Boris Kržan, Jože Vižintin

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TRIBOLOŠKA SVOJSTVA MAZIVA IZ OBNOVLJIVIH IZVORA

Sažetak

Biljna ulja i životinjske masti već se godinama koriste kao maziva. Otkrićem nafte i dostupnošću jeftinih ulja, alternative su postale neprivlačne te su ostavljene po strani. Posljednjih godina povećana pozornost javnosti i ekološka svijest potakle su razvoj velikog broja maziva koja su lako biološki razgradljiva s obzirom na više međunarodno priznatih metoda ispitivanja, te koja se odlikuju niskim stupnjem otrovnosti s obzirom na vodne organizme. Najvažnija osnovna sirovina za formulacije ekološki prilagođenih maziva su biljna ulja, kao i njihovi modificirani esteri.

U radu su ispitana dva tipična estera i dvije formulacije napravljene iz esterne uljne baze, zajedno s odabranom mješavinom aditiva, i to s obzirom na oksidacijsku stabilnost i tribološko ponašanje.

Čak i mineralno ulje i sintetički ester koji sadržava potpuno zasićene masne kiseline pokazali su se stabilniji glede oksidacijske razgradnje. Formulacija s nezasićenim esterom pokazala je bolje tribološko ponašanje kod umjerenih opterećenja. Rezultati upućuju na zaključak da je moguće povezati dugi vijek primjene s visokom razinom radnih svojstava, što je korisno za okoliš, poljoprivredu i potrošače.

1. Uvod

Posljednjih godina opažamo ponovno zanimanje za proizvode na temelju obnovljivih i pridobivih sirovina, poput biljnih ulja i iz njih proizvedenih estera. Tri su glavna razloga za to zanimanje[1]:

- Biljna su ulja lako pridobiva iz obnovljivih izvora:

Biljna su ulja po svojoj kemijskoj naravi dugolančani masnokiselinski triesteri glicerola te osiguravaju većinu poželjih svojstava maziva, poput dobrog graničnog podmazivanja, visokog indeksa viskoznosti, visokog plamišta i niske isparivosti.

Proizvodnja biljnih ulja omogućuje puni potencijal prirodne sinteze, putem energije sunca koja se pritom koristi, tvoreći ciklus u kojem nema neto ispuštanja ugljičnog dioksida.

- Visoki stupanj prekomjerne proizvodnje biljaka čije se sjemenje može koristiti za proizvodnju ulja u industrijskim razmjerima:

U razvijenim zemljama kapaciteti proizvodnje hrane premašuju njezinu potrošnju, omogućujući tako korištenje dijela proizvedenih količina u tehničke svrhe. Svjetska potrošnja prirodnih ulja u 2000. godini je procijenjena na 102 Mt (milijuna tona), od čega je 83 Mt bilo namijenjeno ljudskoj prehrani, 14 Mt u tehničke svrhe, dok je preostalih 5 Mt bilo namijenjeno prehrani životinja. Kao što je vidljivo iz tablice 1, ukupna svjetska proizvodnja biljnih ulja ubrzano raste, približno se udvostručujući svakih 25 godina. Najčešće su korištena biljna ulja sojino (Sj. Amerika), palmino i palmine koštice (JI Azija, J. Amerika), repičino (Kina, Indija, Europa, Kanada) te suncokretovo (J. i Sj. Amerika, Europa). Zasad ove glavne četiri vrste uljarica pokrivaju oko 77 % svjetske proizvodnje biljnog ulja.

U proteklih se nekoliko godina cijena biljnoga ulja znatno smanjila, poradi čega se sada neke cijene biljnih ulja mogu usporediti s onima mineralnih. Međutim, korištenje običnih biljnih ulja je ograničeno niskom toplinskom i oksidacijskom stabilnošću. Maziva na temelju biljnih ulja pogodna su samo za manje opterećene primjene, gdje temperature ne prelaze
70 °C. Za zahtjevnije su primjene bolji modificirani esteri koji se temelje na biljnim uljima. Obično se dobivaju putem reakcije masnih kiselina iz prirodnih ulja s petrokemijski dobivenim alkoholima [3,4].

Tablica 1: Procjena svjetske proizvodnje biljnih ulja u milijunima tona [2].

Biljka uljarica	1970. [mt]	1980. [mt]	1990. [mt]	2000. [mt]
Soja	6,0	15,0	16,0	30,0
Palma i palmina koštica	2,0	4,5	13,0	22,0
Repa	2,0	4,0	9,0	15,0
Suncokret	2,0	4,0	8,0	12,0
Međuzbroj	**12,0**	**27,5**	**46.0**	**79,0**
Kokos	2,4	3,2	3,.0	4,0
Pamuk	2.5	3,2	4,0	4,0
Maslina	2,0	2,0	2,0	2,5
Ostalo	16,1	24,1	25,0	12,5
Ukupno svijet	**35,0**	**60,0**	**80,0**	**102,0**

- Pojačana ekološka svijest rezultirala je strogim zakonodavstvom na području zaštite okoliša, odnedavna uvedenim u brojnim zemljama, u smislu smanjenja opterećenja okoliša izazvana mazivima:

Procijenjeno je kako se između 13 % (EU) i 32 % (SAD) ukupne količine maziva vraća u okoliš, manje ili više izmijenjenih svojstava i izgleda [5]. Godine 1975. Švicarska je donijela prvi propis kojim se nalaže korištenje biorazgradljivih dvotaktnih motornih ulja na jezerima. U proteklih trideset godina doneseni su brojni slični propisi u nekoliko europskih zemalja, kako bi se nametnula uporaba ekološki prilagođenih ulja za lance motornih pila, ulja protiv plijesni, odnosno, hidrauličkih tekućina. Uz navedene propise, neke zemlje podupiru ovakav razvoj događaja putem fiskalnih poticaja, poput propisa VAMIL u Nizozemskoj te incijative Pflanzenöl u Njemačkoj [6].

U radu smo ispitali dva tipična maziva na temelju estera, s obzirom na njihovu oksidacijsku stabilnost te tribološko ponašanje. Svojstva formulacija biljnih ulja obilno su dokumentirana u ranijim radovima te ih ovdje nećemo ponavljati [7,8].

2. Priprava uzoraka

2.1 Uzorci ulja

Bazno ulje za formulaciju Bio 1 bio je trimetilolpropan (TMP)–trioleat, trenutačno najviše korištena bazna sirovina za ekološki prilagođene hidrauličke tekućine. TMP-trioleat pripravljen za ispitivanje sastojao se od 8 % zasićenih, 62 % mono-nezasićenih i 30 % poli-nezasićenih lanaca masnih kiselina. Dok su masne kiseline u potpunosti pridobivene iz obnovljivih izvora, korišteni su alkoholi nastali petrokemijskim postupkom.

Druga formulacija estera Bio 2 temeljila se na složenom zasićenom esteru (CEs). Složeni se ester sastojao od više funkcionalnoga sintetičkoga alkohola, nekih petrokemijski pridobivenih di-kiselina te nekih kratkolančanih (C8 – C10) masnih kiselina iz prirodnih izvora.

Tablica 2: Ispitna maziva

Oznaka ulja	Struktura	Viskoznost pri 40°C [mm²/s]	IV	Biorazgrad-ljivost CEC L33-A-95 [%]	Otrovnost OECD 202 [EC50(mg/l)]
Vrste baznih ulja					
TMP	Nezasićeni TMP-trioleat	46,9	192		
CEs	Zasićeni složeni ester	45,7	153		
Ispitne formulacije maziva					
Bio 1	TMP + aditivi	47,5	186	99	> 1000
Bio 2	CEs + aditivi	46,7	147	76	> 1000
Min 1	Mineralna UTTO formulacija	57,6	143	35	10

EP aditiv za obje formulacije na temelju estera bio je aminski neutralizirani ester fosforne kiseline; uobičajeni EP aditiv opće namjene. Aditiv protiv trošenja bio je dialkil ditiofosfat ester. Antioksidacijski aditiv VANLUBE temeljen na organskim amino spojevima također je uključen u aditivni sustav. Ovaj aditiv je razvijen da osigura odličnu djelotvornost kod visokih temperatura u sintetičkim mazivima.

Obje esterne formulacije Bio 1 i Bio 2 bile su biorazgradljive i niskoga stupnja otrovnosti, tablica 2. Svojstva formuliranih ulja na temelju estera Bio 1 i Bio 2 uspoređena su s konvencionalnim iz nafte pridobivenim univerzalnim zupčaničkim uljem za traktore (UTTO), dostupnim na tržištu te označenim kao Min 1.

3. Ispitna oprema i postupci

3.1 Oksidacijska stabilnost

Oksidacijsko djelovanje ispitnih ulja prikazano je laboratorijskim ispitivanjem nalik na ono Baader, prema DIN 51 554, 3 dio. Ispitna ulja su odstajala šest dana u staklenoj posudi pri konstantoj temperaturi od 95 °C. Stanje je ulja praćeno mjerenjima kinematičke viskoznosti nakon 72 i 96 sati.

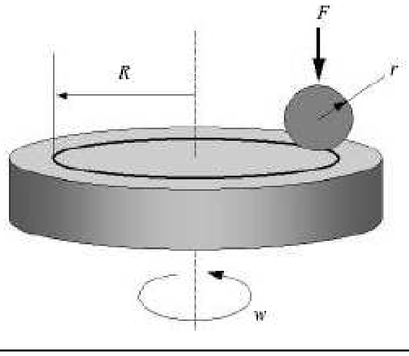
3.2 Ispitivanje trenja i trošenja

Ispitivanje kliznog trošenja provedeno je putem ispitnog uređaja kugle-na-disku, sl. 1. Ispitna se oprema sastojala od visoko ulaštene čelične kugle i rotirajućeg čeličnog diska. Kugle su bile od čelika DIN 100Cr6, 12,7 mm u promjeru, čvrstoće 8,3 GPa i hrapavosti 0,02 μm. Diskovi su bili od čelika DIN 100Cr6, 24 mm vanjskoga promjera, tvrdoće 8,3 GPa i hrapavosti 0,06 μm. Kugla je stavljena pod opterećenje od 10 N, što je izazvalo nominalni pritisak od 0,86 GPa. Kugla i disk u potpunosti su uronjeni u ispitno ulje u komori za uzorke. Sva su ispitivanja izvršena pri sobnoj temperaturi. Uz pomoć odgovarajućeg nadziranja rotacije diska, postignute su efektivne brzine klizanja od 0,004 m/s do 0,24 m/s. Ukupna je klizna brzina iznosila 1750 m. Koeficijent trenja izmjeren je za vrijeme ispitivanja, dok je trošenje utvrđeno nakon ispitivanja, putem profilometrije. Tragovi trošenja na disku i kugli izmjereni su optičkim mikroskopom. Koeficijent trošenja izračunat je putem sljedeće formule:

$$Wear\ coefficient = \frac{(Final\ Worn\ Volume)}{(Load)x(Sliding\ Dis\tan ce)} \qquad (1)$$

/Koeficijent trošenja; konačni obujam istrošenosti; opterećenje; put klizanja/

Slika 1: Konfiguracija kugla-na-disku



Režimi podmazivanja uglavnom su ilustrirani Stribeckovom krivuljom, kada se trenje prikazuje s obzirom na parametar, uključujući brzinu klizanja, viskoznost ulja i opterećenje. Još jedan parametar koji se često koristi kako bi se približili uvjeti podmazivanja jest omjer lambda ili specifična debljina sloja izražena kao [9]:

$$Lambda\ \ ratio = \frac{h_{\min}}{\sqrt{(R_{q,a}^2 + R_{q,b}^2)}}$$

/omjer lambda/ (2)

pri čemu je h_{min} minimalna debljina mazivoga sloja u doticaju, a R_q rms hrapavost površine za uzorke a i b.

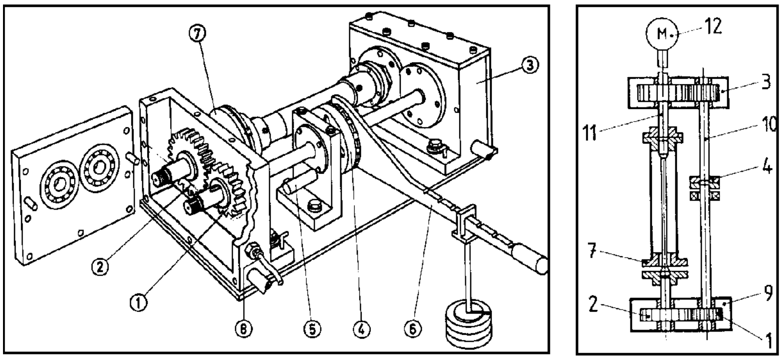
Teorijski, vrijednosti omjera lambda iznad 3 otkrivaju elastohidrodinamično podmazivanje, dok one ispod 1 ukazuju na granično podmazivanje, a između 1 i 3 miješani režim podmazivanja. Miješani uvjeti podmazivanja vrijede samo kod dostatno vielikih kliznih brzina te sve dotle dok hrapavost površine nije pod utjecajem trošenja. Ispitivanje trošenja u ovoj je studiji provedeno u intervalu omjera lambda između 0,1 i 1,6 te u tom smislu uglavnom u graničnome, a djelomice u miješanom režimu podmazivanja.

3.3 Ispitivanje zupčanika

Učinak s obzirom na struganje procijenjen je na FZG ispitnom uređaju u okviru normiranog ispitnog postupka, u skladu s ISO DIS 14635-1. Kao što je vidljivo iz slike 2, ispitni zupčanici, kao i oni radni, povezani su dvjema osovinama. Jedna je podijeljena na dva dijela, a između se nalazi pritezna spojka. Polovica se spojke za postizanje opterećenja među bokovima zuba može učvrstiti za postolje uz pomoć blokirajuće igle, dok se druga okreće, primjerice, uz pomoć poluge. Nakon što se spojka osigura, opterećenje se može ukloniti te se osovina otpušta. Tako se statični moment vrtnje primjenjuje na sustav pokretan elektromotorom. Ispitni se zupčanici stavljaju pod opterećenje postupno, u 12 koraka, između Hertzova opterećenja od 150 do 1800 N/mm^2. Svaki stupanj opterećenja traje 15 minuta pri konstantnoj brzini osovine zupčanika od 1450 o/min te početnoj temperaturi ulja od 90℃, pri uvjetima podmazivanja uranjanjem bez hlađenja. Bokovi ispitnih zupčanika pregledavaju se vizualnim putem nakon svakog stupnja opterećenja, kako bi se procijenila kumulativna šteta pojedinih tragova oštećenja. Stupanj opterećenja koji izaziva prestanak rada nastupa kada bokovi svih zubaca zupčaničkog kola pokazuju zbrojenu ukupnu širinu oštećenih područja koja je jednaka, ili pak premašuje širinu pojedinoga zupca. Ispitivanje vrijedi jedino ukoliko je gubitak težine kola ≤ 20 mg.

Ispitni zupčanici su standardni čelni zupčanici tipa FZG. Zupčanici tipa A projektirani su s velikom modifikacijom profila, što pojačava njihovu osjetljivost na prestanak rada uzrokovan adhezivnim trošenjem. Izrađeni su od čelika DIN 20 MnCr5, površinski kaljeni. Tvrdoća površine nakon popuštanja iznosila je 60 do 62 HRC, a debljina kaljenog sloja 0,6 do 0,9 mm. Hrapavost površine iznosila je 0,35 mikrona za veći, a 0,30 za manji zupčanik.

Slika 2: Shematski prikaz FZG ispitnog zupčaničkog sklopa



1	mali ispitni zupčanik	5	igla za učvršćivanje	9	ispitna zupčanička kutija
2	veliki ispitni zupčanik	6	poluga i utezi opterećenja	10	osovina 1
3	pogonska zupčanička kutija	7	spojka za mjerenje momenta vrtnje	11	osovina 2
4	spojka	8	temperaturno osjetilo	12	elektromotor

4. Rezultati ispitivanja i rasprava

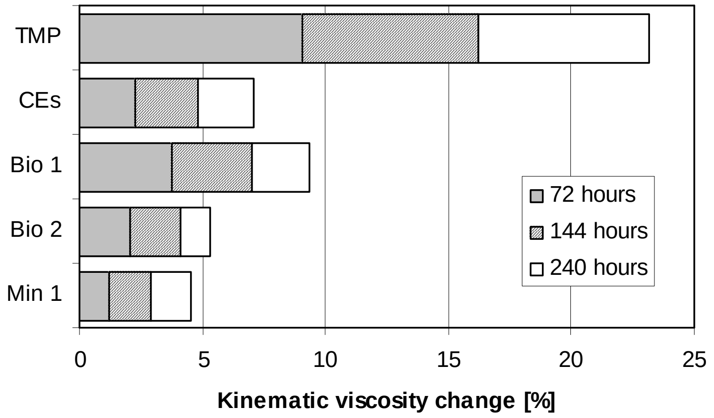
4.1 Oksidacijska stabilnost

Kisik iz zraka reagira s najreaktivnijim mjestom u molekuli maziva. U slučaju nezasićenih TMP, to je na vezi ugljika s vodikom, tik do dvostruke veze unutar ugljičnoga lanca. Iz slike 3 je vidljivo kako je oksidacijska stabilnost TMP daleko niža od one složenih estera CEs, gdje su dvostruke veze u kiselinskoj skupini u potpunosti eliminirane. Nakon prva 72 sata kod 95 °C, porast kinematičke viskoznosti nezasićenih TMP je 22 % viši od porasta viskoznosti zasićenih CEs na kraju ispitivanja od 240 sati. Slijedi kako niža nezasićenost i manja duljina kiselinskoga lanca mogu osjetno poboljšati otpornost na oksidaciju.

Još jedan način poboljšanja oksidacijske stabilnosti jest aditivacija. Antioksidansi usporavaju postupak starenja ulja, radi čega je povećanje viskoznosti formulacija Bio 1 i Bio 2 niže u usporedbi s bezaditivnim uljima TMP i CEs. Bolja otpornost na oksidaciju osobito je vidljiva u usporedbi s rezultatima za TMP i odgovarajuću formulaciju Bio 1, koja predstavlja mješavinu TMP i aditiva. U slučaju CEs i odgovarajuće formulacije Bio 2, poboljšanje svojstava s obzirom na oksidaciju nije toliko vidljivo. Međutim, oksidacijska stabilnost zasićenih složenih estera CEs viša je u usporedbi s onom formulacije Bio 1, čak i uz pojačanje antioksidantima. Svojstva baznog ulja očito imaju veći utjecaj na otpornost spram oksidacije nego aditivi.

Najbolju oksidacijsku stabilnost u ovom ispitivanju pruža mineralno ulje Min 1, osobito poradi naročito niskog porasta viskoznosti u prva 72 sata. Stupanj porasta viskoznosti nakon 72 sata usporediv je s formulacijom Bio 2.

Slika 3: Oksidacijska stabilnost ispitnih ulja



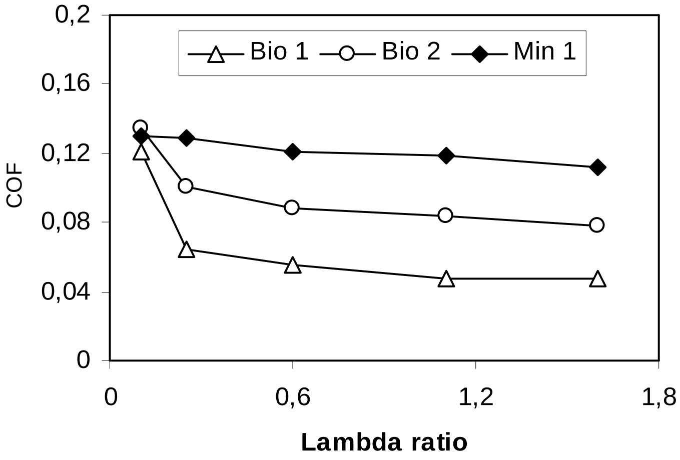
/Promjena kinematičke viskoznosti/

4.2 Mjerenje trenja i trošenja

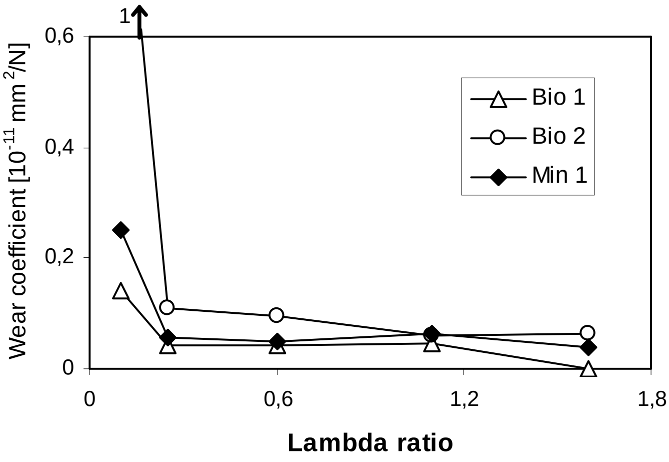
Slika 4 prikazuje trag trenja za formulirana ispitna ulja. Pri vrlo niskom omjeru lambda i niskoj kliznoj brzini, koeficijent trenja (COF) gotovo je identičan za sva ispitna ulja. Međutim, budući da omjer lambda raste iznad vrijednosti od 0,25, očigledna je velika razlika u vrijednosti koeficijenta trenja među uljima. Najveće trenje izaziva ulje Min 1, dok je koeficijent trenja za formulacije na temelju estera ispod 0,1. Formulacija Bio 1 s nezasićenim masnim kiselinama rezultirala je vrlo niskim koeficijentom trenja od približno 0,05. Nezasićeni ester sadrži organske ravne dugolančane spojeve s polarnim krajnjim skupinama. Navedene polarne krajnje skupine bivaju adsorbirane na metalnu površinu, čime se smanjuje površinska sila i izaziva smanjenje koeficijenta trenja [7].

Koeficijent trošenja prikazan je na slici 5. Sva ispitna ulja pokazuju iste tendencije visokog koeficijenta trošenja za omjer lambda do 0,25, kao i značajno niži stupanj trošenja pri njegovim višim vrijednostima. Krivulje imaju isti opći oblik, no formulacija Bio 2 izaziva najviše trošenja. Kod većih brzina, koeficijent trošenja je gotovo isti za sve ispitne formulacije. Međutim, rezultati pokazuju kako najbolju zaštitu protiv trošenja pruža formulacija Bio 1, koja se temelji na nezasićenom esteru. Nezasićeni esteri reagiraju brže od zasićenih, kao i od mineralnih ulja te imaju najviši sadržaj polarnih funkcionalnih skupina koje izazivaju fizičku i kemijsku interakciju s metalnim površinama u kliznom dodiru.

Slika 4: Učinak omjera lambda na koeficijent trenja



Slika 5: Učinak slojnog parametra na koeficijent trošenja

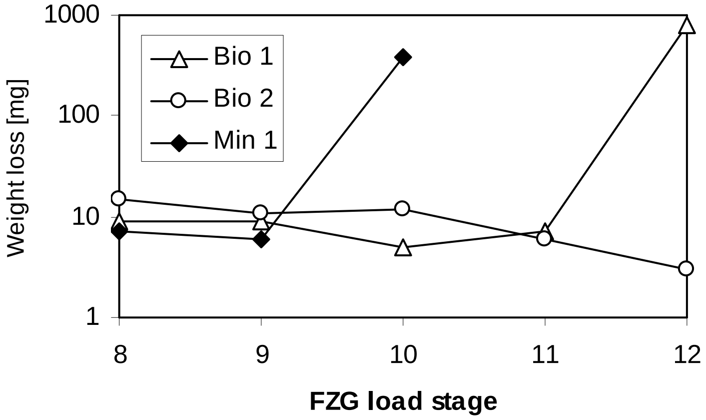


Formulacija temeljena na nezasićenom esteru Bio 1 izaziva manje trenja te posjeduje bolja svojstva protiv trošenja nego zasićena formulacija Bio 2. Polarne funkcionalne skupine u nezasićenoj molekuli ulja na temelju estera u sprezi s interakcijom ulje-aditiv-metal za vrijeme postupka trljanja metalnih površina mogu značajno poboljšati otpornost na trošenje, kao i podmazivanje u uvjetima iznimno visokog pritiska. Nezasićena mjesta brže reagiraju s dodirnim površinama te su se pokazala daleko učinkovitijima za smanjenje trenja i trošenja nego esteri sa zasićenim kiselinskim skupinama. Kratkolančani spojevi zasićenog estera Bio 2 bolji su za oksidacijsku stabilnost od dugolančanih, ali su zato manje učinkoviti u stvaranju zaštitna maziva sloja. Može se primijetiti kako se isti aditivni sustav koristi za obje formulacije temeljene na esteru.

4.3 Sposobnost podnošenja opterećenja zaribavanjem

Nastajanje štete izazvane zaribavanjem pod sve većim opterećenjem prikazano je na slici 6. Gubitak mase zupčaničkoga kola i zupčanika prvi je puta provjereno nakon stupnja opterećenja 8, pa stoga ova vrijednost predstavlja kumulativni zbroj prethodnih gubitaka težine. Nakon stupnja opterećenja 8, ispitni su zupčanici vagani nakon okončanja svakog stupnja opterećenja. Ako gubitak mase ispitnih zupčanika na pojedinom stupnju premašuje 20 mg, dosegnuta je razina štetnog opterećenja te se nerijetko može opaziti prekomjerno trošenje bokova zubaca zupčanika.

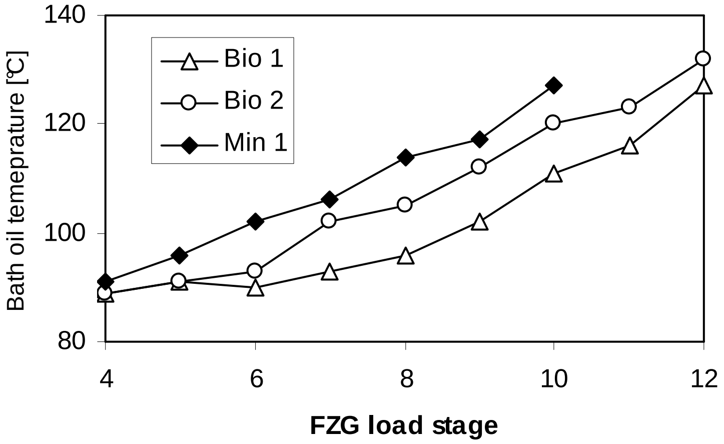
Slika 6: Gubitak mase ispitnih zupčanika



Ulje Min 1 prestaje djelovati kod FZG stupnja opterećenja 10 (1538 N/mm^2); ulje Bio 1 kod stupnja opterećenja 12 (1841 N/mm^2), dok je ulje Bio 2 kadro izdržati i veća opterećenja. Bio 2 može prenijeti opterećenja preko FZG stupnja opterećenja 12, bez prekomjerna zaribavanja, ali je stupanj trošenja 9 pritom najviši. Stupanj trošenja viši je također i u usporedbi s Bio 1 pri stupnju opterećenja 10. Pri ispitivanju kliznog trošenja, kao što je prikazano na slici 5, već je primijećeno kako zasićena složena esterna formulacija Bio 2 pokazuje najveći stupanj trošenja. Čini se kako polarnija i reaktivnija nezasićena formulacija Bio 1 pokazuje bolju zaštitu od trošenja pri umjerenim opterećenjima, dok je zasićeni kratkolančani masnokiselinski sastav baznog ulja Bio 2 primjereniji za visoka opterećenja.

Slika 7 prikazuje razvijanje temperature uljne kupke zabilježene pri kraju svakoga stupnja opterećenja. Od tri ispitna maziva, nezasićena esterna formulacija Bio 1 pokazuje najnižu temperaturu uljne kupke, što upućuje na najniži stupanj trenja pri dodiru. Navedeni rezultati u potpunosti potvrđuju opažanja vezana uz koeficijent trenja prikazana na slici 4, gdje je on zabilježen o ovisnosti o kliznoj brzini.

Slika 7: Temperatura uljne kupke nakon završetka stupnja opterećenja FZG



5. Zaključak

Na temelju ove studije moguće je stvoriti sljedeće zaključke:

- Oksidacijska stabilnost zasićene esterne formulacije daleko je bolja od one nezasićene. Čak i obogaćena antioksidantima, oksidacijska postignuća TMP-trioleatne formulacije ostaju poprilično slaba.
- Formulacije na osnovi estera izazivaju manje trenja od maziva mineralne osnove. Najniži koeficijent trenja pokazuje formulacija na osnovi nezasićenog TMP-trioleata. Ovi se rezultati u potpunosti podudaraju s mjerenjima temperature uljne kupke u zupčaničkome ispitivanju, opravdavajući tako niže temperature postignute formulacijama na osnovi estera.
- Formulacija na osnovi nezasićenih sintetičkih estera pokazuje najbolju zaštitu protiv trošenja, osobito pri niskim kliznim brzinama. Pri većim vrijednostima, koeficijent trenja približno je jednak za sve ispitne formulacije ulja.
- Kapacitet opterećenja zaribavanjem polarnije i reaktivnije formulacije na temelju TMP-trioleata uzrokovao je bolju zaštitu od trošenja pri umjerenim opterećenjima, dok se čini kako je sastav složenih estera zasićenih kratkolančanih masnih kiselina primjereniji za veća opterećenja.

TRIBOLOGICAL PROPERTIES OF LUBRICANTS DERIVED FROM RENEWABLE RESOURCES

Abstract

Vegetable oils and animal fats have been used as lubricants for many years. With the discovery of petroleum and the availability of inexpensive oils, alternatives became unattractive and were left by the wayside. In recent years, the increased public attention and the awareness of environment protection have stimulated the development of a vide variety of lubricants that are readily biodegradable in terms of one of the several internationally recognized test methods, and that have a low toxicity toward water organisms. The most important base stocks for environmentally adapted lubricants formulations are vegetable oils as well as modified vegetable oil esters.

In the present work, two typical esters and two formulations made from ester oil base along with a unique blend of additives were investigated with respect to their oxidative stability, and tribological behavior. Even mineral oil and synthetic ester containing fully saturated fatty acids have proven to be more stable against oxidative attack, unsaturated ester formulation exhibit better tribology performance at moderate loads. Results suggest that it is possible to combine high renewability and high technical performance, which should benefit the world’s environment, the agricultural community and the consumer.

1. Introduction

In recent years, a renewed interest has occurred on the products derived from renewable harvestable resources such as vegetable oils and esters produced from them. Three main reasons for the current interest are [1]:

- Vegetable oils can be readily extracted from renewable resources:

Vegetable oils are by their chemical nature long chain fatty acid triesters of glycerol and provide most of the desirable lubricant properties such as good boundary lubrication, high viscosity index, high flash point and low volatility. The production of vegetable oils provides the full potential of natural synthesis by means of energy from the sun is used and constitutes a cycle in which no net release of carbon dioxide occurs.

- Large overproduction of plants whose seeds could be used to produce oils on an industrial scale:

In developed countries, the possibilities of food production exceed food consumption, what enables to use part of the production for technical purposes. The world’s consumption of natural oils in 2000 has been estimated at 102 mt (million tonnes), of which 83 mt was for human consumption, 14 mt was “for technical uses”, and the remaining 5 mt was for animal feed. As seen from Tab 1, the total world’s production of vegetable oils is growing at a rapid pace of approximately doubling the volume for every 25 years. The most commonly used vegetable oils include soybean oil (North America), palm and palm kernel oil (SE Asia, South America), rapeseed oil (China, India, Europe, Canada) and sunflower oil (South and North America, Europe). At present, these major four oil crops account for about 77% of worldwide vegetable oil production.

In the past five years, the cost of vegetable oils is reduced considerably, making some vegetable oils prices also comparable to mineral oils. However, the use of simple vegetable oils has been limited by low thermal and oxidation stabilities. Lubricants based on vegetable oils are suited only to less stressed applications where temperatures do not exceed 70 °C. For more demanding applications, modified esters derived from vegetable oils have been preferred. They are typically made by reacting fatty acids obtained from natural oils with petrochemical derived alcohols [3,4].

Table 1: Estimated world production of vegetable oils in million tonnes [2].

Oilseed crop	1970 [mt]	1980 [mt]	1990 [mt]	2000 [mt]
Soya	6.0	15.0	16.0	30.0
Palm and palm kernel	2.0	4.5	13.0	22.0
Rape	2.0	4.0	9.0	15.0
Sunflower	2.0	4.0	8.0	12.0
Subtotal	**12.0**	**27.5**	**46.0**	**79.0**
Coconut	2.4	3.2	3.0	4.0
Cotton	2.5	3.2	4.0	4.0
Olive	2.0	2.0	2.0	2.5
Others	16.1	24.1	25.0	12.5
World total	**35.0**	**60.0**	**80.0**	**102.0**

- Increased environmental interest resulted in strict legislation and environmental policy, recently introduced in many countries, to reduce lubricant environmental load:

It has been estimated that between 13% (EU) and 32 % (USA) of all used lubricants return into the environment more or less changed in properties and appearance [5]. In 1975, Switzerland issued a first regulation imposing the use of biodegradable two-stroke engine oils on lakes. Over the last thirty years, a lot of similar regulations have been issued in several European countries to force the use of environmentally adapted chain saw oils, demoulding oils or hydraulic fluids. In addition to these regulations, some countries supported this evolution by fiscal incentives like the VAMIL regulation in Netherlands and Pflanzenöl-Initiative in Germany [6].

In the present work, two typical ester based lubricants were investigated with respect to their oxidative stability, and tribological behavior. The properties of vegetable oil formulations are well documented in earlier works and are not presented here [7,8].

2. Sample preparation

2.1 Oil samples

The base oil for formulation Bio 1 was trimethylolpropane (TMP)–trioleate, which is the most widely applied base stock for environmentally adapted hydraulic fluids at present. TMP-trioleate prepared for the test was composed of 8% saturated, 62% monounsaturated and 30% polyunsaturated fatty acid chains. While fatty acids were completely derived from renewable resources the alcohols used were from petrochemical origin.

The second ester formulation Bio 2 was based on saturated complex ester (CEs). Complex ester consisted of the multifunctional synthetic alcohol, some petrochemical derived di-acids and some shorter chain (C8 – C10) fatty acids from natural resources.

EP additive for both ester based formulations was an amine neutralized phosphoric acid ester; a common type of general purpose EP additive. The AW additive was a dialkyl ditiophosphate ester. VANLUBE antioxidant additive based on organic amine compounds was also included in the additive system. This additive is designed to provide excellent high temperature performance in synthetic based lubricants.

Both ester formulations Bio 1 and Bio 2 were biodegradable and low toxic, Table 2.

The properties of formulated ester based oils Bio 1 and Bio 2 were compared to the conventional petroleum derived universal tractor transmission oil (UTTO) from the market, labeled as Min 1.

Table 2. Test lubricants

Oil code	Structure	Viscosity at 40°C [mm^2/s]	IV	Biodegradability CEC L33-A-95 [%]	Toxicity OECD 202 [EC50(mg/l)]
Base oil types					
TMP	Unsaturated TMP-trioleate	46.9	192		
CEs	Saturated complex ester	45.7	153		
Test lubricant formulations					
Bio 1	TMP + additives	47.5	186	99	> 1000
Bio 2	CEs + additives	46.7	147	76	> 1000
Min 1	Mineral UTTO formulation	57.6	143	35	10

3. Test equipment and procedures

3.1 Oxidation stability

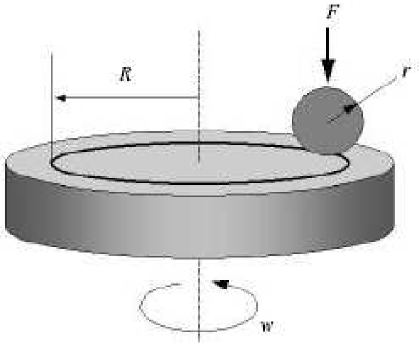
The oxidation performance of test oils has been demonstrated by a laboratory test similar to a Baader test according to DIN 51 554, Part 3. Test oils were aged for six days in a glass vessel at constant temperature of 95 ℃. The condition of the oils was monitored by measurements of kinematic viscosity on 72 and 96 hour periods.

3.2 Friction and wear test

Sliding wear tests were performed using a ball-on-disk wear tester, Fig. 1. The test apparatus was consisted of a highly polished steel ball and rotating steel disc. The balls were DIN 100Cr6 steel, 12.7 mm diameter, 8.3 GPa hardness and 0.02 μm roughness. The disks were DIN 100Cr6 steel, 24 mm outer diameter, 8.3 GPa hardness and 0.06 μm roughness. A load of 10 N was applied to the ball, which gave a nominal pressure of 0.86 GPa. The ball and the disc were completely immersed into the test oil in the sample chamber. All tests were carried out at room temperature. By appropriate control of the rotation of the disc, effective sliding speeds from 0.004 m/s to 0.24 m/s were achieved. The total sliding distance was 1750 m. The coefficient of friction was measured during the test, while wear was determined subsequent to the test by profilometry. The wear scar of disc and ball were measured with an optical microscope. The wear coefficient was calculated through a formula:

$$Wear\ \ coefficient = \frac{(Final\ \ Worn\ \ Volume)}{(Load)x(Sliding\ \ Dis\tan ce)} \tag{1}$$

Figure 1: Ball-on-disc configuration.



The lubrication regimes are mainly illustrated by the Stribeck curve, when the friction is plotted against the parameter including the sliding speed, oil viscosity and the load. Another parameter often used to approximate the lubrication conditions is the lambda ratio or specific film thickness expressed as [9]:

$$Lambda\ ratio = \frac{h_{\min}}{\sqrt{(R_{q,a}^2 + R_{q,b}^2)}} \qquad (2)$$

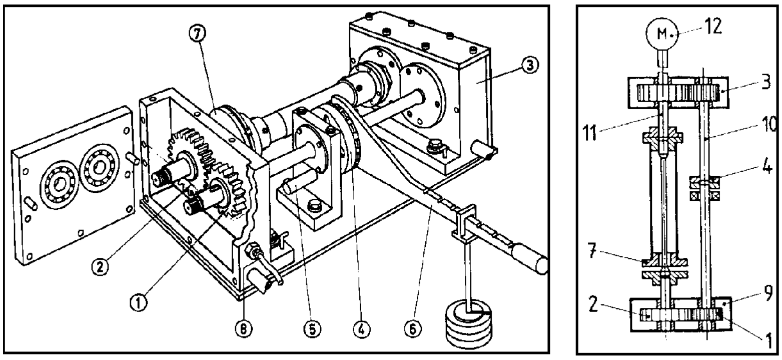
where h_{min} is a minimum lubricating film thickness in the contact and R_q is the rms surface roughness for specimens a and b.

In theory, lambda ratio values above 3 indicate the elastohydrodynamic lubrication, below 1 indicates boundary lubrication and between 1 and 3 mixed lubrication regime. The mixed lubrication condition is only valid at sufficiently high sliding speeds and as long as the surface roughness is unaffected by wear. Wear tests in this study were performed in lambda ratio interval between 0.1 and 1.6, therefore mainly in the boundary and partly in the mixed lubrication regime.

3.3 Gear test

Scuffing performance was evaluated on a FZG back-to-back test rig under standard test procedure according to ISO DIS 14635-1. As it is seen from Fig. 2, the test gears and the slave gears are connected by two shafts. One shaft is divided in two parts with the lock clutch in between. One half of the load clutch can be fixed to the foundation with the locking pin while the other half is twisted e.g. by means of a lever.

Figure 2: Schematic section of the FZG gear test rig.



1	test pinion	5	locking pin	9	test gearbox
2	test gear	6	load lever and weights	10	shaft 1
3	slave gearbox	7	torque measuring coupling	11	shaft 2
4	brace coupling	8	temperature sensor	12	electric motor

After bolting the clutch together the load can be removed and the shaft is unlocked. Thus a static torque is applied to the system which is by an electric motor. Test gears are loaded stepwise in 12 load stages between a Hertzian stresses of 150 to 1800 N/mm^2. Each load stage runs for 15 minutes at a constant pinion shaft speed of 1,450 rpm and starting oil temperature of 90 ℃, under conditions of dip lubrication without cooling. The test gear flanks are visually inspected after each load stage for cumulative damage in particular scuffing marks. Failure load stage is indicated when the faces of all pinion teeth show a summed total width of damage areas which is equal or exceeds one tooth width. The test is only valid if the wheel weight loss is ≤ 20 mg.

The test gears were standard FZG type A spur gears. Type A gears have been designed with a large profile modification, which increases their sensitivity to adhesive wear modes of failure. They were made of DIN 20MnCr5 steel and case carburised. The surface hardness after tempering was 60 to 62 HRC and case depth of 0.6 to 0.9 mm. the surface roughness was 0.35 microns for the pinion and 0.30 for the wheel.

4. Test results and disscusion

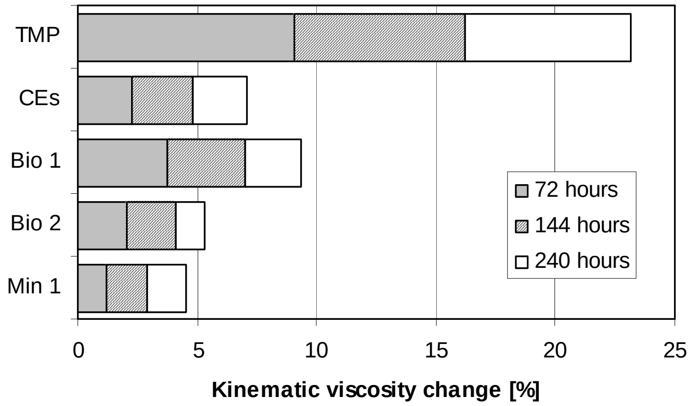
4.1 Oxidation stability

The oxygen from the air reacts with the most reactive site on the lubricant molecule. In the case of unsaturated TMP this is on the carbon hydrogen bond adjacent to a double bond within a carbon chain. It is evident from the Fig. 3, that oxidation stability of TMP is far less than those of complex ester CEs, where double bonds in the acid group are completely eliminated. After first 72 hours at 95 ℃, the kinematic viscosity increase of unsaturated TMP is 22% higher than viscosity increase of saturated CEs in the end of the test at 240 hours. It follows that lower unsaturation and shorter acid chain length can dramatically improve resistance to oxidation.

Another way to improve oxidation stability is additivation. Antioxidant additives slow down the process of oil ageing, therefore the viscosity increase of formulations Bio 1and Bio 2 is lower compared to the additive free oils TMP and CEs. Better resistance to oxidation is especially evident when comparing the results for TMP and corresponding formulation Bio 1, which is blend of TMP and additives. In the case of CEs and the corresponding formulation Bio 2, the improvement of oxidation performance is not so distinctive. However, the oxidation stability of saturated complex ester CEs is higher compared with those of formulation Bio 1, even enhanced with the antioxidants. The base oil properties are obviously more influence factor on resistance to oxidation than additives.

The best oxidation stability in this test provides mineral oil Min 1, particularly because of the very low viscosity increase in first 72 hours period. The rate of viscosity increase after 72 hours is comparable to formulation Bio 2.

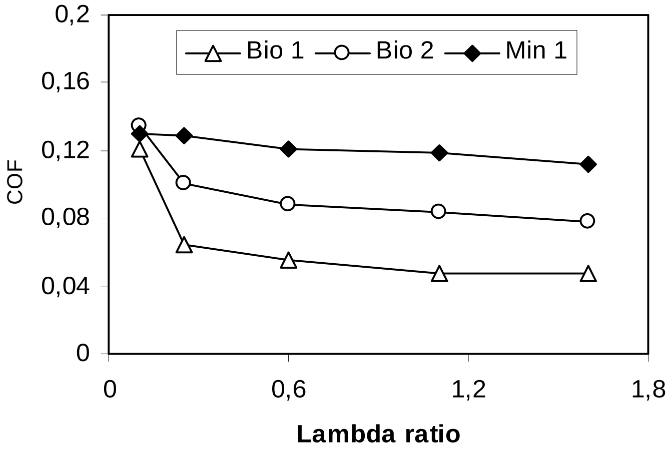
Figure 3: Oxidation stability of test oils



4.2 Friction and wear measurements

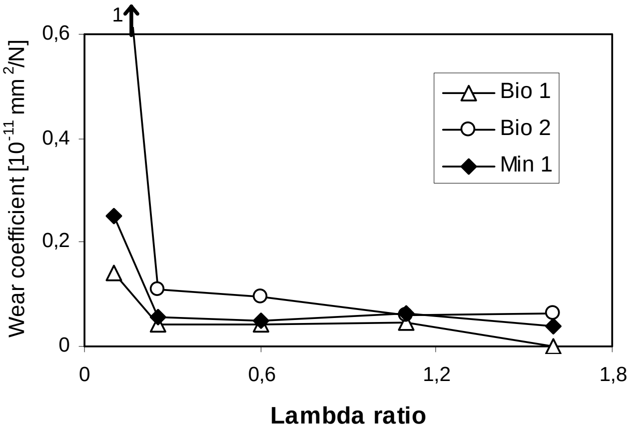
Figure 4 shows a friction trace for formulated test oils. At very low lambda ratio and low sliding speed, the coefficient of friction (COF) is almost identical for all test oils. However, as lambda ratio increases over the value of 0.25 the large difference in coefficient of friction between oils is apparent. The largest friction generates oil Min 1, while COF for ester based formulations is under 0.1. Formulation Bio 1 with the unsaturated fatty acids resulted in very low COF of about 0.05. Unsaturated ester contains organic long straight-chain compounds with polar end groups. These polar end groups are adsorbed on the metal surface, which decreases the surface energy and causes a reduction of the coefficient of friction [7].

Figure 4: Effect of lambda ratio on coefficient of friction



The wear coefficient is shown on Fig. 5. All test oils show same tendencies of high wear coefficient for lambda ratio up to 0.25 and significantly lower wear at higher values. The curves have the same general shape, but formulation Bio 2 is seen to give the highest wear. With higher speed the wear coefficient is about of the same value for all test formulations. However, the results demonstrate that the best anti-wear protection perform formulation Bio 1, based on unsaturated ester. Unsaturated esters react more easily than saturated esters or mineral oils and have the highest content of polar functional groups that make physical and chemical interaction with the metallic surfaces in sliding contact.

Figure 5: Effect of film parameter on wear coefficient

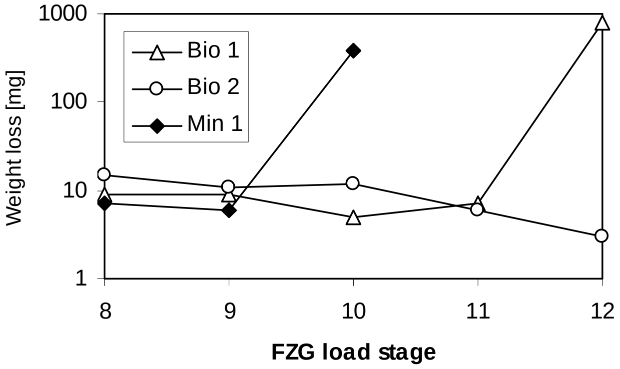


The unsaturated ester based formulation Bio 1 results in lower friction and better anti-wear properties than saturated formulation Bio 2. Polar functional groups in the unsaturated molecule of ester based oil in conjunction with oil-additive-metal interaction during the metal rubbing process can significantly improve the wear resistance and extreme-pressure lubrication. Unsaturated sites react more easily with the mating surfaces and it is found to be much more effective in reducing friction and wear than esters with saturated fatty groups. Short chain compounds of saturated ester Bio 2 are better for oxidation stability than long chain compounds, but are less effective in lubricant protective film formation. Note, that the same additive system is used for both ester based formulations.

4.3 Scuffing load capacity

The evolution of scuffing damage under increasing load is presented in Fig. 6. The weight loss of pinion and gear was first controlled after the load stage 8, therefore the value is the cumulative sum of the previous weight loses. After load stage 8 test gears were weighted at the completion of each load stage. If the test gears weight loss in one stage exceeds 20 mg then the failure criterion is reached and as often as not the excessive wear is observed on pinion teeth flanks.

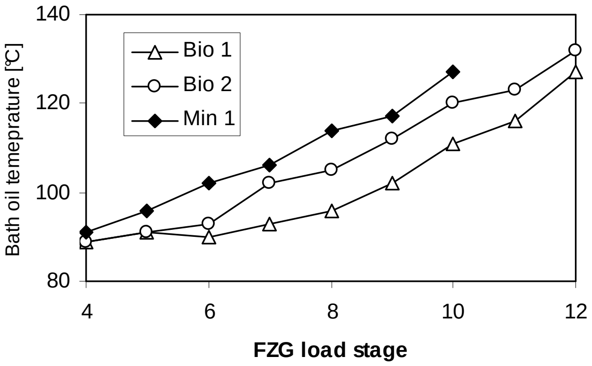
Figure 6:Test gears weight loss



Oil Min 1 collapses at FZG load stage 10 (1538 N/mm^2), oil Bio 1 at load stage 12 (1841 N/mm^2), whereas oil Bio 2 is capable to withstand higher loads. Bio 2 can transmit loads over the FZG load stage 12, without excessive scuffing, but wear rate up to the load stage 9 is the highest. Wear rate is also higher compared to the Bio 1 at load stage 10. On sliding wear test, as shown on Fig. 5, it was already noted that saturated complex ester formulation Bio 2 exhibits the highest wear rate. It appears that the more polar and reactive unsaturated formulation Bio 1 resulted in better wear protection at moderate loads, however saturated short chain length fatty acid composition of base oil Bio 2 is more suitable for high loads.

Figure 7 shows the evolution of bath oil temperature recorded at the end of the each scuffing load stage. Of the three test lubricants, the unsaturated ester formulation Bio 1 results in the lowest bath oil temperature, suggesting the lowest friction in the contact. These results completely confirm the coefficient of friction observations presented on Fig. 4, where COF for the sliding speed was recorded.

Figure 7: Bath oil temperature after completion of the FZG load stage



5. Summary

The following conclusions can be derived from this study:

- The oxidation stability of saturated based ester formulation is significantly better compared to the unsaturated ester based formulation. Even enhanced with antioxidants, the oxidation performance of TMP-trioletate based formulation remains quite poor.
- Ester based formulations exhibit less friction than mineral based lubricant. The lowest friction coefficient shows the formulation based on unsaturated TMP-trioleate. These results are in totally in agreement with bath oil temperature measurements in the gear test, justifying the lower temperatures obtained with the ester based formulations.
- Unsaturated based synthetic ester formulation exhibits the best antiwer protection, especially at low sliding speeds. At higher values, wear coefficient is about the same for all test oil formulations.
- Scuffing load capacity of more polar and reactive formulation based on TMP-trioleate resulted in better wear protection at moderate loads, however saturated short chain length fatty acid composition of complex ester is seen to be more suitable for high loads.

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UDK	Ključne riječi:	Key words:
621.892.31	polusintetičko mazivo ulje biljne osnove	semisynthetic vegetable base lubricating oil
-035.83	biljna ulja, masti, voskovi, kao osnovni materijal	vegetable oils, fats, waxes; as base material
621.892.28	polusintetičko mazivo ulje esterske osnove	semisynthetic esther base lubricating oil
665.765.035	primjenska svojstva mazivih ulja	lubricating oil application properties
620.178.16	ispitivanje trenja i trošenja	friction and wear testing
.001.37	komparativna analiza	comparative evaluation

Autori / Authors:
doc .dr. sc. Boris Kržan, prof. dr. sc. Jože Vižintin
University of Ljubljana, Faculty for Mechanical Engineering, Center for Tribology and Technical Diagnostics, Ljubljana, Slovenia

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