.4	16.7	20.5	29.5	FT-IR
RPVOT	minutes	826	495	370	235	ASTM D 2272

Based on the results shown in Figure 8 it can be concluded that increasing of biodiesel concentration in the oil leads to a significant reduction of the induction period. The induction period is the time from the start of testing until the pressure drop of 175 kPa compared to the maximum pressure. Increasing the content of biodiesel (Figure 9) leads to a significant increase in the amount of carbonyl compounds in absorption at 1710 cm^{-1}.

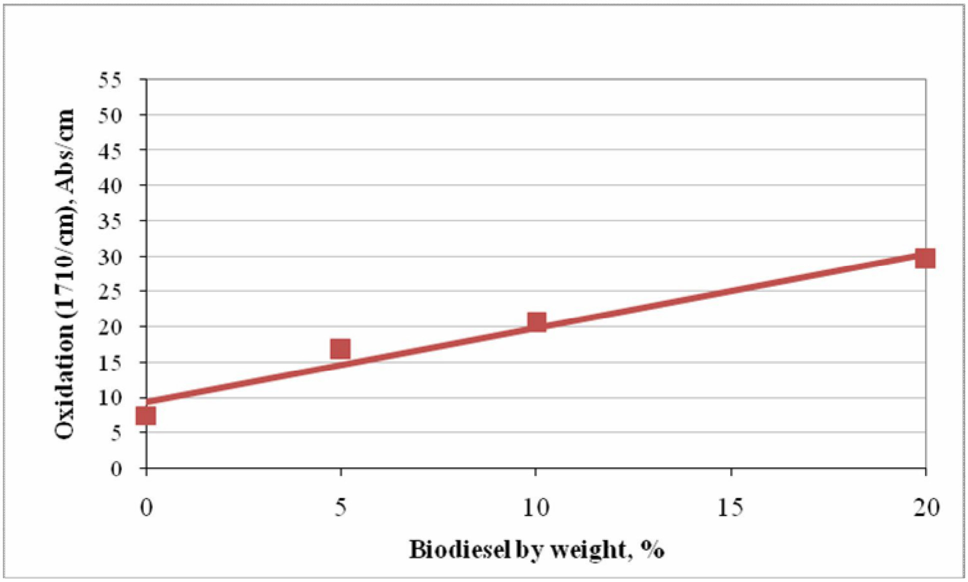

Figure 9: Carbonyl compounds in oil after oxidation

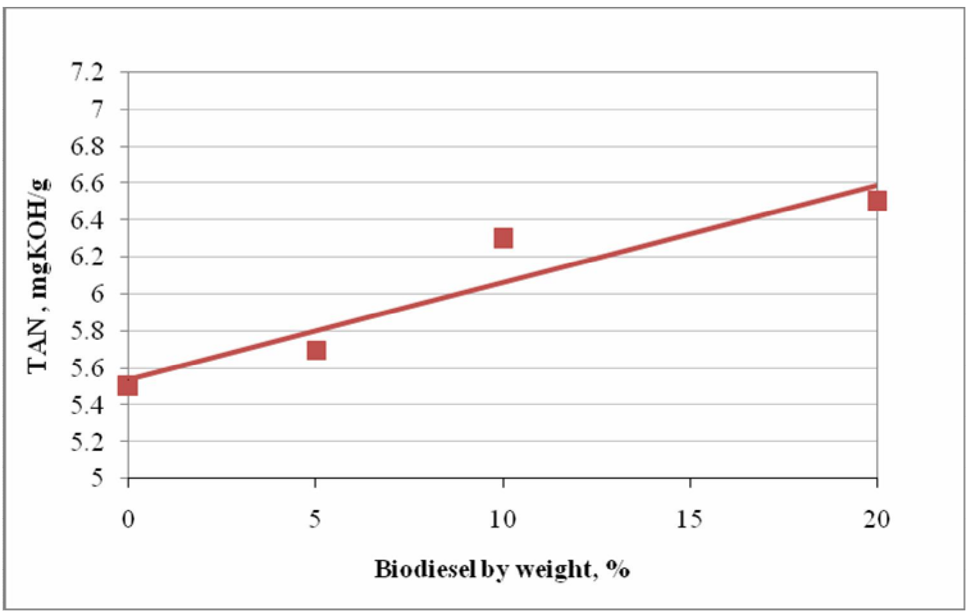

Figure 10: Dependence of total acid number on biodiesel content

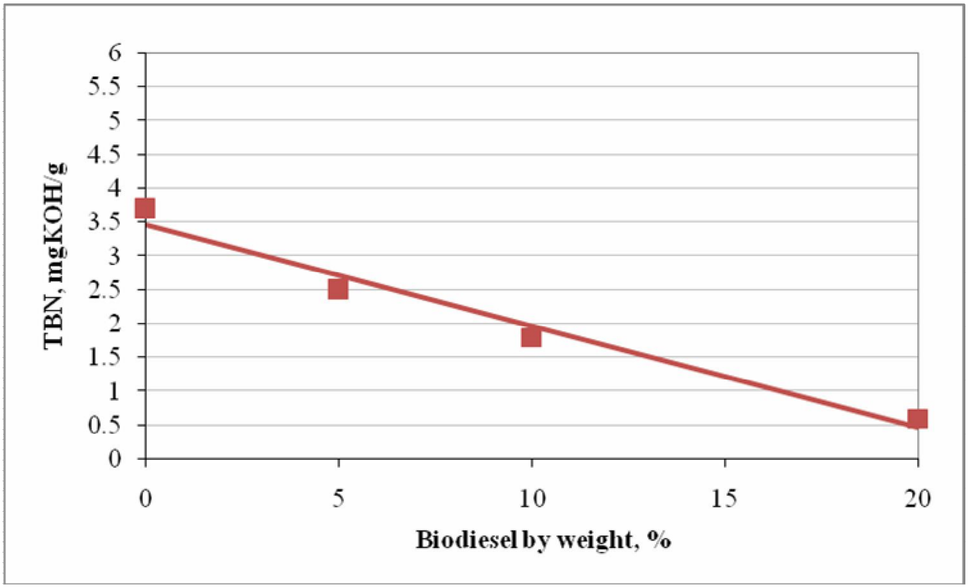

Figure 11: Dependence of total base number on biodiesel content

High value of TAN shows that even without biodiesel there is the complete oxidation of the oil. It is obvious that this method, due to the high temperatures and significant catalytic activity of copper, is not selective and can not determine the impact of biodiesel on the oxidation process. The value of TBN shows that entre aount of additives has been spent for the neutralization of acid products.

Based on the overall results obtained by this method it can be established that biodiesel accelerate the process of oxidation. However, this method is not suitable for the evaluation of engine oil because of severe conditions.

Conclusion

1. The presence of biodiesel has negative infulence on the chemical stability of engine oils.
2. With increasing the content of biodisel the amount of carbonyl compounds is being increased.
3. The presence of biodiesel decreases total base number and increases total acid number.
4. Higher quality oil shows smaller infulence of biodiesel on the oxidative stability.
5. Test method IP 48 can be used for the evaluation of biodiesel infulence on the chemical stability of the engine oil.
6. Modified method ASTM D 2272 has too severe testing requirements and is not suitable for this application.

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