Evaluation of thermooxidation stability of biodegradable recycled rapeseed-based oil NAPRO-HO 2003

M. Kučera[1], M. Rousek[2]

[1]*Department of Forest and Mobile Technology, Faculty of Environmental and Manufacturing Technology, Technical University in Zvolen, Slovak Republic*
[2]*Faculty of Forestry and Wood Technology, Mendel University of Agriculture and Forestry in Brno, Brno, Czech Republic*

Abstract: The paper deals with the problems of introducing biodegradable oils in relation to the environmental protection. In the course of the research, the parameters were tested and improved of a number of rapeseed-based oils. Thus, two groups of oils were created to enable to distinguish raffinates and recycled oils. Recycling can remove the greatest disadvantage of raffinates, namely their thermo-oxidation instability, which becomes evident particularity by the formation of hardenable polymer deposits. The deposits result in the loss of the function of the components of the hydraulic circuit and gearbox. The methods of testing are based on the follow-up of the changes in acid value, kinematic viscosity at 40°C, water content, and peroxide number during the service life test. It has been proved that peroxide number characterises very well the thermo-oxidation stability, which is nearly unsatisfactory in raffinates. Within the cooperation in the international program KONTAKT, compliance tests were carried out of recycled rapeseed-based oil NAPRO 2003 in a hydraulic circuit and gearboxes. Their results are compared with the parameters of the best-recycled oils available.

Keywords: biodegradable oils; hydraulic circuit; gearboxes; recycled oil

Increasing attention to the environmental issues and more restrictive environmental regulations drive the lubricant industry to increase the ecological friendliness of its products. For the last three decades, the industry has been trying to formulate environmentally acceptable lubricants with technical characteristics equal or superior to those of mineral oils. Vegetable oils are a candidate for the replacement of mineral oils due to their inherent biodegradability, non-toxicity, and excellent lubricity. Moreover, vegetable oils are a renewable resource, and their cost is reasonable compared with that of other alternative biodegradable fluids (Kržan & Vižintin 2003).

The possibilities of the environment improvement and consistent decrease of the level of its pollution by filling gearboxes and hydraulic circuits in forest machines were solved by the replacement of mineral oils with biodegradable oils with the focus on rapeseed-based oils (HETG) in the last years; the results were published (Rousek 2003; Skoupý 2004). The results of lifetime tests, development of viscosity number and viscosity were published by Harms (1998), and the influence of biodegradable oils for sealing materials of hydraulic elements was observed by Kučera (2006).

The amount of biodegradable oils in the market is quite small. There is a catch-up to make a stronger pressure for using biodegradable oils as fillings of the hydraulic circuits and gearboxes. It is the fact that the application of biodegradable rapeseed-based oils is doubtful. If operational parameters of recent hydraulic circuits are compared with the older ones, we observe a significant increase of pressure and operational temperatures. And thes limited range of operational temperatures (40°C–70°C) gives limits for the area of their use. On the basis of the circumstances mentioned, conclusions were deduced that it is necessary to direct the application of natural esters to the area of performance where the hydraulic circuits of machines and gearboxes are lower. The reason is the achievement of an economical period of the use for oil filling. The forestry equipment is ideally suited to use vegetable based lubricants, because it operates close to the environment where lubricant can easily come into contact with the soil, ground water, and crops. The area of machines used in forestry and agriculture is that which fulfil the given requirements. The next research is focused on the area of improvement of some parameters of biodegradable oils, and it is mainly the thermo-oxidation stability where the use of recycled biodegradable oils is hopeful.

MATERIAL

Recycled biodegradable oil

Recycled oil is oil made of rapeseed-based raffinate, which was used in production; it was characterised by high temperature loading and was modified for the next mainly technical use. During fritting, oil is superheated up to the temperature of about 150°C–200°C. After the introduction of food into hot oil, water is evaporated and the oil is cooled down. During frying, which takes usually several minutes, the temperature is again increased by several degrees. Considering higher temperatures and the access of air oxygen, the oxidation of unsaturated fatty acids takes place and is followed by polymerisation. The number of double bonds decreases, which is shown by decreased iodine number. This is the way how to decrease the risk of the fast ageing process (Rousek 2003).

Oil is cleaned by dropping, defecation, and filtration. The pure oil is modified by the addition of, stabilisers against oxidation, additional ingredients, which modify the viscosity index Iv, i.e. the dependency course of viscosity on temperature, variance ingredients for the decrease of the point of solidification. The variance ingredients must decrease the point of solidification from the temperature –15°C to the temperature –25°C. The reason of the given modifications is to achieve a higher recovery of the oil which has been temperature stressed before. Recycled oil is recommended for the use as biodegradable liquid in the hydraulic circuits and gearboxes in the forest and agricultural machines (Rousek *et al.* 2005).

On the basis of the given results, it is possible to assume that recycled oil will have a higher acid value but also a much more better oxidation stability, which results from the fact that this oil was temperature overcharged in the previous operation in the past. It is necessary to make lifetime tests because of the assumption that the properties of recycled oil are comparable to those of rapeseed-based raffinates.

Determining the parameters under study

In each of the quality indicators, a limit value is determined which is either generally applicable or possesses specialities given by the operational conditions. Its attainment means the exhaustion of desirable properties and impossibility to fulfil the originally determined function. Such debased oil has to be replaced by a new oil refil. This step occurs by exceeding the limit value of even a single parameter. In the course of the tests carried out previously, it was found that the following parameters rank among the basic indicators of the service life of hydraulic biodegradable oils (Rousek 2003):

(a) kinematic viscosity at 40°C (mm^2/s)
(b) number of acidity (mg KOH/g)
(c) water content (%)
(d) peroxide number (mmol O_2/kg)

The first three parameters can assess the basic properties of oils required in technical conditions of hydraulic liquids. Thermo-oxidation properties of oils manifest themselves in the increased rate of the formation of resinous deposits hardening in the course of time. An important contribution of the work carried out so far is the study of the thermo-oxidation properties of oils by means of peroxide number. Together with iodine number, the value of which is known for rape-seed oils and enables a rough estimate of the thermo-oxidation stability of oil, the peroxide number makes it possible to determine the time of the oil service life by its marked changes during the course of the service life test. Iodine number informs on the number of double bonds causing potential danger of the start of rapid oil ageing. The peroxide number provides information on the amount of fixed oxygen on these double bonds. A slight increase in the peroxide number at the beginning of the operation called the induction period is to be as long as possible. It corresponds to the conception of the chemical service life of oil. An increased degradation of oil is shown by a higher formation of peroxides, the formation of di- and polymers, splitting the ester bond under the formation of free fatty acids and partial glycerols, formation of aldehydes, ketones, oxy- and hydroxy-acids. The tests have shown that the technical service life of oil ends roughly in the domain of the maximum value of peroxide number. In the field of the decrease of peroxide number, i.e. the field of advanced degradation of oil, a marked increase in the formation of polymers and acids occurs showing marked changes (increase) in the oil acid number and viscosity. In recycled oils, due to the previous disintegration of double bonds a slightly increasing course of peroxide number is expected together with a marked decrease in the formation of polymers, which finally results in the substantial improvement of thermo-oxidation stability.

Methodology of determining the parameters is based on the following standards:

The determination of acid value is carried out according to STN 58 8756 Standard operative from 1994. The standard corresponds to ISO 660-1983 without any substantial differences.

The determination of peroxide number in animal and vegetable fats is carried out according to STN EN ISO 3960 from 1994 which is identical with STN 58 0130 Standard.

The determination of the water content is carried out according to STN 65 0330 Standard for oil and oil products. The subject of the standard consists in developing a method for determining trace amounts of water according to K. Fischer.

The determination of density is carried out according to STN 65 6010 Standard – Oil and Oil Products. The methods of determining the density have been operative since 1983. A method for determining the density by areometer was used.

For the purpose of the paper, the method was used of measuring the viscosity by means of Höpler viscosimeter according to DIN 53 015. The quantity measured is dynamic viscosity η. Kinematical viscosity is calculated according to the equation $\nu = \eta/\rho$ where ρ is the specific weight.

METHODS

Set-up of testing apparatus

Loading and ageing process of recycled oil was done in:
– hydraulic testing circuit (Figure 1),
– gearbox ALBOX Alfa.

Samples taking was realised with focus on time, temperature, homogensity of the samples and time period between takings. The evaluation of chemical parameters of recycled biodegradable oil was done according to the standards the following parameters being involved: kinematic viscosity (mm^2/s) at the temperature of 40°C, acid value (mg KOH/g), water content (%), and peroxide number (mmol O_2/kg). The oil sample taken represented the whole filling of a hydraulic circuit and a gearbox providing homogeneity of the whole filling. It was necessary to establish the conditions for taking an important sample of oil filling. After 100 or 300 hours, the oil was taken out for the parameters tests, and after that it was returned back into the hydraulic circuit and the gearbox. The temperature of the oil taken was in the temperature range from 40°C to 65°C. The test was interrupted, following visible degradation of one of the parameters measured. The filling was made of:
– samples of recycled rapeseed-based oils NAPRO-HO 2001 and 2002,
– samples of recycled oil NAPRO-HO 2003.

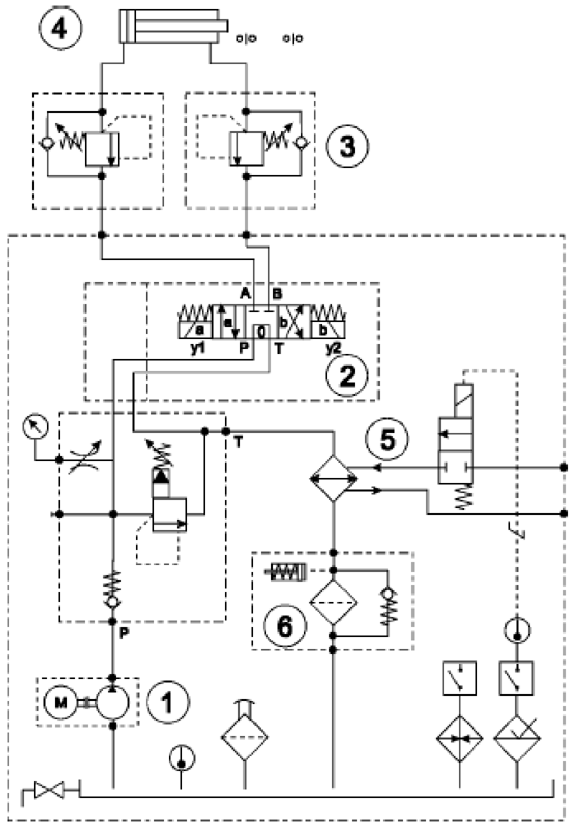

Figure 1. Laboratory hydraulic system
(1) gear pump, (2) directional valve, (3) pressure relief valve, (4) cylinder, (5) water cooler, (6) filter

The working hypothesis was as follows: the properties of the recycled rapeseed-based oil NAPRO-HO 2003 tested in the gearbox and also in the hydraulic circuit will be very similar during the time of at least 1500 working hours, the changes of the principal parameters selected being in the allowed tolerances.

Figure 1 shows the hydraulic testing circuit. A hydraulic trial stand is designed as a simple open hydraulic circuit. Particular kinds of recycled biodegradable oil were tested under various parameters of pressure and temperature, the pressure in the hydraulic circuit being up to 15 MPa, the oil temperature in the tank in the course of the test being kept in the range of 40°C–65°C (Kučera 2003).

On the ground of economy, gearboxes ALBOX, which stress oil mechanically in a similar way as the elements of hydraulic circuits, were used in the tests. A number of ALBOX gearboxes are of modular construction which makes it possible to compose two- and three-stage combinations from six basic one-stage gearboxes. For the purpose of the test, the recommended volumes of oil appear to be very small and, therefore, after consultations with the manufacturer, the oil volume was increased roughly by 50% of the recommended filling. The volume will not substantially affect the process of ageing, however, it will enable to observe the filling service life at required intervals of service hours.

For the purpose of testing, a test block was designed and implemented, consisting of a frame on which two ALBOX Alfa 63/100 gearboxes were mounted by means of screws (marked as green and yellow) driven by separate electric motors. The output shafts of both gearboxes were shouldered by belt pulleys of different diameters and interconnected by three V-belts. In this arrangement, one gearbox drives another, which drags the first one. Thus, both gearboxes are loaded to a full capacity and can be used for testing the oil fillings.

RESULTS AND DISCUSSION

For the purpose of information, we give the results of the service life tests with recycled biodegradable oils NAPRO-HO 200x, viz. the changes in acid number (Figure 2), kinematic viscosity at 40°C (Figure 3), the peroxide number (Figure 4) and water content (Figure 5). The working hypothesis is as follows: the properties of the tested oil will be very good for at least 1500 service hours and the changes in the basic parameters selected will be in the permitted tolerances (Rousek *et al.* 2004).

Evaluation of acid value in the samples of recycled oils NAPRO-HO 200x

In Figure 2, unequal courses are visible of the curves sowing acid values of recycled oil NAPRO 2003, as compared with recycled oils NAPRO-HO 2001 and NAPRO-HO 2002, applied in the gearbox ALBOX Alfa and in the hydraulic circuit as well. Despite this fact, acid value is lower at first sight which is a positive effect. The lowest values were obtained in recycled oil in the hydraulic circuit at TU in Zvolen. It is not possible to say exactly how the recycled oil behaves during increased testing time. The trend is visible in the graph, which shows increasing acid values in the next stage of testing.

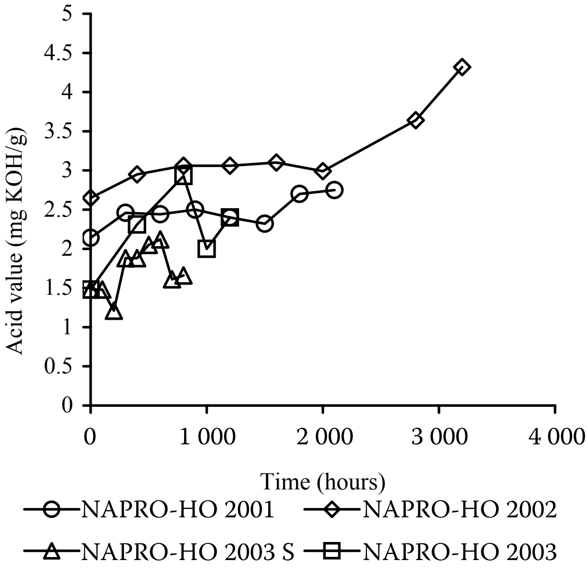

Figure 2. Changes of acid value in a laboratory hydraulic system and in a spur gear test system

Evaluation of kinematic viscosity at 40°C in the samples of recycled oils NAPRO-HO 200x

Kinematic viscosity has an ideal course with recycled oils NAPRO-HO 2001 and NAPRO-HO 2002 at the temperature of 40°C. We can say that the course is nearly constant (Figure 3). As to recycled oil NAPRO-HO 2003, its value oscillates in the gearbox and this state is nearly inconvenient. With recycled oil NAPRO-HO 2003 S, kinematic viscosity starts to increase notably after previous oscillation. This increase is responsible for the end

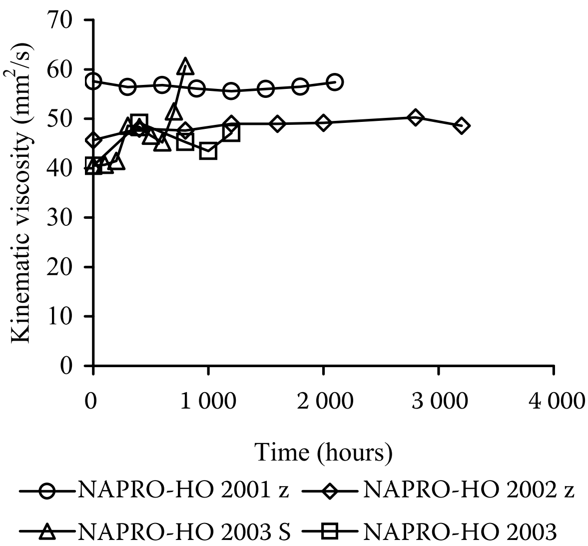

Figure 3. Changes of viscosity at 40°C in a laboratory hydraulic system and in a spur gear test system

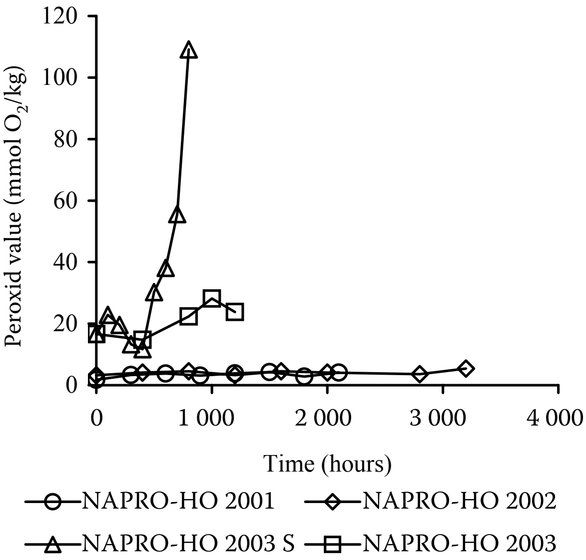

Figure 4. Changes of peroxide number in a laboratory hydraulic system and in a spur gear test system

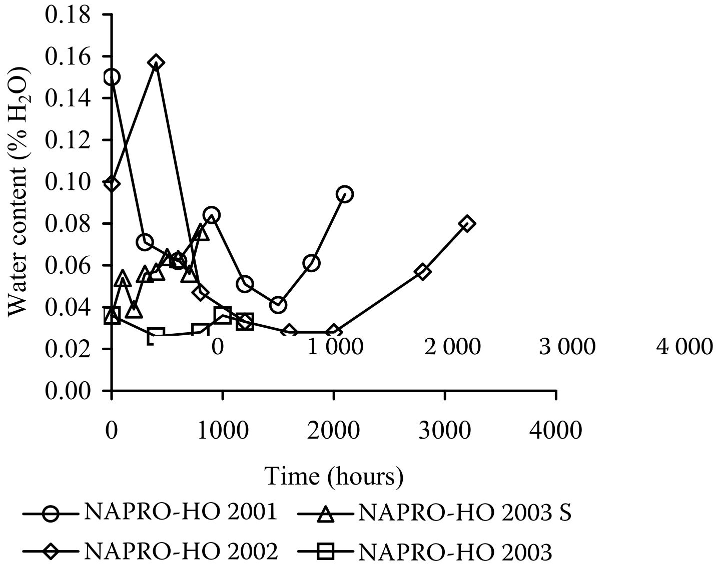

Figure 5. Changes of water content in a laboratory hydraulic system and in a spur gear test system

of this recycled oil life time in the hydraulic circuit after 600 working hours. A lower initial value in recycled oil NAPRO-HO 2003 any can be considered as positive, which is the same as with acid value, and it finally remains without any effect because of the next negative course of kinematical viscosity.

Evaluation of peroxide number in the samples of recycled oils NAPRO-HO 200x

Peroxide number informs about the amount of oxygen bound in double bonds. Double bonds cause a potential risk of creating a fast ageing process in oils, the number of double bonds being defined by iodine number. The oil lifetime is dependent on the changes of iodine and peroxide numbers, and it can be concluded that a lower peroxide number results in a better thermo-oxidation stability. The tests showed that technical lifetime terminates approximately in the area of maximum value of peroxide number.

The lifetime of recycled oils NAPRO-HO 2001 and NAPRO-HO 2002 is not finished after the finish of the tests realised as shown in Figure 4. It is similar with recycled oil NAPRO-HO 2003, whose course has an exponential character but not yet showing any significant failure. First of all, the values decreased in recycled oil NAPRO-HO 2003 S which was positive but in the course of 500 working hours there was an intensive failure, which means the end of lifetime of this recycled oil. An extremely high initial periodic number was also the case with both recycled oils.

The result of all conclusions mentioned above is that during the production of oil, the technological procedure was not kept, and in the tests with the hydraulic circuit undefined reaction occurred with materials coming from the hydraulic circuit or with sealing materials.

Evaluation of water content in the samples of recycled oils NAPRO-HO 200x

Water causes oil foaming, in extreme cases it makes emulsion, it has a tendency to increase the oil viscosity, it also has a negative influence on oil oxidation stability, and it supports the production of dangerous sediments, i.e. it also has an influence on oil hydrolytic stability. The presence of water in oil always degrades the quality of oil, that'is why oil with the lowest amount of water is considered to be of the highest quality from the oil quality assessment point of view.

The amounts of water in recycled oils NAPRO-HO 2001 and NAPRO-HO 2002 were at the beginning of testing higher than that in oil NAPRO-HO 2003 (Figure 5). A relatively low amount of water was contained oil NAPRO-HO 2003, which was visible also after 1000 working hours. In comparison with this oil, NAPRO-HO 2003 S had a tendency to oscillate and increase at the same time. This behaviour was found out as inconvenient. If the quality and lifetime of oil were regarded according to the amount of water, then the given oil would be similar to biodegradable recycled oil NAPRO-HO 2001 or NAPRO-HO 2002 as visible in the graph.

CONCLUSIONS

Peroxide number informs on the amount of active oxygen bound on the double bonds. Iodine number gives information on the number of double bonds causing potential danger of starting rapid ageing. The service life of hydraulic oil is related to small changes in iodine and peroxide numbers: the higher the peroxide or iodine number, the higher oxidation stability can be expected (Rousek 2003). The technical life of hydraulic oil terminates in the area of maximum peroxide number. Comparisons with the behaviour of commonly recommended oils show that recycled hydraulic oils rank among the types of rapeseed oils possessing average properties. However, the thermo-oxidation stability of the oil was substantially improved, peroxide values of recycled oils NAPRO-HO 2001 and NAPRO-HO 2002 were constant and the formation of hardenable polymerised deposits did not occur. It is needed to accent that while the recycled hydraulic oils NAPRO-HO 2001 and NAPRO-HO 2002 were tested after 2000 service hours, the hydraulic oil NAPRO-HO 2003 was tested after 800 service hours in the hydraulic circuit at the Technical University in Zvolen and in the gearbox at the Department of forestry and forest products technology MZLU in Brno, and it had been tested up to 1200 working hours as a reference sample at a smaller mechanical oil stress. This is also an important parameter for the detection of hydraulic oil quality.

From the figures we can evaluate:

- all samples of the recycled hydraulic oils NAPRO-HO revealed viscosity changes for up to 1000 hours in the allowed tolerance, these having been caused by oxidation and temperature instability ± 10%,
- acidity the numbers of the recycled biodegradable oils rose slightly from comprehensible causes. For the recycled hydraulic oil NAPRO-HO 2003 is evident a non-constant course in the face of others,
- water contents in recycled hydraulic oils, whose occurrence in oil always interferes with the quality of hydraulic oil. The shapes of curves of the recycled hydraulic oils NAPRO-HO are almost individual,
- the greatest differences are in peroxide number. The effect of temperature on the course of peroxide number is based onthe fact that at higher temperatures peroxide decompression occurs. The higher the temperature during oxidation, the lower the maximum value of peroxide number.

Peroxides of markedly unsaturated fatty acids are decomposed already at normal temperature. The stability of hydraulic oil at high temperatures plays the same role as at low temperatures in connection with its applicability in hydraulic systems. Ageing (oxidation) should start as late as possible even at high temperatures. In addition to this, no acids causing corrosion must be released and viscosity must not be markedly changed. Through oxidation and temperature instability, various parameters (particularly viscosity) of hydraulic oil can be markedly changed. Thermo-oxidation stability of the recycled oils NAPRO-HO 2001 z a NAPRO-HO 2002 z was good and comparable with that of mineral oils. From Figure 4 can be evaluated that the shape of the curve of the recycled hydraulic oil NAPRO-HO 2003 S geased to be good already after 500 hours. Thence may be deduced that in hydraulic trial stand either mechanical contaminations occur or reactions take place of the recycled biodegradable hydraulic oils with materials coming from the hydraulic components or packages.

References

Harms H.H. (1998): Development trends in a hydraulics of mobile machines. In: Proc. 16th Int. Conf. Hydraulics and Pneumatics. Brno, Tanger, Ostrava, 144–150. (in Czech)

Kržan B., Vižitin J. (2003): Tribological properties of an environmentally adopted universal tractor transmission oil based on vegetable oil. Tribology International, **36**: 827–833.

Kučera M. (2003): Biodegradable hydraulic oils in a hydrostatic systems of forest machines. Acta Facultatis Technicae, **7**: 43–49. (in Slovak)

Kučera M. (2006): Examination of sealing materials in ecologically friendly hydraulic oils – Part 1 – Volume changes. Acta Facultatis Technicae, **10**: 61–68. (in Slovak)

Rousek M. (2003): Characteristics and Parameters of Biologically Degradable Oils. MZLU, Brno. (in Czech)

Rousek M. *et al.* (2004): The use of methods of tribotechnical diagnostics to determine the reliability of biodegradable oils. In: Proc. Colloquium to Grant Work No.1/9260/02. TU Zvolen, 99–107. (in Czech)

Rousek M. *et al.* (2005): The use of methods of tribotechnical diagnostics for testing the parameters of recycled biodegradable hydraulic oil NAPRO 2003. Acta Facultatis Technicae, **9**: 121–135. (in Czech)

Skoupý A. (2004): Biologically degradable oils at working with power saws. Journal of Forest Science, **50**: 542–547.

Received for publication March 17, 2008
Accepted after corrections May 30, 2008

Abstrakt

Kučera M., Rousek M. (2008): **Hodnotenie termooxidačnej stability recyklovaného oleja na repkovom základe NAPRO-HO 2003**. Res. Agr. Eng., **54**: 163–169.

Príspevok sa zaoberá problematikou zámeny olejov biologicky rozložiteľnými v súvislosti s ochranou životného prostredia. V priebehu výskumu boli overené a zlepšené parametre celej rade olejov na repkovom základe, rozoznávame rafináty a recyklované oleje. Recyklácia odstraňuje najväčší nedostatok rafinátov a to ich termooxidačnú nestabilitu, ktorá sa prejavuje hlavne vznikom polymérových usadenín, ktoré vytvrdzujú. Usadeniny vedú k strate funkcie prvkov hydraulických systémov i prevodových skríň. Metodika skúšania spočíva v sledovaní zmien čísla kyslosti, kinematickej viskozity, obsahu vody a peroxidového čísla v priebehu životnostnej skúšky. Bolo preukázané, že peroxidové číslo najlepšie charakterizuje termooxidačnú stabilitu, ktorá je u rafinátov takmer nevyhovujúca. V rámci spolupráce na medzinárodnom programe KONTAKT boli zrealizované skúšky recyklovaného biologicky rozložiteľného oleja na repkovom základe NAPRO-HO 2003 v hydraulickom obvode a prevodovej skrini. Jeho výsledky sú porovnané s parametrami najlepších recyklátov získaných pri minulých skúškach.

Kľúčové slová: hydrostatický obvod; prevodové skrine; biologicky rozložiteľné oleje

Corresponding author:

Doc. Ing. Marián Kučera, Ph.D., Technická univerzita vo Zvolene, Fakulta environmentálnej a výrobnej techniky, Katedra lesnej a mobilnej techniky, T.G. Masaryka 24, 960 53 Zvolen, Slovenská republika
tel.: + 421 455 206 822, e-mail: kucera@vsld.tuzvo.sk