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Modification of rapeseed oil and lard by monoglycerides and free fatty acids

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1. Introduction

Biological plastic lubricants (greases) are lubricating materials based on vegetable (rapeseed, sunflower, soy, flax and other oils) or animal (lard, beef, co-liver oil or other fat) origin. Such lubricants are environmentally friendly taking into account that in the environment no less than 80% of them disintegrate during 21 days while only 15-20% of mineral lubricants do it in the same period [1].

Plastic lubricants are produced of basic materials (oil or fat), thickeners and multipurpose functional additives which strengthen their adequate operating properties.

Thickener is one of the key components as plastic lubricants rendering them the form. Its main prerequisite is that they constitute small-sized particles which are uniformly distributed and are capable to form a sufficiently stable gel structure with the basic lubricant. Its structure may be filamentary (metal soaps), laminar or spherical (non-saponifiable thickeners). Basic lubricant contains about 70-90% of lubricant material and 10-20% of thickener [2-4].

Lately scientists have started emphasizing more and more that oil resources are abating, oil products are polluting the environment, "a greenhouse effect" on the nature and human health is increasing – all this result in the need to expand the use of biological lubricants and fuels. For this reason greater attention is diverted to alternative sorts of biological materials from renewable sources [4-6].

Vegetable oils consist of triglycerides which determine physical and chemical properties of the oil. Triglycerides consist of glycerol with three fat acids. Triglyceride scheme is given in Fig. 1. Fat acids contained in triglyceride may be saturated and unsaturated. In this case (Fig. 1) triglyceride consists of saturated acids: saturated stearic, monounsaturated oleic and polyunsaturated linoleic. Exactly these fatty acids determine lubricating, oxidizing and temperature properties [7-10]. Fatty acids contained in the oils may be saturated, mono- and polyunsaturated.

Saturated fat acids in hydrocarbon chains do not have any double links (Fig. 1) therefore they are resistant to oxidation. They are desirable in lubricating materials for improving their oxidative stability However, when hydrocarbon links stretch; the fatty acids increase the temperature of mixture freezing. Compare: C12:0 (Lauric) fat acid whose freezing temperature is about 44°C and C20:0 (Arachidic) who's freezing temperature is 76°C. It is stated that high freezing temperatures are influenced by long, straight hydrocarbon links capable of occupying very close interposition. In the light of it, fatty acids in lubricating materials operating at low temperatures are unwanted [7, 10].

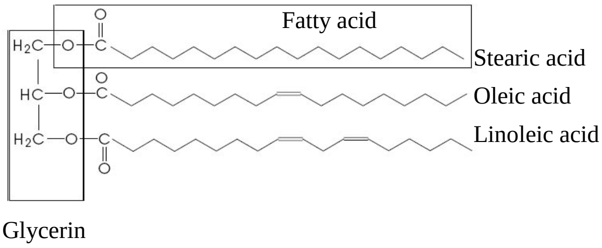


Fig. 1 Schema of typical triglyceride [10]

In addition to oxidative stability saturated fat acids have one more positive property ensuring the limiting lubrication of friction surfaces. Stearic fatty acid contained in palm oil methyl ester is known to constitute on the friction surface the adsorption layer of polar molecules which reliably separates the interactive surfaces [7]. In estimating temperature stability, greater unsaturation always reduces the freezing temperature, and it is due to the geometric structure of unsaturated fat acids.

CIS double link makes fatty acids molecules coil. The greater is the number of CIS double links, the greater deformation of a fatty acid molecule appears. Deformation minimizes the potential of the atoms to distribute closely i.e. to crystallize. Thus, molecules occupying larger volume remain in the liquid form up to the comparatively low temperatures. Compare: the freezing point of oleic C18:1 acid is about 4°C while that of linoleic C18:3 is -11°C, and the freezing point of arachidonic C20:4 is only -50°C [7].

An important property of plastic lubricants is their ability to remain in a friction couple during its operation. It is greatly influenced by both lubricating material and thickener. External mechanical (load, movement speed) and thermal effects have an impact on changes in the lubricant structure and its destruction which determine substantially its mechanical as well as tribological properties. Owing to these factors the thickener texture may be decomposed, the lubricant colloidal structure disrupted and friction surfaces will not be separated from each other, thus friction losses and wear will increase [4, 11].

Friction and wear in the machine elements consume a great part of the energy required. It depends on the properties of the lubricant and acting surfaces as well. Various surface treatment techniques and specific lubricants are suggested [12, 13].

The objective of this work is to investigate the impact of monoglycerols, stearic and oleic acids on tribological and plastic properties of the greases of rapeseed oil (RO) and lard (L).

2. Tested materials

Refined rapeseed oil (RO) and lard (L) and mixtures obtained by modifying with monoglycerols (MG), stearin (SA) and olein acids (OA) were tested. The amount of MG in rapeseed oil and lard was 10 and 20%, respectively, while o SA and OA – 2 % (according to mass).

Monoglycerides are glycerides containing one sort of fat. They are usually used as emulsifiers and stabilizers and as thickeners for increasing consistence [9, 13, 14]. Mixtures were stirred with magnetic blender TK 22. The obtained results were compared to commercial plastic lubricant (reference). High quality universal plastic lubricant with molybdenum disulfide additives for lubrication of various automobile units was taken as reference.

3. Experimental procedures

Penetration was determined according to ASTM D 217-97. A 102.5 g weight penetration cone was used.

A four-ball type tribotester was used to perform tribological tests. The balls of 12.7 mm diameter were made of 100Cr6 bearing steel ($E = 21.98\ 10^4$ MPa; $\nu = 0.3$; 63-66 HRC). The testing procedure was adapted from the standard DIN 51 350, Part 3 [15].

A test oil sample of 22 cm^3 was poured into the sample compartment fully submerging stationary balls. Under the applied load of 150 N and 300 N and the rotation speed of 1420 rpm, the machine was run for 1 hour. Prior to each experiment, all the appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and test balls were washed in an ultrasonic bath with hydrocarbon solvents, and then dried.

The wear scar diameter on three stationary balls was measured with an optical microscope. The results were recorded and reported in millimeters as an average of the wear scar diameter (WSD) of three balls. During the test the friction moment between the balls and the temperature change of the oil sample were recorded.

4. Results and discussion

Results of penetration measurements are given in Table. By modifying rapeseed oil with monoglycerides its consistence was increased up to 00 NLGI class. Having additionally poured stearic or oleic acid, the lubricant consistence increased up to 0 NLGI class. 00 and 0 classes correspond to the consistence of lubricants used for lubricating gearwheels in central lubricating systems.

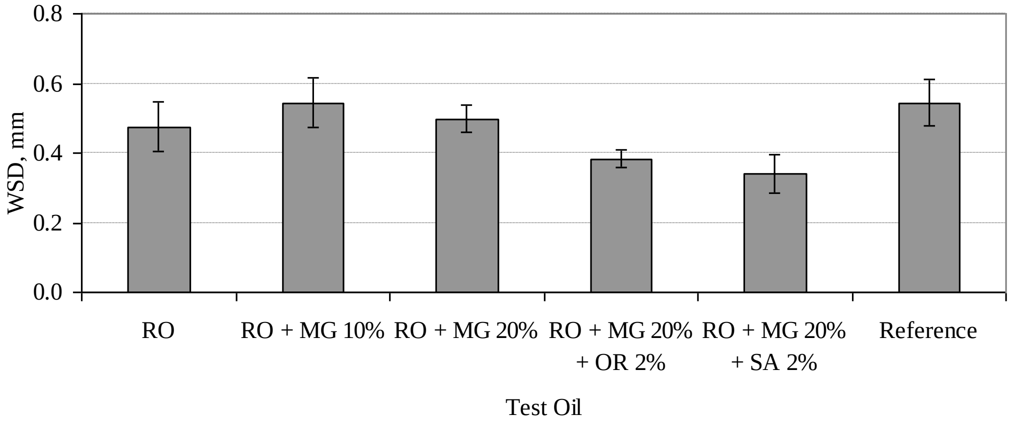
Results of wear analysis are given in Figs. 2 and 3 when lubricating with rapeseed oil and lard and after modifying them with stearic and oleic acids and monoglycerides. The diagrams show that modification with stearic and oleic acids and monoglycerides improved the antiwear properties of the lubricants. Modification of rapeseed oil and lard only with monoglycerides had no significant effect on anti-wear characteristics. Only rapeseed oil modified with 10 % monoglycerides stands out when the wear trace diameter increased 1.1 times comparing to that of pure rapeseed oil. The biggest antiwear efficiency was reached by modifying rapeseed oil and lard with monoglycerides (20%) and stearic acid (2%). Comparing the ball wear of pure lard and rapeseed oil to the modified lubricants the difference is evident – after modification the wear decreased 1.4 times. The modified lard and rapeseed oil have shown similar results as the reference oil. The reason may lie in stearic and oleic fat acids. They are attributed to polar molecules which make up an absorption layer. Oleic acid is known as an additive for improving lubricating properties of rapeseed oil, this acid making favorable conditions to formation of the limiting oil layer. During the experimental work under larger load (300 N, contact load 1325 MPa) and lubricating with rapeseed oil modified with monoglycerides (20%) and stearic acid (2%), the ball wear was 1.3 times greater than that when it was lubricated with modified lard. Wear resistance of modified lard was close to that of the reference oil. It testifies good antiwear characteristics of modified lard.

Different images of traces have been observed when analyzing the worn surfaces with an optical microscope. On the picture of the wear trace surface when pure lard was used (Fig. 4, a) many small scars are seen. The situation changes when monoglycerides (20%) (Fig. 4, b) are added – the number of scars substantially decrease and distinct relieves appear on the trace surface. With another addition of 2 of oleic acid there are less scars and trace relief becomes more distinct. These changes may occur when the microhardness of the deforming surface decreases because of impact of fat acids. The microhardness in wear trace is 8.25 GPa (at 5.1 mN loading) when using the lard. The modification of the lard with 20% monoglycerides and 2% oleic acid reduces the microhardness up to 5.76 GPa.

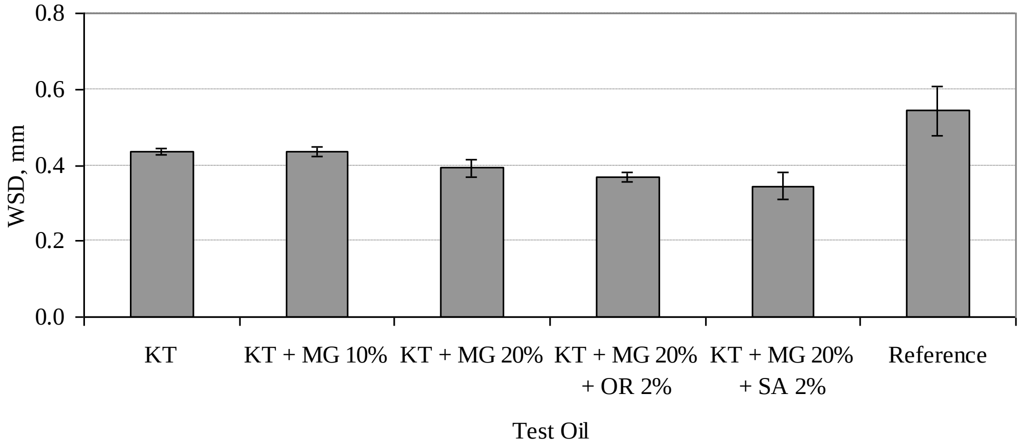
Table

The penetration number of tested materials (according to ASTM D 217 – 97)

Tested materials	RO + MG 20 %	RO + MG 20 % + OA2 %	RO + MG 20 % + SA 2 %	L	L + MG 10 %	L + MG 20 %	L + MG 20 % + OA 2 %	L + MG 20 % + SA 2 %	Reference
NLGI class	00	0	0	1	2	4	2	2	3
Penetration at 25ºC	400–430	355-385	355-385	310-340	265-295	175-205	265-295	265-295	220-250



a



b

Fig. 2 Wear of the specimens when experimenting with additives modified: a) rapeseed oil, b) lard (load 150 N, contact load 1050 MPa)

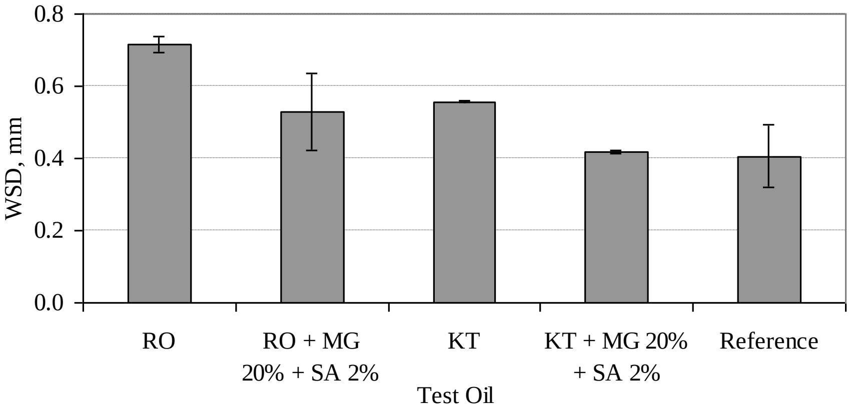
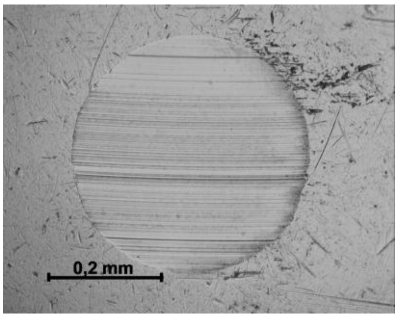


Fig. 3 Wear of the specimens when experimenting with additives modified rapeseed oil and lard, (load 300 N, contact load 1325 MPa)

It is likely to be Rebinder's effect (decrease in strength of the absorption surface layer). Compared to the reference oil (Fig. 4, e) the wear traces at modified lard (Fig. 4, b, c, d) are significantly smaller.

In Fig. 5 the images of wear traces which appear when lubricating with modified lard and rapeseed oil are presented. They are obtained with SEM microscope. The boundaries of wear traces indicate that the wear was so negligible that the traces of the ball surface treatment remained in the wear zone. It testifies about especially good wear resistance characteristics of these materials.

Diagrams of variation of the friction moments during experimentation are given in Fig. 6. They demonstrate that modification of rapeseed oil and lard with monoglycerides (MG) and stearic acid (SA) considerably (1.5 times) reduces the average friction moment. It should be noted that modification with MG and SA, besides the reduction in friction losses, substantially changes the friction moments variation during the experiments. When testing pure RO under 150 N load, the friction moment increases insignificantly and after three quarters of the testing time the friction moment suddenly increases 1.5 times.



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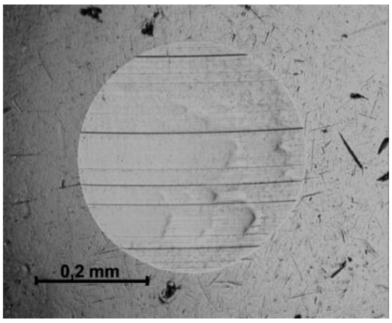

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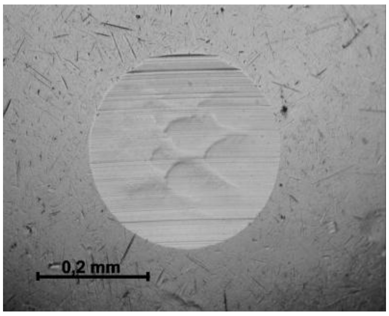

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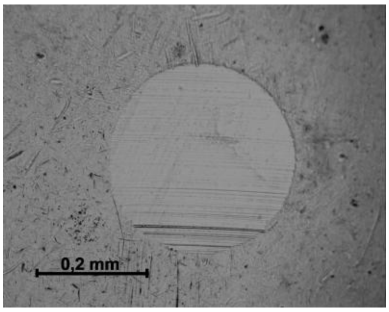

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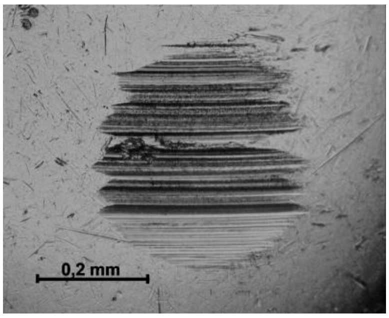
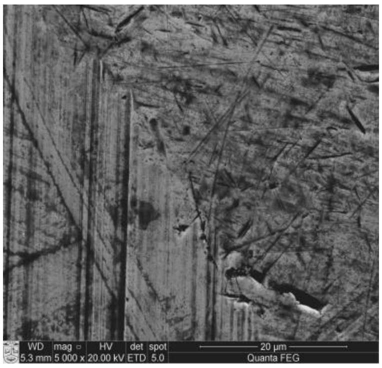


e

Fig. 4 Optical images of wear traces of balls lubricated with L (a), L+MG 20 % (b), L+MG 20 % + OR 2 % (c), L+MG 20 % + SA 2 % (d), reference (e) (150 N load)



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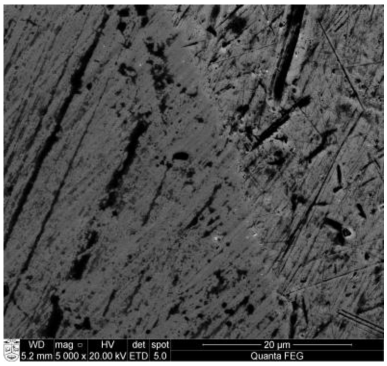

b

Fig. 5 Images of wear traces of balls lubricated with L + MG 20 % + OR 2 % (a), RA + MG 20 % + OR 2 % (b), obtained by SEM (150 N load)

When testing pure lard, the increase in friction moment begins sooner, namely, in the first third of the testing time. Having increased by 40%, it remains stable. While testing RO at 300 N load, the increase in friction moment begins earlier and later it stabilizes. The stable friction moment during the whole testing period is typical for the lard, but it is greater than testing RO. Having modified RO and L with monoglycerides and stearic acid, the friction moment is decreasing during the whole testing period. When testing the modified RO and L under bigger (i.e. 300 N load), the variation of the friction moment is analogous to the lower load, whereas a greater initial (static) friction moment is typical for modified rapeseed oil and not for modified lard (100 mNm and 75 mNm, respectively). The decrease in friction moment and its greater instability during testing is typical for the reference oil and the average friction moment is greater than testing both modified RO and modified lard.

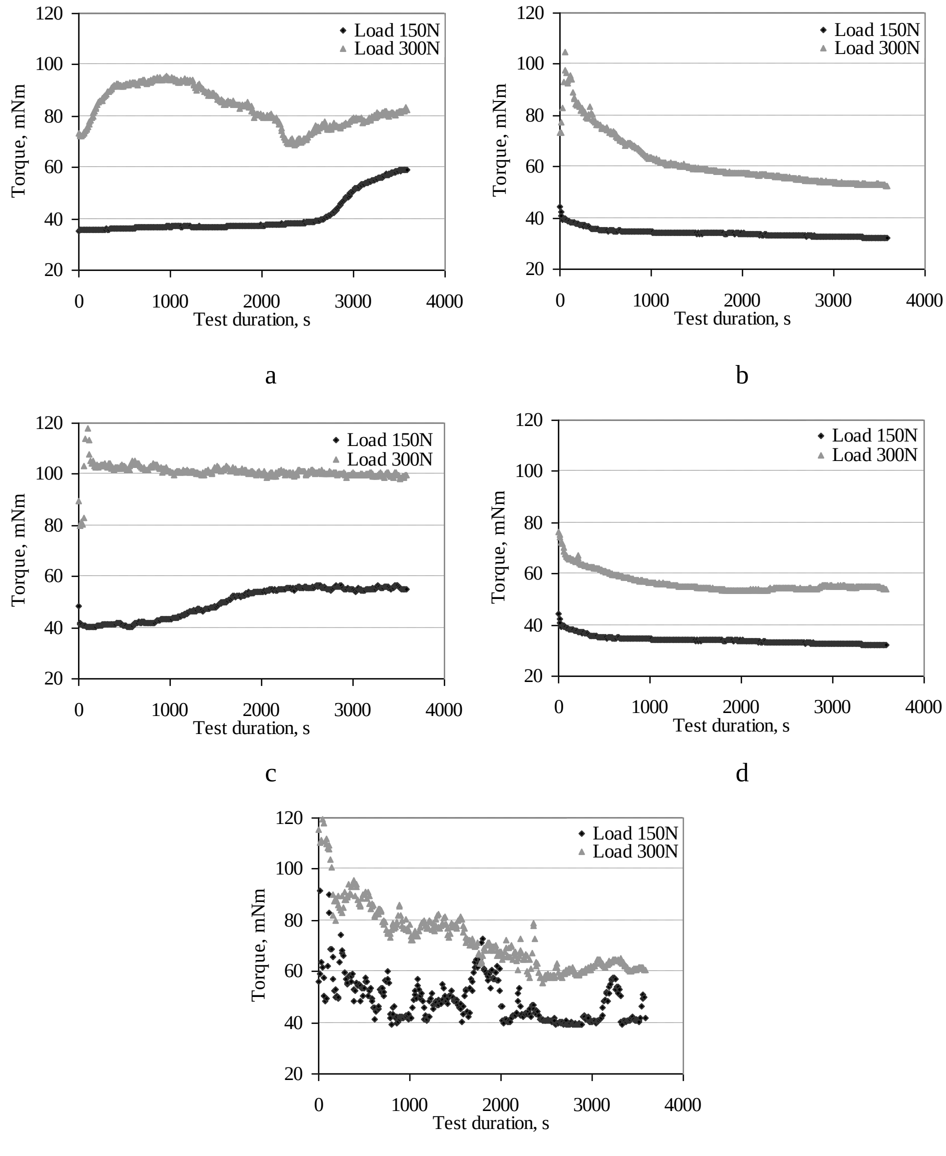

Fig. 6 Diagrams of friction moment during the tests under 150 N (contact load 1050 MPa) and 300 N load (contact load 1325 MPa): a – RO, b – RO + MG 20 % SA 2 %, c – L, d – L + MG 20 % SA 2 %, e – Reference

5. Conclusions

1. Concentration of monoglycerides has a direct impact on the consistence of both rapeseed oil and lard. Additional modification with stearic and oleic acid (2%) increases the rapeseed oil consistency, but decreases that of lard. It testifies to different interaction of these acids with the basic lubricating material.

2. When testing at 150 N loads, 10 % monoglyceride additive has no impact on wear resistance characteristics of lard but increase the wear at rapeseed lubricants. Under this load the best characteristics are demonstrated by the compositions consisting of basic lubricating material (RO or L) with 20% monoglycerides and 2% stearic acid.

3. When testing at 300 N loads, the best antiwear characteristics are demonstrated by the lard modified with 20 % monoglycerides and 2% stearic acid. Wear resistance characteristics of this lubricating material are close to those of the reference plastic lubricant.

4. Modification of rapeseed oil and lard with monoglycerides and stearic acid decreases the average friction moment (about 1.5 times) and also changes the friction moment variation - it tended to decrease during testing. The average friction moment of modified rapeseed oil and lard is significantly lower than lubricating with reference oil.

5. Decrease in friction losses and wear of lubricating compositions of basic material (RO or L), monoglycerides (20%) and stearic acid (2%) may be explained by strength decrease in the adsorption layer (Rebinder's effect).

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RAPSŲ ALIEJAUS IR KAULIŲ TAUKŲ MODIFIKAVIMAS MONOGLICERIDAIS IR LAISVOSIOMIS RIEBALŲ RŪGŠTIMIS

R e z i u m ė

Darbo tikslas buvo ištirti monogliceridų, stearino ir oleino rūgščių įtaką tribologinėms bei plastinėms rapsų aliejaus ir kiaulių taukų savybėms. Tyrimai atlikti standartiniu keturių rutulių metodu, naudotos 150 ir 300 N apkrovos. Tyrimų rezultatai parodė, kad, naudojant monogliceridus kaip tirštiklį, galima padidinti rapsų aliejaus ir kiaulių taukų plastiškumą, atitinkantį įvairias plastinių tepalų konsistencijos klases. Tribologiniai tyrimai parodė geras jų dilimo slopinimo ir trinties nuostolių mažinimo savybes. Išskirtinis kompozicijų, sudarytų iš rapsų aliejaus arba kiaulių taukų, modifikuotų monogliceridais bei stearino rūgštimi, pranašumas yra tai, kad jas naudojant trinties momentas bandymų metu turi tendenciją mažėti.

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MODIFICATION OF RAPESEED OIL AND LARD BY MONOGLYCERIDES AND FREE FATTY ACIDS

S u m m a r y

The objective of this work is to investigate the impact of monoglycerols, stearin and olein acids on tribological and plastic properties of the greases of rapeseed oil and lard. A four-ball type tribotester was used to perform tribological tests under the 150 and 300 N load. The test results show that the use of monoglycerides could increase the consistence of both rapeseed oil and lard according to the different consistence categories of greases. Tribological tests presented good properties of such lubricants to decrease the wear and friction. Special advantage of rapeseed oil and lard greases modified by stearin and olein acid is the ability to change the friction coefficient during the tests – it has the trend to decrease.

Keywords: rapeseed oil, lard, monoglycerides, free fatty acids.

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