THE ANALYTICAL COMPOSITION OF THE BIODEGRADABLE UNIVERSAL TRACTOR OIL BASED ON THE VEGETABLE OILS

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1. INTRODUCTION

Lubricating oils contain up to 80 % of base oils and the properties such as viscosity, oxidation stability, pour and flash point, volatility and others depend on them. Lubricating oils can contain up to 20 % additives which improve base oil characteristics or bring some new properties thus increasing exploitation and technical properties. Lubricants made out of mineral base oils originating from the crude oil, are the most widely used. However, these lubricants are very often toxic and are not readily biodegradable, thus being environmentally aggressive. The annual consumption of lubricants in the world is around 40 million tons out of which less than 40% are collected and properly processed, meaning regeneration, re-refining and controlled incineration, while the rest is disposed without control thus contaminating soil, water and atmosphere. It has been proved that 1 liter of spent oil contaminates 1 million liter of water or one tone of spent oil contaminates the river water as much as waste water from a 40 000 men town.

Due to the aforementioned potential dangers, during some last twenty years the ecologically acceptable oils are more and more used. Ecologically acceptable oils are the oils which in contact with the environment produce the minimum of harmful effects [1-7]. The conditions for the ecological acceptance are biodegradability and no toxicity of lubricants. Besides, ecologically acceptable lubes are produced from the renewable sources (vegetable oil) thus reducing the dependence of mineral oils.

The disadvantages of vegetable oils versus mineral oils are low oxidation stability, low fluidity on low temperatures, low hydraulic stability and the price which is 1.5 to 2 times higher than the price of mineral oils [8-13].

The features of oils based on rapeseed oil, sunflower oil, soybean oil and a mixture of rapeseed oil with mineral oil were, after the corresponding testing, compared with the features of the commercially available mineral-based universal tractor oil, UTTO (Table 1).

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Table 1 Oil Samples

Sample number	Oil name	Oil code
1.	Rapeseed oil without additives	RE
2.	Soybean oil without additives	SO
3.	Sunflower oil without additives	SU
4.	Rapeseed oil with additives	REA
5.	Soybean oil with additives	SOA
6.	Sunflower oil with additives	SUA
7.	Rapeseed oil + additives + 10% SN150	REAM10
8.	Rapeseed oil + additives + 20% SN150	REAM20
9.	Mineral UTTO	MIN

The ASTM D 4951 and ASTM D 4927 AAS methods have been applied to obtain the elemental composition of the additives used in the test oils, as shown in Table 2 and Figure 1.

Table 2 The elemental composition of the additives used in the test oils

	P	Ca	Zn	S
	% m/m			
REA	0.07	0.08	0.13	0.19
SOA	0.06	0.07	0.14	0.19
SUA	0.06	0.07	0.14	0.19
REAM10	0.08	0.15	0.14	0.23
REAM20	0.09	0.18	0.15	0.28
MIN	0.11	0.34	0.15	0.54

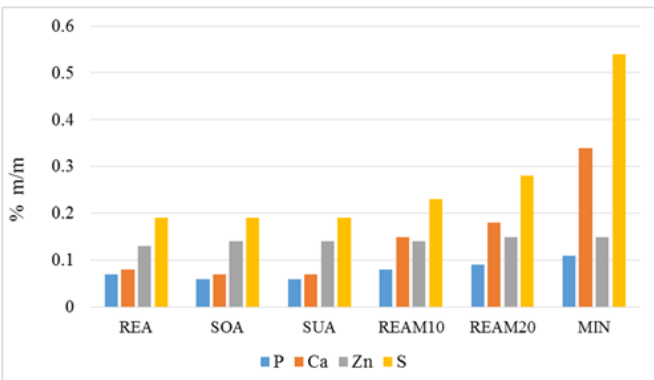

Figure 1 The elemental composition of the additives for the test oils

Vegetable oils are generally less additivated than mineral oils, because they possess good lubricating properties due to their polar nature. This makes them good solvents for sludge and dirt, which would otherwise deposit on metal surfaces [14-17]. Because of these properties, it is possible to reduce the amount of friction modifiers, antiwear additive package, and dispersants, when formulating biodegradable universal tractor oils.

2. PHYSICAL AND CHEMICAL PROPERTIES OF THE TRACTOR OIL

The physical and chemical properties of the vegetable oils were examined in accordance with standard methods (Table 3).

Table 3 Laboratory test methods

Method No.	Physical and chemical properties	Test method
1.	Density, kg/m^3	ASTM D 1298
2.	Kinematic viscosity at 40 °C, mm^2/s	ASTM D 445
3.	Kinematic viscosity at 100 °C, mm^2/s	ASTM D 445
4.	Viscosity Index	ASTM D 2270
5.	Pour point, °C	ASTM D 97 or ISO 3016
6.	Flash point, °C	ISO 2592, ASTM D 92
7.	Foaming, ml/ml 24 °C; 94 °C; 24 °C	ASTM D 892
8.	Deaeration, minutes	DIN 51381
9.	Oxidation stability, minutes	ASTM D 2272
10.	Corrosion on copper, 3 hours at 121 °C	ASTM D130
11.	P content, %	ASTM D 4927
12.	S content, %	ASTM D 2622
13.	Ca content, %	ASTM D 4628
14.	Zn content, %	ASTM D 4628
15.	Wear, (1h; 65 °C; 40 kg and 1500 rpm), mm	ASTM D 4172
16.	4-ball EP test - scuffing, kg	ASTM D 2783

The results of experimental testing of physico-chemical properties are presented in Table 4. Experimental work was carried out in accordance with the manufacturer specifications and proper standards, by using the necessary testing equipment.

Table 4 Physico-chemical properties of oils

Physico-chemical properties	Measuring unit	Methods	RE	SO	SU	REA	SOA	SUA	REAM 10	REAM 20	MIN
Density at 15°C	kg/m³	ASTM D1298	916	918	920	918	921	922	912	907	877
Kinematic viscosity at 40°C	mm²/s	ASTM D 445	34.8	32.7	35.1	42.3	37.7	38.6	42.0	41.0	70.5
Kinematic viscosity at 100°C	mm²/s	ASTM D 445	7.9	7.82	7.93	9.49	9.17	9.27	9.23	9.18	10.05
Viscosity Index		ASTM D2270	210	224	209	218	227	226	211	201	126
Flash point	°C	ASTM D 92	322	326	328	254	260	250	248	246	234
Pour point	°C	ASTM D 97	-8	-13	-11	-23	-25	-24	-26	-27	-36
Foaming, I sequnce, 24ºC II sequence, 94ºC III sequence 24ºC	ml	ASTM D 892	0/0 0/0 0/0	0/0 0/0 0/0	0/0 0/0 0/0	25/0 20/0 20/0	15/0 20/0 20/0	30/0 20/0 10/0	25/0 20/0 10/0	20/0 20/0 10/0	5/0 20/0 5/0
Deaeration	minutes	DIN 51381				6	5	6	5	7	1
Oxidation stability, RBOT	minutes	ASTM D2272	13	8	10	109	60	70	120	149	214
Wear, (1h;75ºC;40kg and 1200 rpm)	mm	ASTM D 4172	0.66	0.69	0.68	0.38	0.39	0.37	0.39	0.39	0.36
4-ball EP test - scuffing	kg	ASTM D 2783				200	200	200	200	160	100
Protection against corrosion, Test B		ASTM D 665	pass	pass	pass	pass	pass	pass	pass	pass	pass
Corrosion on copper, 3 hours at 121 ° C		ASTM D130	1A	1A	1A	1A	1A	1A	1A	1A	1A

2.1 Kinematic viscosity

Most tractor lubricants possess kinematic viscosity between 9 and 11 mm^2/s at 100 °C. This viscosity is found to provide sufficient thickness to promote good protection for the transmission system and anti-squawk performance, yet still to be a suitable viscosity for the hydraulic system.

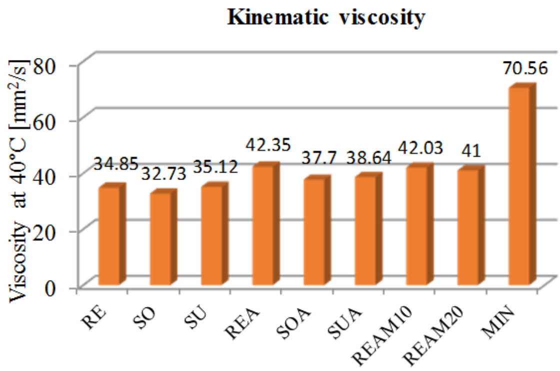

Figure 2 Kinematic viscosity at 40°C, ASTM D 445

As can be seen from Table 4, viscosity of vegetable oils produced from oil seeds falls between 32,7 and 42,3 mm^2/s at 40 °C, and between 7,8 and 9,4 mm^2/s at 100 °C.

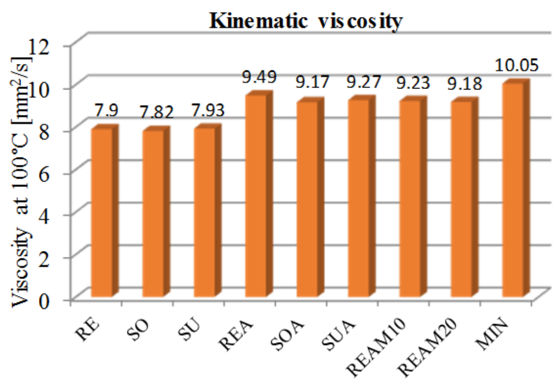

Figure 3 Kinematic viscosity at 100°C, ASTM D 445

2.2 Oxidation stability

Most vegetable oils are triglycerides constituting a complex mixture of fatty acids with different chain length and instauration content [18-24]. The alcohol component (glycerine) is the same in all vegetable oils. The fatty acid components are plant-specific and therefore variable. The fatty acids differ in chain length and number of double bonds. From the fatty acid composition of the oils, it is observed that chain length C18 is dominating (Table 5). Main fatty acids with double bonds are linolenic, linoleic and oleic. The oxygen absorption rate is 800:100:1 respectively, therefore less double bonds in a carbon chain result in better oxidation stability [16]. Generally the oxidation stability of vegetable based oils decreases with the increased level of instauration.

The content of polyunsaturated fatty acids (C18:2) is rather high for soybean (SO) and sunflower (SU) oil. Under thermal conditions, the double bonds in polyunsaturated fatty acids polymerize much faster than monounsaturated (C18:1 and C22:1) or saturated (C16:0 and C18:0) fatty acids. Unfortunately, the saturation of fatty acid degenerates the low temperature behaviour or pour point of the oil.

Iodine value characterizes particular oil on the base of unsaturated fatty acids. Oils with high iodine values are more problematic for oxidation processes, however values fewer than 100 are not recommended since such oils are more problematic for changing the characteristics at lower temperatures.

Table 5 Fatty acid content and iodine value of vegetable base oil

Physico-chemical properties	Unit	Rapeseed oil	Soybean oil	Sunflower oil
Iodine value	$gI_2/100g$	118.41	126.2	131.2
Fatty acid content	%			
C14:0 (Myristic acid)		0.06	0.05	0.04
C16:0 (Palmitic acid)		6.58	10.24	6.35
C16:1 (Palmitoleic acid)		0.36	0.15	0.13
C18:0 (Stearic acid)		2.88	5.24	5.35
C18:1 (Oleic acid)		53.10	29.33	27.13
C18:2 (Linoleic acid)		28.72	47.95	58.53
C18:3 (Linolenic acid)		6.54	5.35	0.16
C20:0 (Arachidic acid)		0.41	0.52	0.41
C20:1 (Eicosenoic acid)		0.73	0.29	0.20
C22:0 (Behenic acid)		0.28	0.65	1.31
C22:1 (Erucic acid)		0.17		
C24:0 (Lignoceric acid)		0.10	0.20	0.35

The oxidation stability of oil samples was examined by the ASTM D2272 test (RBOT - Rotating Bomb Oxidation Test). As concerning the neat vegetable oils (without additives), rapeseed oil (RE) shows better oxidation stability as compared to the soybean (SO) and sunflower (SU) oil. The reason is a high content of oleic acid and a low iodine value present in rapeseed oil. The oxidation stability of vegetable oils without additives is very low.

The improvement of the oxidation stability of vegetable oils was accomplished by adding the antioxidant additives and the mineral base oil. The concentration of the additives was the same for all vegetable oils. The oxidation stability values determined by RBOT method for neat vegetable oils, vegetable oils with additives and vegetable oils with mineral base oil, were compared with the values for commercial UTTO oil, as it is shown in Figure 4.

The best oxidation stability shows sample REAM20 (149 minutes). The oxidation stability is improved by adding the antioxidant additive: for rapeseed oil, the improvement is more than eightfold. The stability is further increased by adding a mineral oil, but the biodegradability is reduced.

A low oxidation stability of newly formulated biodegradable oils limits their use for the production of motor oils and other oils that require high oxidation stability. Therefore, such oils may be used in the fields where the high oxidation stability is not required (flow lubricating oils, hydraulic oils, universal tractor oils), or in the agriculture and forestry, where a low toxicity and biodegradability of lubricants is mandatory [25-29].

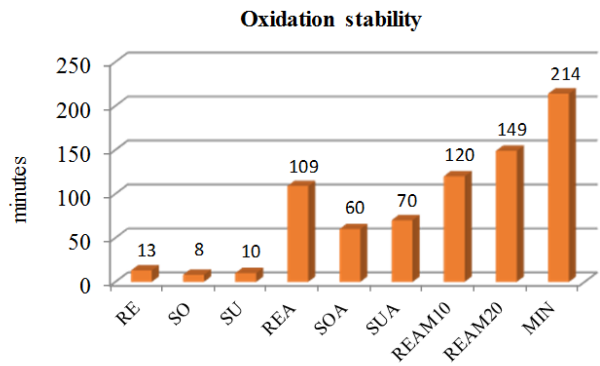

Figure 4 Oxidation stability, ASTM D2272 (RBOT)

2.3 Flash point

Flash point is important in transport and storage due to risk of fire. Vegetable oils have higher flash point values in comparison with mineral oils (Figure 5).

Flash point for vegetable oils is higher than 300 °C. By adding a package of additives and mineral oil according to the formulation, the flash point is reduced, but it is far above the allowed values according to the specifications of tractor manufacturers (Massey Ferguson CMS M1141, Massey Ferguson_CMS M1143; John Deere J20C: Flash point ≥ 200 ^{0}C).

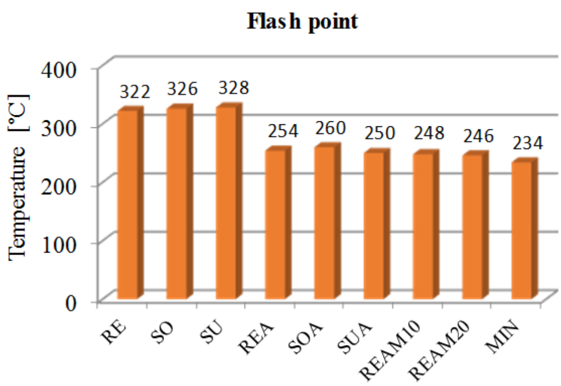

Figure 5 Flash point, ASTM D 92

2.4 Pour point

The flowability of vegetable oils at low temperatures is extremely low, which limits their use at low operating temperatures (Figure 6). Vegetable oils form crystal structures at low temperatures, by agglomeration of triglycerides, wherein the oil flowability is reduced. In order to improve the low-temperature characteristics, vegetable oils are added additives labeled as pour point depressants (PPD). The function of these additives is to prevent the crystallization of the triglyceride molecules at low temperatures and their further grouping. The optimal concentration of additive PPD of 1% in the final formulation of vegetable oils, significantly improves their low temperature properties.

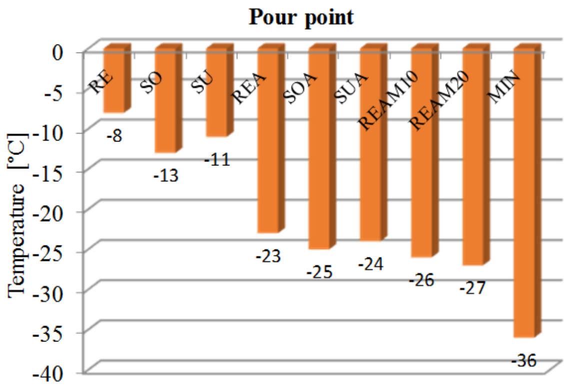

Figure 6 Pour point, ASTM D 97

2.5 Abrasion and high pressures resistance

Tests of the abrasion and high pressures resistance were carried out on the device with four balls ("four ball" test), and the results are shown in Table 6. The wear resistance testing was carried out according to the method ASTM D 4172.

The test conditions were as follows: the pressing force is 392 N, the top ball is rotated at 1200 rpm for 60 min., and the temperature of the test lubricant is regulated at 75°C. The limiting value of the scar diameter worn on the ball is maximum 0.4 mm for UTTO oil, according to the Massey Ferguson MF 1135 specification. The vegetable oil samples without additives (RE, SO, SU) did not pass the standard test, because the wear intensity was 70% higher than allowed. The wear parameters for other samples are presented in Figure 7, and it is seen that they are quite uniform, and within the allowed limits (< 40mm).

The measurement of extreme-pressure properties was performed according to the ASTM D 2783 (Four-ball method). The load is steadily increased until welding occurs, and the welding value of load is recorded as a maximum load which can be carried out by lubricant. The results in Table 6 indicate that vegetable based UTTO oils possess higher load values comparing to mineral oils, which means that they can better withstand extreme pressures and suddenly applied stress. The laboratory tests by using four-ball method have revealed that vegetable oils free of EP additives, possess even better results than mineral oils with the additives, as it is seen in Figure 8.

Table 6 The wear resistance test parameters and results

Characteristics	Unit	RE	SO	SU	REA	SOA	SUA	REAM10	REAM20	MIN
Wear	mm	0.66	0.69	0.68	0.38	0.39	0.37	0.39	0.39	0.39
4-ball EP test	kg	140	140	140	200	200	200	200	160	100

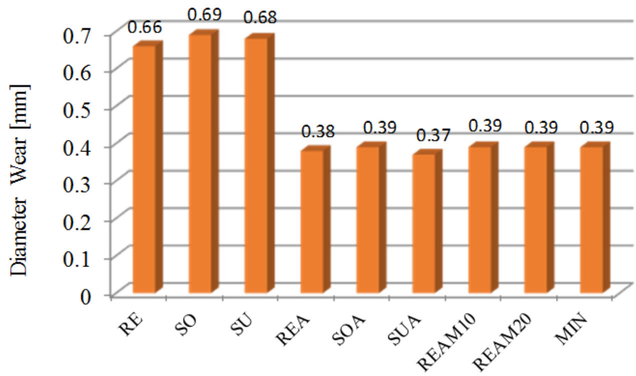

Figure 7 Wear resistance of vegetable oils and their mixtures

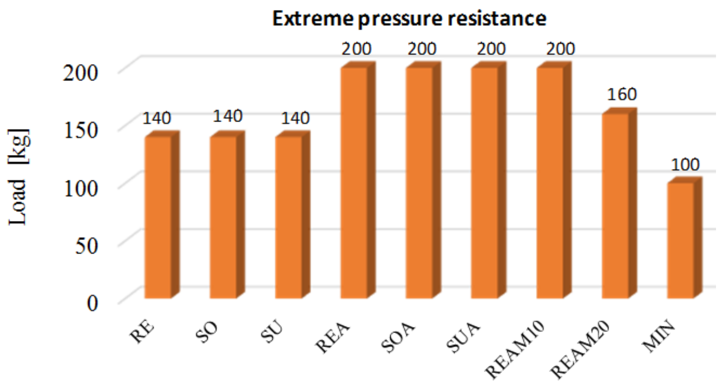

Figure 8 Extreme pressure resistance of vegetable oils and their mixtures

4. CONCLUSIONS

According to the obtained results for physico-chemical properties of various oil samples, it may be concluded that almost all the investigated properties of biodegradable universal tractor oils, satisfy the John Deere and Massey Ferguson specifications, and some characteristics are even better when compared to the properties of universal mineral based oil. The vegetable oils show considerably higher viscosity index (VI > 200) than mineral oils, allowing a reliable tractor operation at wider temperature changes. Flash point is higher for vegetable oils as compared to the mineral. Low temperature fluidity of vegetable oils is far from satisfactory, thus limiting their use at low temperatures. However, PPD additive lowers pour point for these oils to -15 0C or even -23 0C, and these values satisfy most standards. Some of the additives used (PPD and EP) increase foaming above the allowed limits, but after the addition of antifoaming agent, good results are obtained. Oxidation stability of vegetable oils without additives is very low. For instance, the result from RBOT test for additive free soybean oil is only 8 minutes. The improvement of this characteristic of vegetable oils has been accomplished by adding the antioxidant additive and mineral based oil. The mineral oil addition enhances the oxidation stability, but lowers the biodegradability of vegetable oils. The best oxidation stability was found for the rapeseed oil sample (REA=109 minutes), which was the expected result.

The wear resistance tests were performed on “four ball” device. The results from this examination were quite uniform for all samples and within the standard limits (< 40 mm). The extreme pressure (EP) resistance was tested by using “four ball” device. The vegetable UTTO oils show much higher ability to withstand extreme pressures as well as shock loads, in comparison to mineral oils. The laboratory tests give evidence that even vegetable oils without EP additives show better results than mineral oils with the additives.

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