

Results of the development of biodegradable oils suitable for forest machines

M. ROUSEK

*Mendel University of Agriculture and Forestry, Faculty of Forestry and Wood Technology,
Brno, Czech Republic*

ABSTRACT: The paper is a response to the problem of the environment pollution by oil product spills from mechanisms of forest and agricultural machines. The problem can be dealt with through the replacement of mineral oils by biodegradable oils. Information concerning the measurement of parameters of these oils was published by the author. It has been demonstrated that the parameters are broadly suitable with the exception of thermooxidation stability. The paper is, therefore, aimed at improving the thermooxidation stability of biodegradable oils of HETG type. Oil raffinates based on rape oil, methyl esters are delivered in various quality, mostly with a service life of 600 to 2,000 service hours at a temperature of max. 70°C. Methods of testing are based on monitoring the change in acid value, viscosity, water content and peroxide number during the service life test. It has been proved that peroxide number characterizes very well thermooxidation stability which is nearly unsatisfactory in raffinates. A method for improving the thermooxidation stability has been proposed using high superheating of oils at the beginning of use and their subsequent treatment. Thus, deep-frying oils (HETG) characterized by a short-term thermal stress appear to be suitable. Through filtration and other treatment three types of samples were developed and tested. The advantage of the procedure consists in the fact that esterification does not occur. Results of the tests are evaluated and compared with properties of traditional raffinates. It is possible to conclude that thermooxidizing stability of the oils has been substantially improved, other parameters in additivated samples are comparable with raffinates.

Keywords: biodegradable oil; leakage; environment pollution; hydraulic circuit; gearbox; thermooxidation stability

PRESENT CONDITION

Possibilities of improving the condition of the environment and decreasing the level of its pollution by fillings of gearboxes and hydraulic circuits of forest machines replacing mineral oils by biodegradable oils with an emphasis to HETG oils (rape seed oil esters, triglycerols where the acronym means Hydraulic fluid Ecological TriGlycerol) were dealt with in previous years and results were published (ROUSEK 2000, 2001). BIOMIL PR has appeared to be of the best quality and, therefore, it is used as an etalon.

Basic findings on the type of oils were published by BUSCH (1989) and all other papers refer to it. Results of service life tests, the development of acid value and viscosity were published by HARMS (1998). A number of findings concerning the use of oils was published by BARTOŠKA (1999), KUČERA (1999), MARKO (1997) and SKOUPÝ (2001). Untreated recycled oils specified as NAPRO-HO 9901 were tested in 2000 and results were published (ROUSEK 2001). Based on the results of the tests it has been concluded that from the technical viewpoint it is necessary to focus the application of a natural methylester (rape-seed oil) to the field of

hydraulic circuits of machines and gearboxes with low working load. Therefore, further research was oriented to the field of improving some parameters of rape-seed oils, thermooxidation stability in particular. Analysis of possibilities of treatment is given in chapter Material. For testing oil properties the already used deep-frying oil was applied both from practical and ecological reasons short-term temperature stress being typical of the oil. In the first stage of testing, samples were not treated with the exception of filtration. Because the samples are only little satisfactory from the viewpoint of quality particularly small thermooxidation stability where the use of 'recycled food biodegradable oils' appears to be promising, in the second stage of tests the treatment of oils was carried out by decreasing the initial acidity and bleaching and in the third stage using antioxidants and other additives of oils.

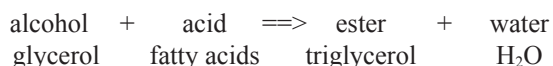
The creation of a stable, functional network of subjects gathering used food oils and within an ecological contribution for the environment utilizing them in a reproduction process is a basis for the attractive cost of a product. Another possibility consists in the treatment of rape-oil raffinates by industrial methods which of course will affect the increase of production costs.

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MATERIAL

It is possible to state that rape is a plant species of the genus *Brassica* belonging to the family *Brassicaceae* (*Cruciferae*). Its scientific name is *Brassica napus*.

Various forms where it can occur affect phylogenetic, anatomic and morphological properties. For the purpose of a technical use, *Brassica napus oleifera* is important as a source of oil. Oil is obtained through the multiple extraction of seed. The procedure of further processing can be carried out in the following stages: sediment disposal, hydration, neutralization, bleaching and deodorization. The objective of raw oil processing is to produce a raffinate which is a basic raw material for the production of other products mostly through additives. Keeping the quality of the pursuance of particular production stages markedly affects the raffinate quality. Rape oil ranks among the group of lipids consisting predominantly from glycerolesters of higher carbonaceous acids molecules of which are composed from an alkyl group (C_nH_{2n+1}) and a carboxyl group (COOH). In addition to a glycerolester the natural oil includes free fatty acids, phosphatides and non-saponifiable components. The glycerolester consists of trivalent alcohols three OH groups of which can be esterified to a triglycerol. The process of esterification can be depicted as follows:



The rape-seed triglycerol molecule contains more kinds of fatty acids and literature mentions that the content of oleic acid is 50–66%, linoleic acid 18–31% and linolenic acid 6–14% (molecule weight 282 g/mol). Ageing which is manifested by the increase of free fatty acids can be assessed in the technical rape-seed triglycerol by determining the acid number as the acidity of oleic acid. Another problem is thermooxidation stability which is assessed by means of peroxide number.

Problems of the attainment of high thermooxidation stability of rape raffinates and the effect of particular factors influencing the stability consists in understanding the oxidation processes occurring in the oils. Main oxidation processes were described by VELÍŠEK (1999). As for his findings, the list of particular possibilities of oxidation but particularly problems of antioxidation factors are necessary to be accepted. A fundamental finding deserving attention is a chapter on reactions occurring in rape-seed oil raffinates and deep-frying oils.

Oxidation reaction – classification

Oxidation refers to reactions of carbohydrate chains and, therefore, they are common to free fatty acids and their esters. Carboxyl of free fatty acids accelerates, of course, the decomposition of hydroperoxides and can react with some products.

Several types of lipid oxidation reactions can occur in oils:

- Autooxidation by aerial oxygen (triplet)
- Oxidation by hydroperoxides or hydrogen peroxide
- Oxidation by singlet oxygen (usually refers to photo-oxidation)
- Oxidation catalyzed by enzymes (lipoxygenases)
- Oxidation by heavy metals of higher valence.

Autooxidation

Autooxidation of fatty acids is the most usual type of oxidation under conditions occurring during treatment or storage. Under usual temperatures, unsaturated fatty acids only are oxidized by aerial oxygen. Under higher temperatures corresponding to temperatures in stressed hydraulic circuits, generally also during baking, frying and roasting autooxidation of unsaturated fatty acids also occurs. Autooxidation of the hydrocarbon chain of fatty acids and also other hydrocarbons is a radical chain reaction occurring in three stages.

The first stage of the reaction is the origin of a free hydrogen radical (hydrogen atom, H·) and the free radical of a fatty acid (R·) which originate by homolytic splitting of the covalent C-H bond of the carbohydrate chain. The energy necessary for splitting the bond can be obtained by the fatty acid molecule from various sources, e.g. thermal energy (warming), ultraviolet radiation or radioactive radiation, visible light (under the presence of a sensitizing agent it refers to two-electron oxidation by singlet oxygen).

The splitting is also caused by the reaction with another free radical (immediate reactions of a hydrocarbon chain directly with oxygen are difficult from the viewpoint of thermodynamics) or reactions with metals of transition valence. This first stage is named 'initiation stage of an autooxidation reaction'. The originated free radical of a fatty acid (R·) is very reactive so that it can easily combine with a molecule of oxygen being virtually a biradical. Thus, a peroxy or peroxide radical originates (R-O-O·). The peroxy radical is again very radical so that it can sever the hydrogen atom from another molecule of an unsaturated fatty acid. Thus, a hydroperoxide (R-O-OH) and another free radical of a fatty acid will occur (R·). This second stage of autooxidation reaction is called 'propagation stage'. The sequence of above-mentioned two reactions of the propagation stage can repeat once, several times and even many times. Chains were observed amounting to more than thousands links. Therefore, autooxidation is called chain reaction. Reaction of the free radical of a fatty acid with oxygen is much faster than reaction of a peroxy radical with the lipid hydrocarbon chain. The peroxy radical reacts with the lipid molecule relatively slowly and this reaction determines, therefore, the rate of autooxidation.

If the concentration of free radicals in the reaction system is rather high it is probable that two free radicals will react under conditions of the origin of a non-radical

relatively stable product and thus the reaction chain will be completed. This third stage is called the termination stage of an autooxidation reaction.

Unsaturated fatty acids

In unsaturated fatty acids, the splitting off of hydrogen is relatively easy, at least for hydrogen from a methylene group neighbouring with a double bond. Even smaller energy is necessary for splitting off hydrogen from diene and triene fatty acids.

Hydroperoxides are the primary reaction products of autooxidation. The number of double bonds remains unchanged but the double bond is usually shifted by one atom of carbon either to a carboxyl or terminal methyl. The shift in diene or triene fatty acids is particularly easy. The free radical originates between two double bonds being stabilized by mesomerism. In a reaction with oxygen, a peroxy radical originates on one end of the mesomeric system. In the shift of double bonds, the double bond transposes simultaneously from *cis* configuration to a more constant *trans* configuration.

Saturated fatty acids

Splitting the bond between carbon and hydrogen in a saturated hydrocarbon chain requires considerable activation energy (422 kJ/mol) and, therefore, under lower temperatures it is not virtually taken into consideration. Under higher temperatures, however, corresponding to baking, frying and roasting the reaction is possible. In addition to the last atom of carbon all other atoms are roughly equally prone to the formation of a free radical by splitting the C-H bond, the third carbon and to a lesser extent the second and the fourth carbon somewhat more than the other. Oxygen bonds to new free radicals, peroxy radicals originate and reaction runs similarly as in hydroperoxides of unsaturated acids. Since in saturated acids, a free radical can be formed in many places of the hydrocarbon chain the composition of oxidation products tends to be very varied.

Hydroperoxides

Hydroperoxides of fatty acids are primary products of autooxidation. Hydroperoxides, particularly of diene and triene acids are very unstable and split off either a hydrogen or hydroxyle radical. Both the free radicals can initiate the chain reaction of fatty acids. From the viewpoint of time course, the autooxidation reaction is mostly initiated by heat or radiation so that the initiation rate is small at the beginning. The stage of reaction is called induction period. Hydroperoxides gradually accumulate in the system causing the formation of other radicals and thus the rate of initiation reaction increases with increasing concentration of peroxides. Therefore, the reaction is called autocatalytic. Provided sufficient amount of oxygen is available the rate of reaction rapidly increases until it reaches its maximum. Reactive

groups in the reaction environment gradually decrease and the reaction slows down. In slowing down the formation of further hydroperoxides the importance of disintegration of hydroperoxides by the mechanism mentioned above increases. The disintegration is not dependent on the presence of oxygen or the presence of non-reacted lipids. From a certain moment, the rate of hydroperoxide disintegration exceeds the rate of their formation. Then the amount of hydroperoxides gradually decreases in the system.

Secondary products of autooxidation

Hydroperoxides of fatty acids and their radicals can fundamentally react in secondary reactions by three ways. According to the type of originating products we can distinguish:

- Reactions which do not result in the change of the number of atoms of carbon in a molecule (e.g. in the origin of cyclic peroxides and endoperoxides, epoxyacids, hydroxyacids and oxoacids).
- Reactions when a molecule splits and products with the lower number of carbon atoms originate (e.g. reactions resulting in the origin of aldehydes, hydrocarbons or oxoacids).
- Polymerization reactions when the number of carbon atoms in a molecule increases.

Polymeric secondary products

Reactions when the number of carbon atoms in a molecule increases are a very important group of secondary reactions of oxidized fats. In technical practice, these reactions are not quite exactly termed oxypolymerization.

Polymers usually originate by interactions of two free radicals. If both radicals are alkyl dimer originate where both fatty acids are bound by a simple bond C-C between two carbon atoms.

Inhibitors of oxidation

All matters decreasing the rate of oxidation regardless of the mechanism of their action are termed inhibitors of oxidation. Antioxidants, synergists, chelating substances and compounds disintegrating hydroperoxides by a non-radical way rank among them. Also substances stabilizing hydroperoxides can decrease the reaction rate because they hamper the formation of free radicals.

Antioxidants

Antioxidants are substances which can react with free radicals of an autooxidation chain with peroxy radicals in particular. Hydroperoxide or another non-radical lipid product originates during the reaction. The antioxidant moves into the form of a free radical which, however, tends to be rather stable so that it is not able to continue in an autooxidation reaction. Thus, the role of antioxidants consists in shortening the autooxidation chain and

increasing the rate of termination reactions. During the reaction the antioxidant is depleted. When all the antioxidant is used the autooxidation proceeds in such a way as though no antioxidants were present. Thus, antioxidants cannot completely stop autooxidation reactions but can slow them, in an ideal case up to the rate of an initiation reaction.

The most frequently used antioxidants are phenol derivatives which are substituted by two or three phenol groups in ortho- or para-positions. Natural antioxidants are mostly substituted in ortho-position and, therefore, they are more effective. Synthetic antioxidants are largely substituted in para-position because they are less toxic in the position. Instead of one hydroxyl group a methoxy group can be present or at least a furcate alkyl. The substitution of a benzene nucleus by another alkyl or by two alkyls increases effectiveness. Antioxidants with a nitrogen heterocycle (e.g. dihydropyridine or dihydroquinoline compounds) are used less frequently, particularly due to their higher toxicity.

In natural fats and oils, natural antioxidants tend to be present, most frequently tocopherols. Phenol and other compounds belong to further common natural antioxidants.

Changes during frying

During frying, fat is preheated to a temperature of about 150–200°C, the procedure proper during frying is double and, therefore, we distinguish:

- Frying in the thin layer of fat;
- Frying in a layer of fat more than 50 mm high (usually between 100 and 200 mm) so that the fried food is immersed in fat or swims on it.

The second method is more usual today being also called deep-frying. After the insertion of fried foodstuff, water vaporizes in contact with warm fat while the fat cools. During frying taking usually several minutes the temperature increases again by several tens of degrees. Processes occurring in a fat bath during frying can be classified into several groups of reactions:

- Hydrolytic processes which come by the effect of warm steam (released from the fried foodstuff) on the warm fat represent main processes occurring during frying; free fatty acids originate by hydrolysis the acids being adsorbed to a greater extent to the fried foodstuff or escape to the air.
- Oxidation processes which are very quick at frying temperatures, oxygen dissolved in fat is, however, absorbed, so that further oxidation proceeds only slowly depending on the rate of further oxygen diffusing from air, the rate of diffusion is, however, substantially increased if the fat begins to foam because a contact area between the fat and air increases by foaming.
- Polymerization processes caused on the one hand by reactions between free radicals and on the other hand by interactions of carboxyl groups of free fatty acids with hydroxyl and epoxide groups of oxidized fatty acids of fats.

- Pyrolytic processes, e.g. dehydration of oxidation products or their reactions with proteins and other components of a fried foodstuff when sensorially markedly active substances originate, glycerol (released by hydrolytic processes) dissociation to acrolein belongs to pyrolytic reactions.

Processes described in the analysis result in an idea to use deep-frying oils (of HETG type) as a raw material for recycling oils resistant to the rapid course of oxidation. The reason consists in a fact that recycled oil, i.e. oil produced on the basis of a rape-seed raffinate subject to operation characterized by high thermal load was treated to further predominantly technical use. Thus, at this conception, esterification need not be carried out and the fact appears to be a source of financial savings. By mixing palm oil (20%) with rape-seed raffinate (80%) 'deep-frying oil' is obtained which is distributed into a trade network. Existing companies aimed at the collection of utilized food oil subject to thermal load accumulate the oil in tanks and treat it according to the requirements necessary for further technical use.

During the time, three types of samples were prepared and tested. In the first stage of testing, the samples were not treated with the exception of filtration (a sample marked NAPRO 9901). Because the samples are only little satisfactory from the viewpoint of quality, in the second stage of testing, the treating of oils was carried out by means of decreasing the initial acidity and bleaching and the sample was marked NAPRO 2001 and in the third stage, antioxidants and other oil additives were used and the sample was marked NAPRO 2002.

In the final part of the paper, results are evaluated of the service life test and present possibilities are assessed of the recycled variants.

The processes mentioned above result in an idea to use deep-frying oils as a raw material for recycling oils resistant to the rapid course of oxidation. The reason consists in a fact that a recycled oil, i.e. an oil manufactured on the basis of a rape-seed raffinate subject to an operation characterized by high thermal load was treated to the further predominantly technical use. By mixing palm oil (20%) with rape-seed raffinate (80%) we can obtain 'deep-frying oil' which is distributed into the trade network. There are enterprises which focus their activities on the collection of used food oils, gather them in tanks and carry out their necessary treatment and adjustment required by further technical uses.

METHODS

To assess the service life of recycled oils a verification test has been proposed and elaborated based on the theory of abridged tests when the selection of suitable physical and chemical parameters of a liquid is carried out and their degradation is observed up to the limiting state of usability. The methodology has proved its worth and serves also for recycled oils. Prior to beginning the work some preconditions were uttered. Basic conditions

that the starting values of acid number will be higher and that oxidation stability of the tested oil will be better have been proved by the tests. An assumption that the water content would not be markedly increased due to the use of oil before its recycling has been also fulfilled by accomplishing the service life test.

Determining the parameters under study

In each of the quality indicators a limiting value is determined either with general validity or with respect to specific operational conditions. Its attainment means total exploitation of desirable properties and impossibility to fulfil originally set functions in the future. The debased oil has to be replaced by a new oil filling. Exceeding the limiting value even in the only one parameter is sufficient for the radical step.

In the course of already previously carried out tests it was found that the following parameters ranked among the basic indicators of the service life of hydraulic biodegradable oils:

1. Viscosity (mm^2/s) at 40°C ;
2. Acid number (mg KOH/g);
3. Water content (%);
4. Peroxide number ($\text{mmol O}_2/\text{kg}$ or $\mu\text{g/g}$).

The first three parameters are able to assess basic properties of oils required in technical conditions of hydraulic liquids. Thermooxidation 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 so far carried out work is the study of thermooxidation properties of oils by means of peroxide number. Together with iodine number the value of which is known for rape-seed oils enabling rough estimate of the thermooxidation stability of oil the peroxide number makes possible by its marked changes during the course of the service life test to determine the time of the oil service life. Iodine number informs on the number of double bonds causing potential danger of the origin 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 operation called induction period is to be as long as possible. It corresponds to the conception of the chemical service life of oil. Increased degradation of oil is shown in the higher formation of peroxides, formation of di- and polymers, splitting the ester bond under the formation of free fatty acids and partial glycerols, origin 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 in marked changes (increase) in the acid number and viscosity of oil. In recycled oils due to the previous disintegration of double bonds, slightly increasing course of peroxide number is expected together with marked decrease in the formati-

on of polymers which finally results in the substantial improvement of thermooxidation stability.

In the final part of the paper, results are assessed of the service life test and present possibilities are evaluated of particular variants of samples of recycled oils given at the end of the chapter Material. Terminology and terms are used according to CSN and ISO Standards and corresponding content is assigned to them.

On the ground of economy, gearboxes ALBOX which stress oil mechanically in a similar way as elements of hydraulic circuits are used in the tests. A number of ALBOX gearboxes is of modular construction which makes possible to compose two- and three-stage combinations from six basic one-stage gearboxes. A two-stage combination, specifically of size 63/100 driven by an electric motor of 4 AP 90L – 8 type mounted by means of a distance piece, power 0.55 kW, engine speed 930 min and moment of torsion 190 Nm was chosen for the tests. In the oil filling of each of the stages, a gear wheel or a gear pinion run in oil. For the purpose of filling, draining and control of oil table, a filler plug, a drain plug and an inspection level screw are in a gearbox of each of its stages. The inner space of particular stages is tighten in the place of a gear pinion and output shaft by GUFERO shaft packing which is of polyurethane being resistant to the effect of triglycerols. A working position does not affect oil filling, however, the oil has to be filled up to the inspection level screw. For the purpose of the test, the recommended volumes of oil appear to be very small and, therefore, after consultations with a 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 in required intervals of service hours.

For the purpose of testing, a test block has been designed and implemented consisting of a frame on which two ALBOX Alfa 63/100 gearboxes are mounted by means of screws (marked as green and yellow) driven by separate electric motors. Output shafts of both gearboxes are shouldered by belt pulleys of different diameter 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 oil fillings.

Both gearboxes, i.e. gearbox 1 (yellow) and 2 (green) were run in by BIOMIL PR oil because the oil appeared to be a quality one during previous applications in hydraulic systems. Thus, it could be potentially used in gearboxes. The filling was then replaced by recycled oil based on rape seed. According to a working hypothesis, properties of tested oils (NAPRO) will be very good for a period of min. 1,500 service hours and changes in basic selected parameters will be in allowed limits. In case of fulfilling the precondition (see results and evaluation), the service life test will continue and the parameters will be assessed. Thus, oil is taken for testing the parameters in determined intervals and after their accomplishment its residual part is returned to a gear-

box. At the same time, a rule is taken into consideration that the temperature of taken oil ranges between 40 and 65° C. Attention is paid to the purity and dryness of the sample box which is carefully closed and equipped with a key. Samplings are recorded in a book of tests. The test is interrupted after the obvious degradation of one of the parameters.

Corresponding attention was also paid to sampling in tests when methodology was based on generally applicable principles.

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

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

Determination of peroxide number in animal and vegetable fats is carried out according to ČSN ISO 3960 from 1994 which is identical with ČSN 58 8765 Standard.

Determination of the water content is carried out according to ČSN 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.

Determination of density is carried out according to ČSN 65 6010 Standard – Oil and oil products. Methods of determining the density operative from 1983. A method for determining the density by areometer was used.

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

RESULTS AND DISCUSSION

Tabular data (see Tables 1 and 2 for NAPRO-HO 9901, Tables 3 and 4 for NAPRO-HO 2001, Tables 5 and 6 for NAPRO-HO 2002 and Table 7 for selected comparative oil which is the most quality oil methylester manufactured by the standard BIOMIL PR technology) from reports on tests were converted to diagrams created as a continuous chart of the measured data of particular parameters and then converted to diagrams

Table 1. NAPRO-HO 9901 yellow gearbox

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O kg)	Water content (% H ₂ O)
0	64.2	2.28	5.31	0.800
300	63.1	3.75	6.74	0.700
600	63.1	3.62	3.63	0.670
900	68.6	5.11	5.51	0.610
1,200	63.8	4.76	7.41	0.660
1,500	89.9	7.31	11.30	0.790

Table 2. NAPRO-HO 9901 green gearbox

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O kg)	Water content (% H ₂ O)
0	63.2	2.25	5.14	0.780
300	63.1	3.15	5.90	0.710
600	63.0	3.52	3.90	0.650
900	63.5	4.73	5.34	0.600
1,200	63.7	4.70	7.12	0.640
1,500	63.9	4.78	7.41	0.560
1,800	69.1	5.56	5.83	0.800

Table 3. NAPRO-HO 2001 yellow gearbox

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O kg)	Water content (% H ₂ O)
0	57.6	2.14	1.76	0.150
300	56.4	2.46	3.31	0.071
600	54.7	2.44	3.94	0.065
900	53.7	2.44	3.45	0.062
1,200	53.5	2.42	3.75	0.057
1,500	53.8	2.36	4.58	0.042
1,800	54.3	2.70	3.36	0.063
2,100	67.8	5.88	12.90	0.116

comparing parameters of viscosity, acid number, peroxide number and water content (Figs. 1 to 4). According to recommendations of standards it is possible to state that the main parameter under investigation is viscosity changes of which must not be $> \pm 10\%$. The requirement is observed in NAPRO-HO 1999 samples minimally to a value of 1,500 service hours and in NAPRO-HO 2001 and 2002 samples minimally to a value of 1,800 hours. According to a precondition, greater increase in the water content did not occur during the tests because the development of peroxide number indicates that the oil occurs in a condition when due to its recycling the peroxide number increases only slightly so that the creation of polymers increases only moderately as indicated

Table 4. NAPRO-HO 2001 green gearbox

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O kg)	Water content (% H ₂ O)
0	57.6	2.14	1.76	0.150
300	56.4	2.46	3.31	0.071
600	56.8	2.44	3.81	0.062
900	56.1	2.50	3.14	0.084
1,200	55.6	2.40	3.86	0.051
1,500	56.0	2.32	4.24	0.041
1,800	56.5	2.70	2.83	0.061
2,100	57.4	2.75	4.10	0.094

Table 5. NAPRO-HO 2002 yellow gearbox

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O/kg)	Water content (% H ₂ O)
0	45.7	2.65	3.20	0.099
400	48.1	2.85	4.50	0.067
800	47.3	3.26	6.90	0.060
1,200	48.6	3.12	3.30	0.033
1,600	50.9	3.59	5.70	0.027

Table 6. NAPRO-HO 2002 green gearbox

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O/kg)	Water content (% H ₂ O)
0	45.7	2.65	3.20	0.099
400	48.0	2.95	4.10	0.157
800	47.6	3.06	4.50	0.047
1,200	49.0	3.06	3.30	0.033
1,600	49.0	3.10	4.50	0.028

by the development of viscosity, however, hydrolysis of ester bonds did not yet occur.

These results are also corroborated by the measurement of iodine numbers. The iodine number of rape-seed methylester ranges about 110 mg I₂ 100g, in recycled oils a little more than 100 mg I₂ 100g were measured which is promising because decreasing the value provides a realistic presumption to decrease the recycled oil thermooxidation instability. Further evaluation of the tests confirms the assumption.

After elapsing the time, the course of the diagram shows that oil degradation occurred in the yellow

Table 7. BIOMIL PR

Time (hour)	Kinematic viscosity (mm ² /s)	Acid number (mg KOH/g)	Peroxide number (mM O/kg)	Water content (% H ₂ O)
0	35.3	0.66	0.00	0.56
500	35.5	0.65	6.23	0.45
800	36.1	0.61	13.77	0.39
1,000	36.3	0.74	17.21	0.24
1,500	37.3	1.04	26.87	0.29
2,000	38.6	2.56	28.10	0.26

gearbox which could be explained by the effect of unsuitably used metals or decomposition of unsuitable materials of packing. Acid number which informs on the change by its growth changed substantially in the yellow gearbox and in the second gearbox, it changes proportionally with an acceptable trend in growth. Increase in acid number is explained by the increase in the content of free fatty acids being not desirable for the gearbox operation. However, effects have not been proved of packing from recommended materials on the loss of functionality. On the contrary, if the packing is from an unsuitable material it obviously does not cause total degradation of oil within 1,500 service hours. Emphasis laid on decreasing the initial acid number and improving the colour in preparing the recycled product and adding additives results in improving the thermooxidation stability and other parameters. Peroxide number slightly increases, however, its rapid increase and reverse did not occur. An assumption has been corroborated that the oil is (due to its heat load during deep-frying) already beyond the region of its steep increase and decrease not containing greater

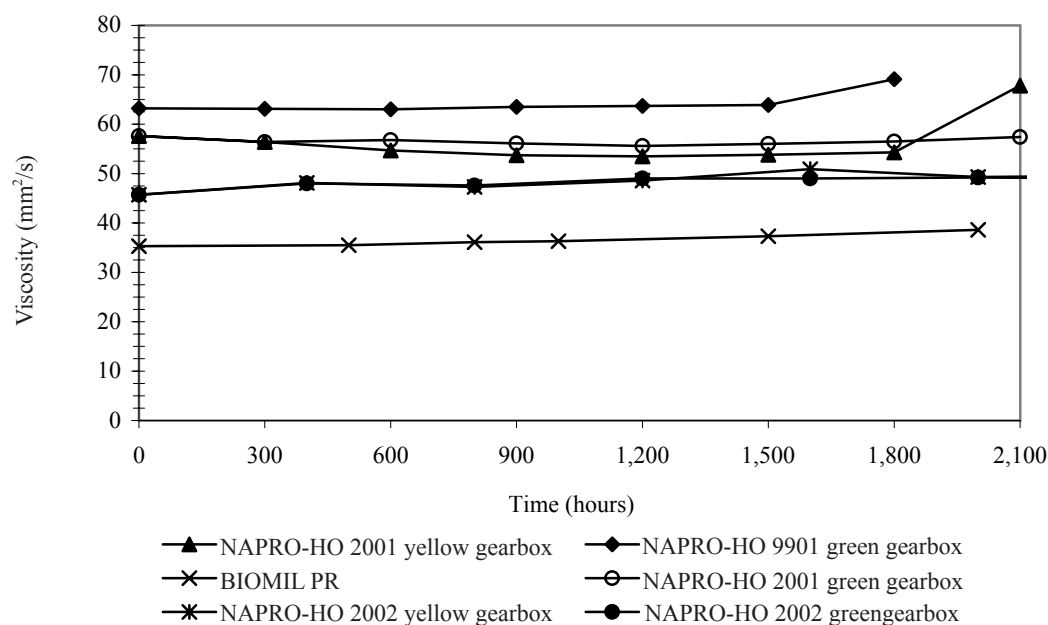


Fig. 1. Graph of time dependence of viscosity

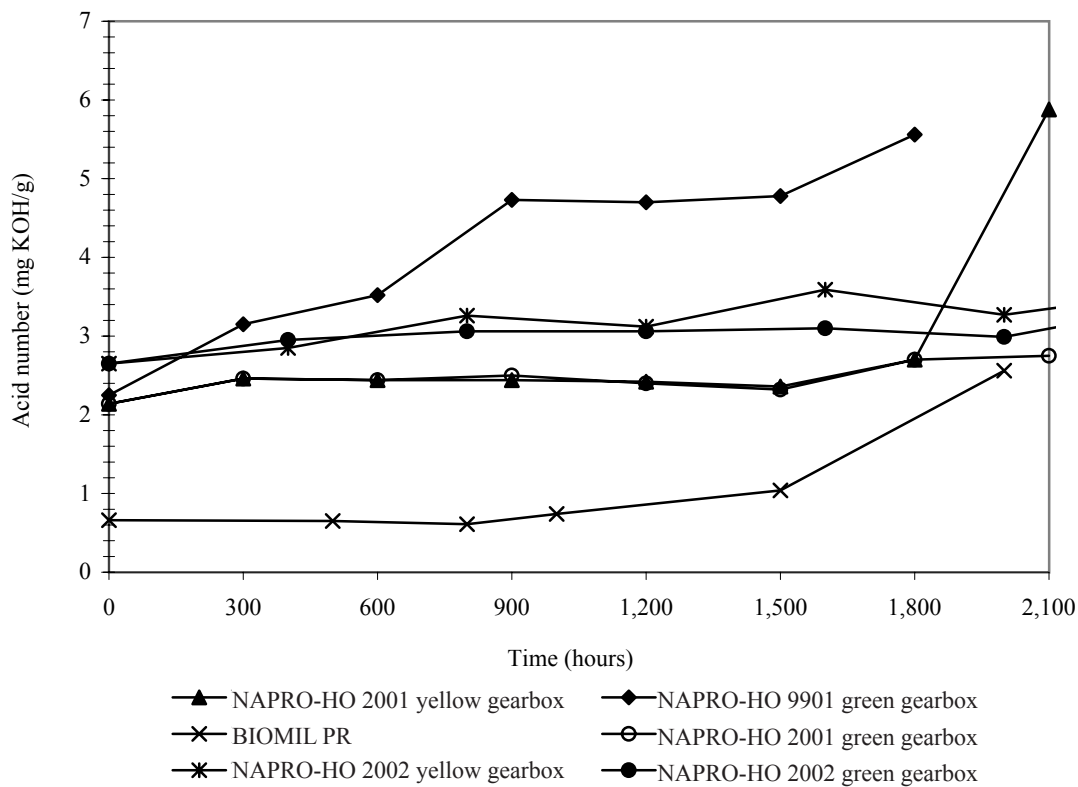


Fig. 2. Graph of time dependence of acid number

amounts of double bonds which could cause oxidation instability. Increase in viscosity with operation time changes only little but a permitted tolerance was exceeded in the yellow gearbox only. So far, effects of

additives are indemonstrable (until the conclusion of tests of NAPRO-HO 2002 samples), however, there is a realistic assumption to increase the oil service life to a limit of 2,500 service hours.

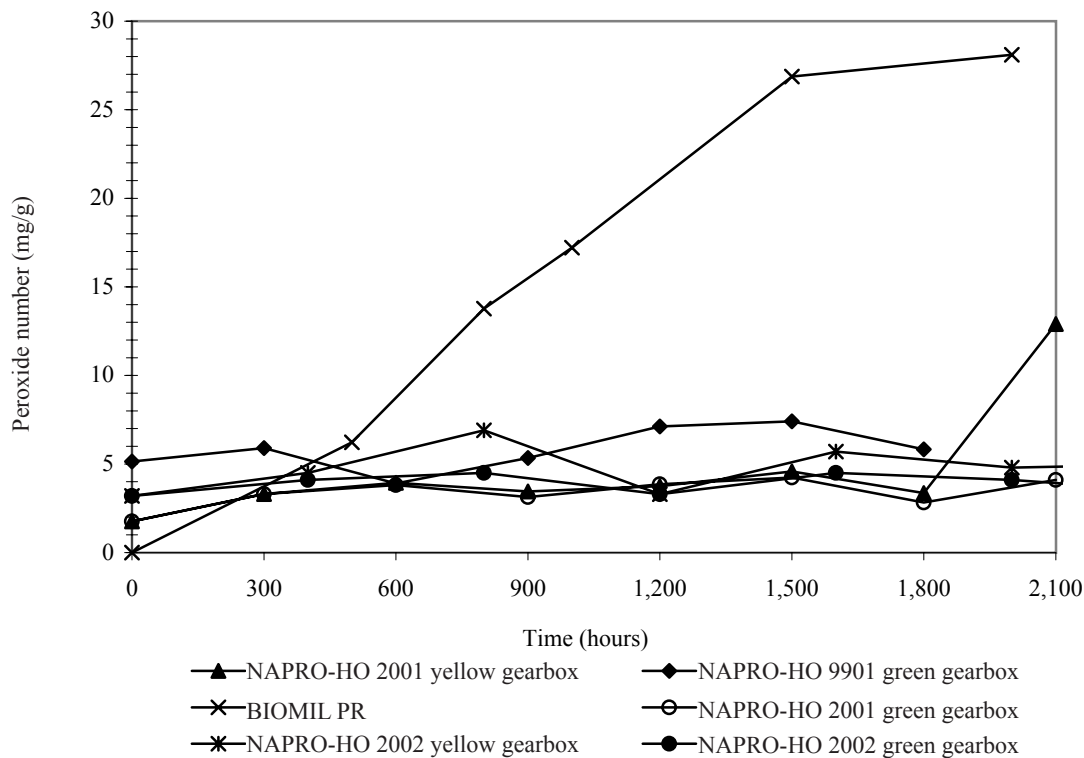


Fig. 3. Graph of time dependence of peroxide number

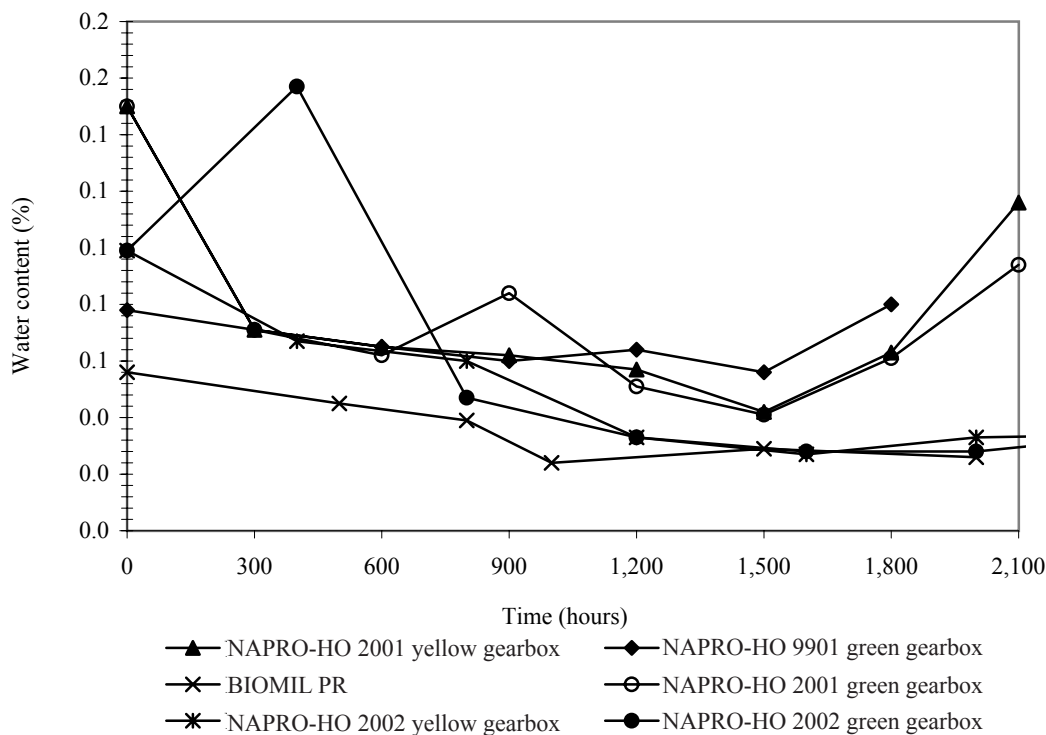


Fig. 4. Graph of time dependence of water content

CONCLUSION

The paper deals particularly with the possibility of improving the thermooxidation stability of rape-seed oils of HETG type. One of the possibilities which corresponds to the state programme of useful, economic but mainly ecological solution of the problem of oil wastes in agreement with Law No. 125/97 Gaz. on wastes and its novella No. 167/98 Gaz. is the collection and subsequent recycling of rape-based oils. Particularly deep-frying oils which underwent considerable thermal load in kitchen operation appear to be suitable for recycling. The basic idea consists in an assumption that through the thermal load considerable number of double bonds decreased. The bonds are the basic source of polymerization reactions, i.e. thermooxidation instability of oils. Such an oil, observing other important physical and chemical parameters, can be used after recycling as a filling of gear boxes or even less stressed hydraulic circuits.

In Introduction, the origin and some important properties of raffinates of rape-based oils are discussed. Further, possibilities are evaluated of recycled oils on rape-seed basis (HETG) after the first use and their treatment for using in gear boxes, methodology is given for studying and assessing the technical condition of recycled products. Values of basic parameters and the course of their changes during time indicating the reliability of recycled oils with respect to the technical service life of fillings are presented in tables and diagrams.

The service life test corroborated that NAPRO-HO 9901 oil was in good condition for a period of 1,500 service hours and that the oil could be recommended as

a filling into gear boxes. The service life of NAPRO-HO 2001 samples is minimally 1,800 service hours and in NAPRO-HO 2002 samples, it is possible to suppose a service life of 2,400 hours. Comparisons with the behaviour of usually recommended oils (pure raffinates) show that the NAPRO oil ranks among types of rape-based oils with average properties. The thermooxidation stability of oil was, however, improved substantially, i.e. peroxide number does not change markedly and the origin of hardenable polymerized deposits did not show. Other parameters degrade, however, more rapidly than values of top-class raffinates. In the operation of gearboxes, it is suitable to recommend yearly terms of exchange.

In conclusion, I think it is correct to give the value of biodegradability degree according to the CEC L-33-A-93 test which amounts to 96.8% in NAPRO-HO 9901 oil.

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Výsledky vývoje biologicky odbouratelných olejů vhodných pro lesnické stroje

ABSTRAKT: Příspěvek je reakcí na problematiku znečišťování životního prostředí úniky ropných výrobků z mechanismů lesnických i zemědělských strojů. Řešení problému je možné náhradou minerálních olejů biologicky odbouratelnými oleji. Informace týkající se měření parametrů těchto olejů již autor publikoval. Prokázalo se, že parametry jsou vcelku vyhovující kromě termooxidační stability. Příspěvek je proto zaměřen na zlepšování termooxidační stability biologicky odbouratelných olejů typu HETG. Dosud používané rafináty olejů na řepkovém základu, metylestery, jsou dodávány v různé kvalitě, většinou s životností 600 až 2 000 provozních hodin při teplotě do 70 °C. Metodika zkoušení spočívá ve sledování změn čísla kyselosti, viskozity, obsahu vody a peroxidového čísla během životnosti zkoušky. Prokázalo se, že peroxidové číslo nejlépe charakterizuje termooxidační stabilitu, která je u rafinátů téměř nevyhovující. Byla navržena metoda pro zlepšení termooxidační stability, využívající vysokého přehřátí oleje v počátku používání a jeho následných úprav. Fritovací oleje (HETG), u kterých je typický krátkodobý tepelný stres, jsou vhodné. Filtrací a úpravami byly vyvinuty a odzkoušeny tři typy vzorků; přínosem postupu je, že odpadá esterifikace. Výsledky těchto zkoušek jsou vyhodnoceny a porovnány s vlastnostmi klasických rafinátů. Lze konstatovat, že došlo k podstatnému zlepšení termooxidační stability, ostatní sledované parametry jsou u aditivovaných vzorků srovnatelné s rafináty.

Klíčová slova: biologicky odbouratelné oleje; průsak; znečištění životního prostředí; hydraulický obvod; převodová skříň; termooxidační stabilita

Corresponding author:

Doc. Ing. MIROSLAV ROUSEK, CSc., Mendelova zemědělská a lesnická univerzita, Lesnická a dřevařská fakulta, Ústav lesnické a dřevařské techniky, Lesnická 37, 613 00 Brno, Česká republika
tel.: + 420 545 134 104, fax: + 420 545 211 422, e-mail: rousek@mendelu.cz
