ISSN 1392 - 1207. MECHANIKA. 2011. 17(2): 203-207

Modification of rapeseed oil with free fatty acids

J. Padgurskas*, R. Kreivaitis, A. Kupčinskas***, A. Žunda******

**Lithuanian University of Agriculture, Studentu 15, 53362 Akademija, Kauno r., Lithuania,*
E-mail: juozas.padgurskas@lzuu.lt
***Lithuanian University of Agriculture, Studentu 15, 53362 Akademija, Kauno r., Lithuania,*
E-mail: raimondaskreivaitis@gmail.com
****Lithuanian University of Agriculture, Studentu 15, 53362 Akademija, Kauno r., Lithuania,*
E-mail: arturas.kupcinskas@lzuu.lt
*****Lithuanian University of Agriculture, Studentu 15, 53362 Akademija, Kauno r., Lithuania,*
E-mail: audrius.zunda@lzuu.lt

crossref http://dx.doi.org/10.5755/j01.mech.17.2.341

1. Introduction

At present ecological requirements are in the great importance. A lot of studies had been made in the field of bio fuels, trying to reduce pollution by exhausted gases and use renewable resources [1, 2]. At the same time tribological properties ate important too. Friction and wear in the machine elements consumes a great part of the energy required. Various surface treatment technologies and specific lubricants are suggested [3, 4]. Nevertheless from the ecological point of view rapeseed oil is remaining as most attractive basis for the production of environmentally friendly lubricants. This attractiveness is caused by biodegradable properties together with comparably good lubricating characteristics [5].

Vegetable oils have naturally good lubricating properties, but the reliable wear protection forces the use of appropriate additives. Vegetable oils modified with additives have lubricating properties equal to those of equivalent mineral oils [6].

Modification of environmentally friendly lubricants is strongly regulated by different ecological marks: The European Eco-label, The German „Blue Angel“, Nordic countries „White Swan“, Canadian „EkoLogo“ a.o. [7, 8]. These standards regulate the amount of additives, restricted materials and elements etc. In order to fulfil these requirements, it is necessary to look for the possibility of using those additives which would be natural, non-toxic and easily degradable in the environment. One of such additive types is free fatty acids (FFA).

The effectiveness of free fatty acids in mineral oils has been known for a long time. Its use for the modification of plant oils has been investigated too [4, 6, 9, 10].

It is predicated that saturated and unsaturated fatty acids (FA) effectively improve the lubricating properties of base oils. However its effectiveness depends a lot on the compatibility of the modified base oil and free fatty acids. The temperature at the contact zone of the lubricated surface is very important too [4].

Saturated and unsaturated fatty acids have different operating mechanisms. The action of saturated fatty acids is based on the formation of an absorbed layer. Directly and vertically to surface oriented molecules of saturated fatty acids form the dense layer which separates the surfaces. This is the reason why such layers have good friction reducing properties [11]. It is believed that unsaturated fatty acids can not locate so densely at the surface because of their double bonds. Therefore the efficiency is lower. It is supposed that unsaturated fatty acids could oxidize between interacting surfaces and loose their lubricating properties [4]. However there are opinions that, at higher temperatures, the unsaturated fatty acids can come between lubricated surfaces forming the tribo-polymeric layer which reduces the friction and wear [9].

This investigation shows that free fatty acids ensure good lubrication at boundary lubrication conditions. However their extreme pressure (EP) properties are not good enough comparing them to reference oils. Therefore it is proposed to use it together with poly-atoms of S and N, which could ensure the EP properties. The combination of sulphur atoms with fatty acids increases the synergetic effect – fatty acids reduce the friction and sulphur ensures the EP properties and reliable wear protection. Additionally, those elements have a low toxicity which is very important for environmentally friendly lubricants [6].

The aim of this research is the investigation of the influence of free fatty acids, provided by LUBRIZOL Company, on the lubrication properties of rapeseed oil. The results should be compared to commercial environmentally friendly lubricants.

2. Tested materials

Pure rapeseed oil and rapeseed oil modified with free fatty acids (FA) were investigated. The refined rapeseed oil from the market was investigated without any processing or modification with inhibitors. Free fatty acids were received from LUBRIZOL Company as the oil additive (ADX 18) for improving the lubricating properties of environmentally friendly oils. Free fatty acid concentrations of 0.5; 1 and 2% were used for the modification of rapeseed oil. The test results were compared to the commercially available environmentally friendly lubricant produced on the basis of rapeseed oil. The physical and chemical properties of the investigated materials are presented in Table.

3. Testing procedures

Tribological tests were performed using a four-ball type tribotester. The balls of 12.7 mm diameter were made of 100Cr6 bearing steel ($E = 21.98 \cdot 10^4$ MPa; $\nu = 0.3$). The testing procedure was adapted from the standard method DIN 51 350, Part 3 [12].

Loads of 150 N and 300 N were used. The test runs 1 hour. Prior to each experiment, all the appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and the test balls were washed in an ultrasonic bath and then dried.

The diameters of the wear scars on three stationnary balls and the friction surfaces were measured and analyzed with an optical microscope. For each run the scar measurements were reported as an average of the Wear Scar Diameter (WSD) of the three balls in millimetres. The copper corrosion test was performed using standard method ISO 2160.

Table

Physicochemical properties of tested oils

Property	Material		
	Rapeseed Oil	Rapeseed Oil + 1% FA	Reference
Viscosity, cSt: at 40°C at 100°C	 34.7 8.0	 35.1 8.1	 63.2 13.9
Viscosity index	213	217	231
Acidity, mg KOH/g	0.07	0.75	n.d.
Copper corrosion	A1	A1	n.d.

4. Results and discussion

Tribological investigations of rapeseed oil modified by free fatty acid show the efficiency of this additive for wear and friction reducing. However the results for operation at the higher load (300 N) are different to those at the lower loading (150 N) regimen.

Wear of the balls in the higher load regimen decreased 1.4 times (Fig. 1) when lubricated with rapeseed oil modified with 0.5% concentration FA. A further increase in additive concentration does not influence significantly the wear decrease – the use of 1 and 2% concentration FA reduces the wear by 1.45 and 1.48 times.

There are several theories explaining the influence of FFA on the lubricating properties of oil [4, 9]. In this case, the adsorption of FA on the lubricating surfaces is the most likely. Higher protection of lubricating surface is most probably ensured by the formation of a dense adsorbed layer of FA [4, 13].

Usually such adsorbed layers have good friction reducing properties and are known as „friction modifiers" [7]. However, in our case the friction increased – the using of 0.5% concentration FA additive slightly increased the average torque, compared to pure rapeseed oil. Increasing the amount of FA slightly reduces the friction and, at 2% concentration, it becomes lower than when lubricating with pure rapeseed oil. The test revealed that average torque is significantly lower when using the modified and non-modified rapeseed oil compared to the reference oil.

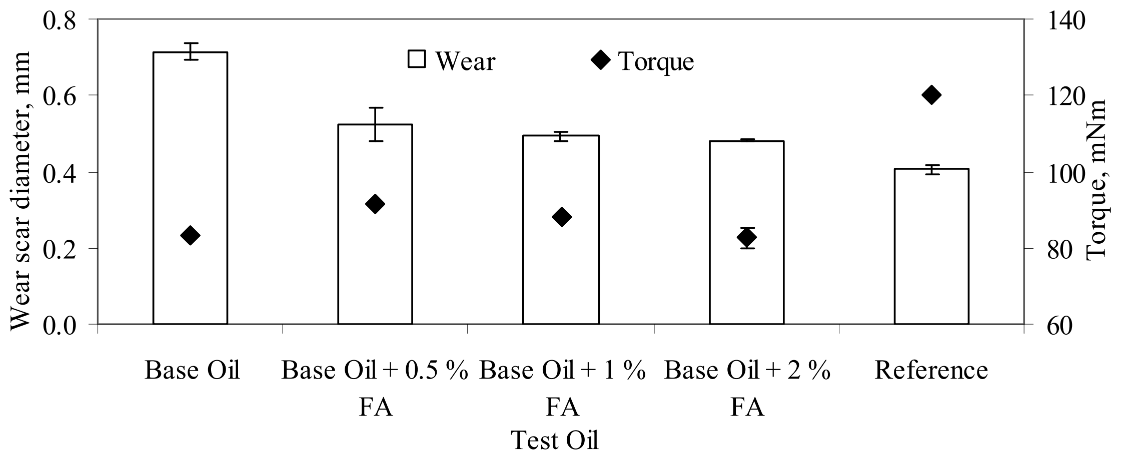


Fig. 1 Wear and torque results in the high load (300 N) four ball test

FFA additives not only change the average value of friction but also its variation during the operation (Fig. 2). There is no torque variation tendency when lubricating with pure rapeseed oil – torque increases at the beginning, after that decreases and, at the end of tests, starts again to increase. Such changes in torque are characteristic for non-stable lubrication of friction pairs and are followed by high wear. After modification of rapeseed oil with FA, the friction had a tendency to increase. That is also the sign of bad lubrication conditions, but it is better than non-stable conditions [4].

The evaluation of torque stability shows that the most stabile torque occurs when rapeseed oil is modified by FA at 0.5% concentration. The friction change has a different character when lubricating with reference oil. In this case, friction torque increases significantly at the beginning, after that it stabilises and, for the most part of the investigation, stays constant.

The friction decrease occurs at the beginning of tests at the high load (300 N) when lubricating with FA modified rapeseed oil (Fig. 2). This is not usual for rapeseed oil lubrication. This decrease occurs for longer when the FA concentration is increasing. This phenomenon could be related to temperature of the contacting surfaces. The oil temperature at the beginning is usually 30°C and increases during the test until 70°C at the test end. However the oil temperature does not reflect the temperature in the contact zone. Therefore it is possible that the FA loses their efficiency and the friction torque starts to increase when the temperature in the contact zone is much higher that oil temperature. Other researchers predicate that there are transfer temperatures which indicate the operation limits of the adsorption layer which is created by FA. This layer decays when the transfer temperature is exceeded – the wear intensity and friction increases [4, 9]. Higher viscosity of FA modified oil could also influence the reduction in torque (Table).

The temperature of 67°C, which is recommended by LUBRIZOL for dissolving the FA mixture, supposes the biggest part of the mixture consists of saturated long chain fatty acids. After creating mixtures of rapeseed oil and varying concentrations FA additives, it was detected that, at 1% concentration, the FA mixture separates at room temperature. The mixture jells, hardly remaining fluid at the concentration of 2%. Only a 0.5% concentration of FA does not cause these changes to rapeseed oil. Therefore, 2% concentration of FA is not appropriate for the modification for rapeseed oil.

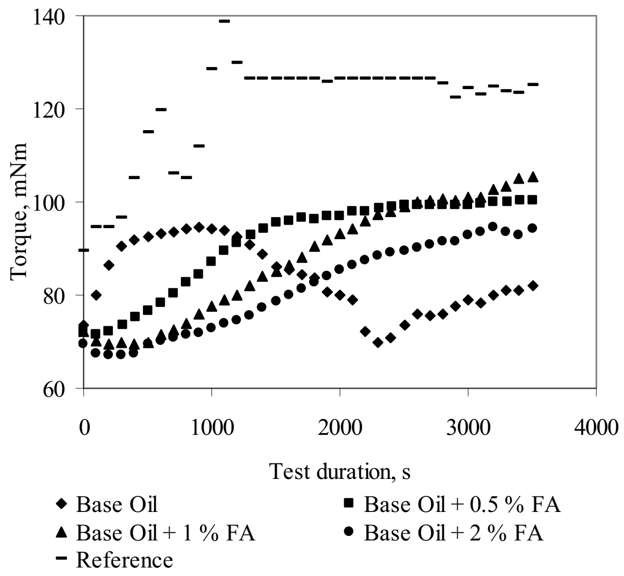


Fig. 2 Torque variations during the high load four ball test (300 N) lubricating with pure and free fatty acid modified rapeseed oil

The evaluation of friction of 0.5 and 1% concentration mixtures at higher load shows lower friction of the 1% concentration mixture. Therefore, taking into consideration the reasons mentioned above, it was decided to investigate only the 1% concentration mixture at lower loads.

Evaluation of wear reducing properties of investigated lubricants at lower loads (150 N) reveals that a 1% concentration FA mixture decreases the wear of test balls by 1.75 times (Fig. 3). This is also 1.12 times more efficient than the reference oil. These wear reduction values show that the modification of rapeseed oil with 1% concentration FA mixture is sufficient for the wear protection of machine elements operating at this regime.

Taking into consideration the 1.33 times lower friction coefficient of FA mixture comparing to reference oil at lower loading, the formation of absorbic layer is the most probable [7]. Rapeseed oil modified with 1% FA mixture reduces the average torque up to 1.2 times and essentially changes the process of friction variation (Fig. 4). The friction value varies considerably during the tests when lubricating with pure rapeseed oil, the same was as at the higher load. The FA modified oil preserves regular friction between the lubricated surfaces throughout the test. Such a torque characteristic is desirable in friction pairs. Friction torque is also stable when lubricating with the reference oil, but at the beginning we have a significant rise (Fig. 4).

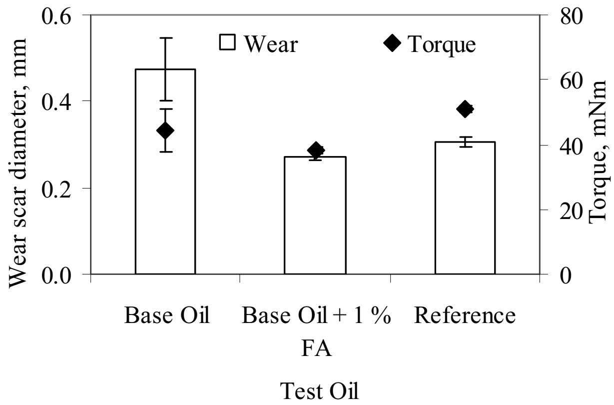


Fig. 3 Wear and torque results in the low load (150 N) four ball test

The results of wear tests at a higher load regime show that the wear protection provided by FA modified rapeseed oil is lower than for reference oil (Fig. 1), but, at the lower load, the FA modified oil is more efficient (Fig. 3). Despite the lower friction of the modified oil, the unstable torque at higher load shows that such FA modified oils could be used only for friction surfaces which operate at lower loads.

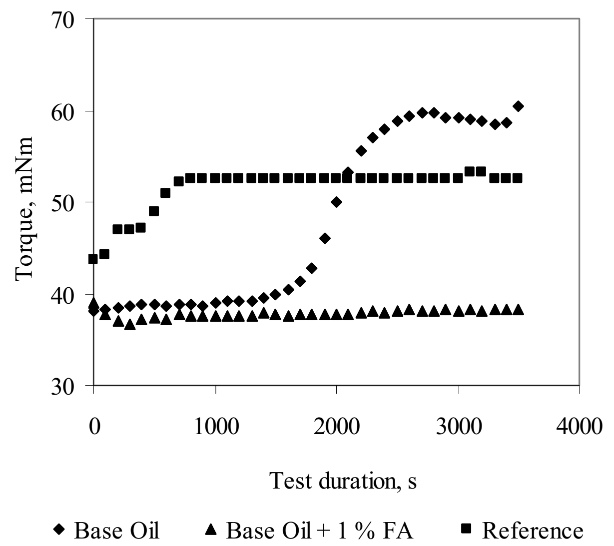
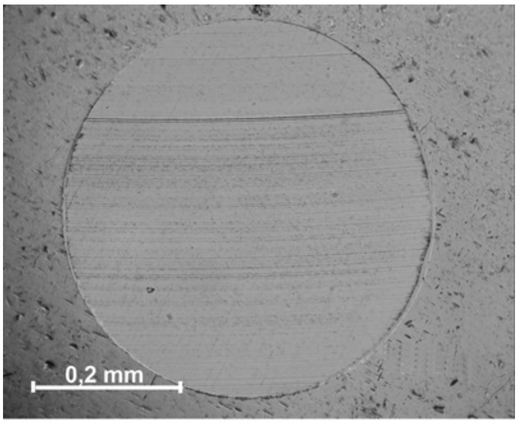


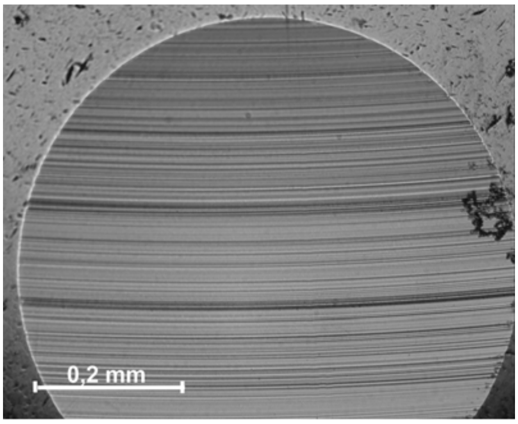
Fig. 4 Torque variations during the low load four ball test (150 N) lubricating with pure and free fatty acid modified rapeseed oil

Fig. 5 presents the wear surfaces after tests with pure rapeseed oil lubrication and lubrication with FA modified rapeseed oil. Apparent difference in wear scars is clearly seen for those two types of lubrication which applies both for lower and higher loading. Wear scar is very small when lubricating with FA modified oil and applying the lower loads (Fig. 5).

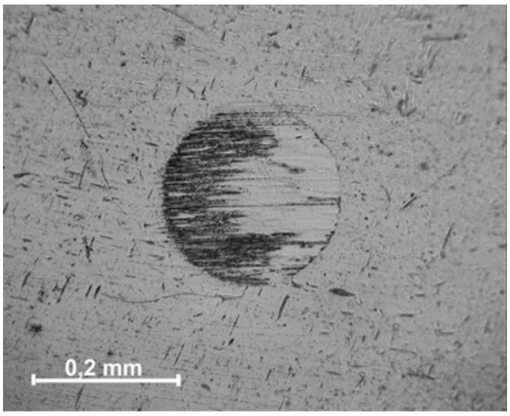
A part of wear scar is covered by remained wear protection layer. Such picture correlates to the torque results – lower friction correspond to small and even wear surface.



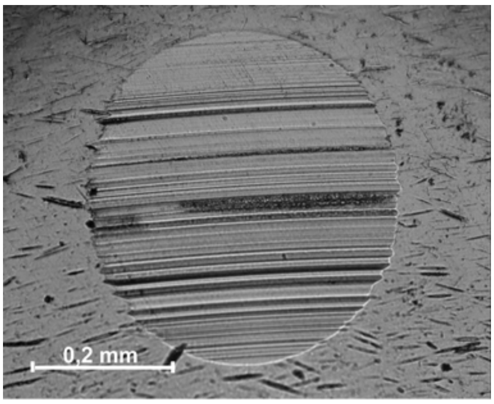
a



b



c



d

Fig. 5 Optical microscopic views of the wear scars when lubricating with a, b – pure rapeseed oil, and c, d – free fatty acid modified rapeseed oil at 150 and 300 N load respectively

Surfaces have much more scratches if they operate at higher loading. Operation with FA modified rapeseed oil caused much more scratches (Fig. 5, d). Higher friction reflects in this picture even if the wear value was lower.

It confirms that the modification of rapeseed oil with FA additives is not efficient at the lubrication of friction pairs which operate on higher contact loads.

5. Conclusions

The modification of rapeseed oil with free fatty acid is effective regarding the reduction of friction and wear. The investigated mixtures are more efficient at the lower load compared to the reference oil. However the wear decreasing at higher loads is not sufficient. The use of rapeseed oil, modified with free fatty acid, can ensure wear protection of machine elements and reduces the friction losses at low load conditions.

Acknowledgement

The authors thank LUBRIZOL Company for the research materials.

References

1. **Kadarohman, A.; Hernani, Khoerunisa, F.; Astuti, R.M.** 2010. A potential study on clove oil, eugenol and eugenyl acetate as diesel fuel bio-additives and their performance on one cylinder engine, Transport 25(1): 66-76.
2. **Lebedevas, S.; Lebedeva, G.; Makarevičienė, V.; Kazanceva, I.; Kazancev, K.** 2010. Analysis on the ecological parameters of the diesel engine powered with biodiesel fuel containing methyl esters from camelina sativa oil, Transport 25(1): 22-28.
3. **Zdravecka, E.; Suchanek, J.; Tacova, J.; Trpcevska, J.; Brinkienė, K.** 2010. Investigation of wear resistance of high velocity oxy-fuel sprayed WC-Co and Cr_3C_2-NiCr coatings, Mechanika 4(84): 75-79.
4. **Jankauskas, V.; Belyaev, S.** 2010. Influence of conterbody surface hardness of a friction part "steel-steel" on tribological behaviour of zinc nanopewder in oil, Mechanika 3(83): 45-50.
5. **Fox, N.N.; Tyrer, B.; Stachowiak, G.W.** 2004. Boundary lubrication performance of free fatty acids in sunflower oil, Tribology Letters 16(4): 275-281.
6. **Cao, Y.; Yu, L.; Liu, W.** 2000. Study of the tribological behavior of sulfurized fatty acids as additives in rapeseed oil, Wear 244: 126-131.
7. **Mang, Th.; Dresel, W.** 2007. Lubricants and lubrication. 2nd Edition. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. 847p.
8. **Bartz, W.J.** 2006. Ecotribology: Environmentally acceptable tribological practices, Tribology International 39: 728-733.
9. **Murakami, T.; Sakamoto, H.** 2008. Elucidation of lubrication mechanism of vegetable oils and their effective application, Tribology Online 3(5): 274-279.
10. **Kreivaitis, R.; Padgurskas, J.; Jankauskas, V.; Kupčinskas, A.; Makarevičienė, V.; Gumbytė, M.** 2009. Tribological behavior of rapeseed oil mixtures with mono- and diglicerides, Mechanika 5(79): 74-78.
11. **Hsu, S.M.** 2004. Molecular basis of lubrication, Tri-

bology International 37: 553-559.
12. **DIN 51350-3.** 1977. Testing of lubricants - Testing in the four-ball tester- Part 3: Determination of wearing characteristics of liquid lubricants (In Germany).
13. **Pawlak, Z.** 2003. Tribochemistry of lubricating oils. ELSEWIER. Netherlands. 368p.

J. Padgurskas, R. Kreivaitis, A. Kupčinskas, A. Žunda

RAPSŲ ALIEJAUS MODIFIKAVIMAS LAISVOMIS RIEBALŲ RŪGŠTIMIS

R e z i u m ė

Griežtėjant pasaulio ir Europos Sąjungos aplinkosaugos reikalavimams vis daugiau dėmesio skiriama aplinkai draugiškų alyvų tyrimui, gamybai ir naudojimui. Ieškoma būdų, kaip sumažinti alyvų daromą žalą aplinkai, taip pat ir pačių alyvų gamybos savikainą. Abu šiuos tikslus galima įgyvendinti alyvų gamyboje naudojant efektyvias natūralias medžiagas. Šiame darbe buvo tirta natūralaus trintį ir dilimą mažinančio priedo ADX 18, gauto laisvųjų riebiųjų rūgščių pagrindu, įtaka rapsų aliejaus tepamosioms savybėms. Tyrimai atlikti standartiniu keturių rutulių metodu, naudotos 150 ir 300 N apkrovos. Gauti rezultatai rodo, kad tirtas priedas pagerina rapsų aliejaus tepamąsias savybes, tačiau esant skirtingiems apkrovų režimams jo efektyvumas skiriasi. Mažos apkrovos sąlygomis tirti mišiniai dilimą mažina efektyviau už etaloninę alyvą, o didelės apkrovos sąlygomis jų dilimo slopinamosios savybės nėra pakankamos. Tepant tirtu priedu modifikuotu rapsų aliejumi trintis tiek didelės, tiek mažos apkrovos sąlygomis yra mažesnė nei tepant etalonine alyva. Tirtą tepamąją medžiagą naudojant mažų apkrovų sąlygomis, mechanizmai būtų patikimai apsaugoti nuo dilimo ir sumažėtų trinties nuostoliai.

J. Padgurskas, R. Kreivaitis, A. Kupčinskas, A. Žunda

MODIFICATION OF RAPESEED OIL WITH FREE FATTY ACIDS

S u m m a r y

Presently strickt World and European environmental requirements made force on research, manufacture and use of environmentally friendly lubricants. Scientists lucking for the ways to reduce harm of lubricants to environment and the cost of lubricants too. Both these problems can be solved using efficient natural lubricating materials. In current study the natural free fatty acid additive ADX 18 was used to reduce friction and wear lubricating with rapeseed oil. Tests were performed with standard four ball tribometer. The load was 150 N and 300 N. The results show positive influence of free fatty acid additive. However the effect in different loads is not equal. In the low loads (150 N) the wear reduction effect of additive is superior in comparison with reference oil. In the high loads (300 N) the wear reduction ability is not sufficient. Nevertheless the friction in both loads is less in comparison with the reference. The use of free fatty acid loaded rapeseed oil can reduce friction and wear in mechanisms with low load condition.

Ю. Падгурскас, Р. Крейвайтис, А. Купчинскас, А. Жунда

МОДИФИКАЦИЯ РАПСОВОГО МАСЛА КИСЛОТАМИ СВОБОДНЫХ ЖИРОВ

Р е з ю м е

При более строгих экологических требованиях в мире и в Европейском Союзе все большее внимание уделяется научным исследованиям, производству и использованию биологических смазочных материалов. Исследуются возможности как снижения ущерба от загрязненности окружающей среды, так и снижения себестоимости производства биологических масел. Обе эти цели можно достичь при использовании для производства масел материалы натурального происхождения. В работе представлены результаты исследований влияния присадки натурального происхождения на основе свободных жирных кислот ADX 18 на смазочные свойства рапсового масла. Исследования проведены по стандартной методике четырех шариков при нагрузке 150 Н и 300 Н. Полученные результаты показывают, что исследованная присадка значительно улучшает смазочные свойства рапсового масла, но при различных нагрузках эффективность присадки разная. Смеси рапсового масла с присадкой при небольших нагрузках (150 Н) снижают износ эффективнее эталонного масла, в то время как при больших нагрузках (300 Н) эти смеси снижают износ недостаточно эффективно. Потери на трение при смазке смесью, как при небольших, так и при больших нагрузках меньше потерь при смазке эталонным маслом. Смазывание смесью рапсового масла с присадкой ADX 18 (~1.0%) может обеспечить надежную защиту механизмов от изнашивании и снизит потери на трение.

Received September 30, 2010
Accepted March 15, 2011