BIODEGRADABLE OILS AND PROTECTION OF THE ENVIRONMENT

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ABSTRACT

The paper deals with the possibility of substituting mineral oils by biodegradable oils. After the analysis of properties and possibilities of the use of rape-seed oils of HETG type, it is stated that these oils show generally very low thermooxidation stability. One of the possibilities of dealing with the present conditions which corresponds to the Czech governmental programme of useful, economic but above all ecological solution of oil waste problems according to Law No. 125/97 Gaz. on wastes and its novella No. 167/98 Gaz. is the collection and subsequent recycling of oils on the rape-seed base. The objective is to improve thermooxidation stability of the oils. A basic idea consists in an assumption that through thermal load, considerable amount of double bonds decreased the bonds being the basic source of polymerization reactions, in other words thermooxidation instability of oil. Such an oil, under conditions of observing other important physical and chemical parameters, can be used after recycling as a filling for gearboxes or less loaded hydraulic systems of forest machines fulfilling strict requirements of Czech laws concerning forest protection. Results are presented of service life tests of raffinates and recycled oils. Comparisons with the behaviour of commonly recommended oils show that recycled oils rank among types of rape-seed oils with average properties. However, the thermooxidation stability of the oil was substantially improved, peroxide number was constant and the origin of hardenable polymerized deposits did not occur.

Keywords: biodegradable oils; environment protection; gearbox; hydraulic circuits, recycling oils, reliability

INTRODUCTION

Possibilities of improving the environment conditions and decreasing the level of its pollution by fillings of gearboxes and hydraulic circuits of forest machines through sub-

stituting mineral oils by biodegradable oils particularly by rape-seed oils (HETG) were dealt with in recent years results being published by ROUSEK (2000). Results of service life tests, development of the acid number and viscosity were published by HARMS (1998) and effects of biodegradable oils on packing were studied by KUCERA (1999).

The paper deals with problems of introducing the oils in connection with the environment protection. After the analysis of basic chemical, physical and technical properties of refined biodegradable oils based on a rape seed basis of HETG type possibilities are studied of improving their properties for technical purposes, above all their thermooxidation stability. One of the possibilities to improve the property according to the state programme of a useful, economic but above all ecological handling the problem of oil wastes conformable with Law No. 125/97 Gaz. on wastes and its novella No. 167/98 Gaz. is collection and subsequent recycling of food oils based on rape seed. Particularly deep frying oils which were exposed to considerable thermal load in kitchen operations appear to be suitable. A basic idea consists in an assumption that through thermal load, considerable amount of double bonds decreased the bonds being the basic source of polymerization reactions, in other words thermooxidation instability of oil. Such an oil, under conditions of observing other important physical and chemical parameters, can be used after recycling as a filling for gearboxes or less loaded hydraulic systems. At the same time, in co-operation with SETUZA Olomouc Co., possibilities were tested and verified to use recycled oils as an admixture for a raw material charge for the production of methylester which is one of the basic components of biodiesel fuel of the second generation. Thus, in this threefold use of rape-seed raffinate it is possible to see a required conclusion of the rape reproduction cycle from the production of rape seed up to combustion in exhaust gases which are much less carcinogenic than products of diesel oil combustion. Therefore, it is necessary to create a more intensive pressure for introducing biodegradable oils. It is a fact that application of rape-seed oil in hydraulic systems is rather problematic and a temperature range of 40 to 70oC limits the field of their use. Based on circumstances mentioned above conclusions were deduced that from the technical point of view it is necessary to direct applications of natural esters (rape-seed oils) to the field of using in hydraulic circuits of machines and gearboxes of low load.

ECOLOGICAL ASPECTS OF THE PROBLEMS

Increasing the ecological safety of the operation of wood-processing or forest machines became (in consequence of the adoption of the Forest Law) one of the main problems of the operation of forest machines and equipment. In § 32 dealing with forest protection and particularly in a section concerning the responsibility of an owner to protect the forest against pollutants occurring in the course of forest management increased requirements are put to deal with sudden leakage of fillings of hydrostatic circuits and gearboxes of machines into the natural environment. A transition to biodegradable oils mastered in the context of all aspects would contribute to strengthen

ecological safety of forest operations.

The following arguments contribute to substituting mineral oils by vegetable oils on the basis of rape-seed triglycerides:

- the present trend of the development of prices in mineral oils indicates that it is of gradual but continuously increasing character,
- mineral oils are obtained from natural sources (crude oil) which are, unfortunately, non-renewable,
- the present state agricultural policy motivates rape producers through subsidies,
- crop production as a source of rape seed shows favourable conditions in our geographical latitudes as well as a support based on experience obtained by many-year tradition,
- through Law No. 289/95 Gaz. on forests, a duty has been enacted to introduce biodegradable oils into forest operations.

On the ground of economic reasons it is advantageous to tend to biodegradable oils based on rape seed basis. In biodegradable oils produced by traditional refining procedures there is a number of problems in the field of technical use. The paper deals with methods of their solution. It refers particularly to improving the poor thermooxidation stability of raffinates manifesting in the origin of hardenable polymer deposits which show a fundamental effect on the loss of the machine mechanism function. A quite original procedure of treatment has been proposed consisting in overheating the rape-seed oil to a high temperature, subsequent removing the oil sludge and next treatment including additive addition which markedly improve the instability. Thus, in this connection, the use of food oils subject to food-processing operations is directly offered.

Good lubricating and viscosity-temperature properties, resistance to corrosion (low water content), tolerance to materials of hydraulic circuits, low setting temperature, stability of a liquid with a limited creation of sludge and sticky substances rank among criteria used for assessing the suitability of fluids for a function in hydrostatic mechanisms.

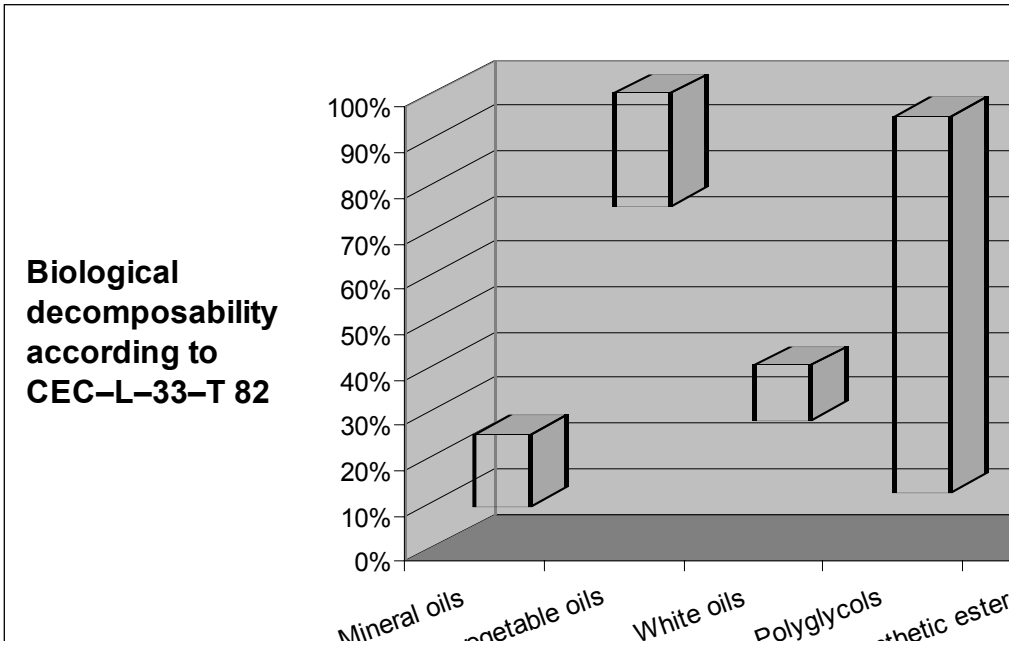
Biologically easily degradable hydraulic fluid is such a product which is biologically sufficiently quickly degraded and which is not toxic (both the fluid and products of its degradation) for flora and fauna.

In carbonaceous substances, aerobic and anaerobic processes of degradation are known. In aerobic degradation, fatty acids are decomposed by the action of oxygen, water and bacteria to water and carbon dioxide a product being both energy and biomass. Anaerobic degradation is characterized by the decomposition of fatty acids by means of bacteria and water to methane and carbon dioxide and also energy and biomass originate. At present, results are known of the decomposition of fluids of both plant and synthetic origin which are to be substituted for mineral fluids (Fig. 1). It refers to fluids based on polyalkyleneglycols and synthetic esters which are degradable after a period of 21days, according to a type from 10 to 100% and natural rape-seed oils degradable from 75 to 100%. As compared with mineral oils which are degradable only from 10 to 30% a promising shift is evident.

Above all, it is suitable to explain briefly the essence of ecologically favourable

properties of biodegradable oils. It refers to substances easily degradable by microorganisms. Under the effect of oxygen and microorganisms which exist in every normal soil the conversion of oil to biohumus (dead microorganisms) and products of degradation occurs which are water and gases (largely carbon dioxide) in a final stage. The rate of decomposition is cardinal in the process. Advantages of easy biological degradation of the fluids are thus based on their rapid transformation to carbon dioxide, water and biomass after their penetration into soil or water. Due to the fact, a rapid decontamination of the affected environment occurs. However, it is not a case of leakage of large volumes of the fluids on small areas of soil or water.

Biodegradation can be defined as a biologically directed reduction of complex chemicals (substances of both natural and anthropic origin). In case of a total degradation of a chemical to primary mineral components (CO2, N, C, P etc.) biodegradation is identical with mineralization. Biodegradation of hydraulic oils is nearly exclusively assessed by a test designated as CEC L-33-A-93 from 1995. The standard has become part of a direction of the Czech Republic Ministry of the Environment No. 15 - 96. Up to 1995, the standard CEC L-33 -T-82 was in operation. The test is carried out in the water solution of oil under the use of a strain of bacteria from a cleaning device.



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 phytogenetic, 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 desodorization. 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 implementation 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 (CnH2n + 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:

alcohol	+	acid	==>	ester	+	water
glycerol	fatty acids			triglycerol	H2O	

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-1). Ageing which is manifested by the increase in 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.

As for the content of fatty acids for technical purposes (not only for the production of biooils), rape with the original content of erucic acid (40 - 50%) which shows antioxidation properties and is without linolenic acid would be more acceptable. Although it is possible to ensure separate growing and processing two types of rape, the present practice is different.

The fact emphasizes the importance of oxidation stability of hydraulic fluids. Oxidation stability is the capability of oil to resist to the effect of oxygen which in relation to environment temperature causes a number of chemical changes in the TAG molecule.

It refers particularly to reactions on a double bond in the chain of fatty acids. The higher the degree of unsaturation of fatty acids the more sensitive the acids to oxidation. It is the main reason of rape breeding to the low content of linoleic and linolenic acid. A number of substances, e.g. oxygen (particularly of singlet type), heat, light, occurrence of metals (particularly Cu, Fe and Mn) and antioxidants (natural and synthetic) effects oxidation and antioxidation properties. Of fundamental importance are the level

and quality of refining processes, methods and conditions of storage (inert atmosphere) etc. The process of ageing vegetable oils can be briefly described as a chemical reaction starting with the formation of peroxides (oxidation) and hydroperoxides (autooxidation) on a double bond, formation of dimers and polymers (polymerization), splitting the ester bonds and formation of free fatty acids and partial glycerol esters (esterification), formation of aldehydes, ketones, oxy - and hydroxy acids. By virtue of the knowledge of some chemical characteristics it is possible to conclude that the oil is liable to the changes.

Iodine number gives information on the number of double bonds causing potential danger of starting rapid ageing. Peroxide number informs on the amount of bound active oxygen (peroxides) on the double bonds. At the beginning of operation it increases, initiation rate is small and it is desirable this stage of reaction (induction period) to be as long as possible because in this stage the oil is chemically constant. In the stage of advanced degradation a turn occurs which is related to the process of polymerization, formation of polymers in a fluid. In the process of polymerization, decrease in double bonds occurs in the TAG molecule with unsaturated fatty acids. Chain grouping takes place of particular TAG molecules. However, starting the moment oil viscosity begins to increase, and iodine number decreases. Polymerization plays a crucial role in oil desiccation.

Acid number increases with the hydrolysis of ester bonds (KOH consumption for buffering free fatty acids). General conclusions that determination of iodine or peroxide number is of importance have to result in comparisons of the numbers (ROUSEK, 1996). Oleic acid shows about 90 mg I2/100 g, linoleic acid 181 mg I2/100 g and linolenic acid 273 mg I2/100 g. Iodine number of synthetic esters oxidation stability of which is evaluated as comparable with mineral oils is given about 10 mg I2/100 g. It is possible to notice a certain dependence which has to be, however, verified experimentally in the course of the service life test. Actually, it is possible to suppose that the oil service life is related to small changes in acid number, iodine and peroxide number and the higher the peroxide or iodine number the higher oxidation stability can be expected (ROUSEK 1996).

Effects of temperature on the course of peroxide number is based on a fact that at higher temperatures peroxide decomposition 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 a normal temperature. The more unsaturated the acids the faster decomposition of the peroxides. Stability of hydraulic oils at high temperatures plays the same role as at low temperatures in connection with their 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 not be released and viscosity must not be markedly changed. Through oxidation and temperature instability various parameters (particularly viscosity) of a hydraulic fluid can be markedly changed. Saponification number shows how many mg KOH is consumed for saponification (splitting) of ester bonds. High saponification number corresponds to TAG with a short chain. The number characterizes rather the composition of fatty

acids and according to the number it is possible to reason the type of oil.

Unsatisfactory peroxide number of raffinates resulted in the elaboration of a method leading to its improvement. The procedure was operationally termed recycling because an idea to use high overheating of oil at the beginning of use for the purpose of removing polymers can be easily applied in the treatment of deep-frying oils. The procedure consists in a fact that after overheating the oil undesirable substances are removed, the raw material is bleached, its acid number is decreased and additive addition follows. Recycled biodegradable oil preserves properties comparable with biodegradable oils based on rape seed.

Under the term recycled oil we understand oil produced on the basis of using the rape raffinate subject to operation characterized by high temperature load which was treated for further mainly technical use. Through mixing palm oil (20%) and rape oil (80%) so called deep-frying oil is obtained. The oil is predetermined for frying in small deep fryers or in large devices of public canteens and dining rooms. Law No. 125/97 Gaz. on wastes sets categories of classification and procedures for waste disposal. Rape-seed oil disposal is carried out according to a key for wastes which includes exclusively vegetable oils. Through the publication of an amendatory bill No. 167/98 Gaz. on wastes an obligation of the user is enacted to document the method of used oil disposal.

METHODS

While up to now, oil in various machine mechanisms is exchanged after elapsing obligatory lawful replaceable periods without any relationship to its serviceable properties, implementation of the measurement of basic indicators makes possible to achieve more economical use of hydraulic and gearbox oils. Theory of technical diagnostics is used to monitor and evaluate the measurements. There is a close relationship between theory of reliability and technical diagnostics. In the application of methods of technical diagnostics already in the stage of monitoring the reliability (of an experiment) it is evident that indicators of reliability will not be related only to moments of the origin of disorders and defects as in the case of standard reliability but on the period of the machine operation related to the achievement of a certain value of a diagnostic signal. Through optimization calculations, it is possible to determine the optimum technical condition of oil for various measures of maintenance and thus to build a system of preventive diagnostic maintenance. The objective is to predict a time when it will be necessary to carry out renewal (treatment, repair or exchange) on the basis of the knowledge of actual technical condition of the machine element. It is necessary to define indicators of a failure-free condition as the function of a technical condition. Within a test of the service life of a machine element we will monitor not only the operation time t but also a suitable diagnostic signal S which is called an indicator of the technical condition of a studied parameter.

Determination of studied parameters

In each of the quality parameters a limit value is determined either with general applicability or with respect to given operational conditions. Its achievement means depletion of desirable properties and impossibility to fulfil the originally determined function. A fluid debased in such a way has to be replaced by a new oil filling. To exceed the limit of even the only parameter is sufficient for the radical step. On the basis of using the findings from previous service life tests of biodegradable oils standard methods of evaluation were used.

In the course of previous tests it was proved that following parameters ranked among basic indicators of the service life of hydraulic biodegradable oils:

1) Viscosity (mm2.s-1) at 40°C
2) Acid umber (mg KOH.g-1)
3) Water content (%)
4) Peroxide number (mmol O2/kg)

Layout of the test equipment

The tests were carried out in hydraulic trial circuits and gearboxes. A hydraulic trial stand is designed as a simple open hydraulic circuit. Particular kinds of oils were tested under various parameters of pressure and temperature, pressure in the hydraulic circuit up to 7 Mpa, oil temperature in the tank in the course of test was kept in a range of 40 - 65°C.

On the ground of savings of financial costs, gearboxes are also used in the tests which load the oil mechanically similarly as elements of hydraulic circuits. Relatively small weight of gearboxes, the size of transferred power per kg of weight, wide range of powers from 0.37 to 30 kW and prefabricated construction predetermine them for wide use and, therefore, they were chosen for testing the service life of biodegradable oils. The combination of construction sizes of 63/100 with an electric motor of 4 AP 90L - 8 type fixed by means of a distance piece of 0.55 kW power, 930 r.m-1 and torque 190 Nm was selected for tests. For testing, a trial stand was designed and implemented consisting of a frame on which two gearboxes ALBOX Alfa 63/100 were installed by screws ALBOX Alfa 63/100 driven by a separate electric motor. Output shafts of both gearboxes are fitted with pulley wheels and interconnected by wedge-shaped belts. Moreover, an arrangement was carried out ensuring a condition when one gearbox loads the second one. Thus, both gearboxes are fully loaded and can be used to test oil fillings.

Sampling

The basis of sampling is a condition that the sample of oil represents the whole filling of a gearbox. All operations affecting the sampling have to correspond to the fact. All tribological methods stem from a condition of the homogeneity of whole filling. However, in the course of operation, the filling need not be homogenous particularly after idle time. From the point of view of diagnostics, it is necessary to determine conditions for taking the necessary sample of oil filling. There are general rules given in literature. After 300 hours, oil is sampled to test parameters and after their implemen-

tation its remaining part is given back to the gearbox. A rule is observed that the temperature of a sampled oil ranges between 40 and 65oC. The test is interrupted after the evident degradation of one of the measured parameters.

The filling is formed by raffinates of BIOMIL type and a recycled oil on rape-seed basis, samples NAPRO - HO. A working hypothesis is as follows: properties of a tested oil will be very good for at least 1500 service hours and changes in basic selected parameters will be in permitted tolerances.

RESULTS AND DISCUSSION

For the purpose of information we give results of service life tests in recycled NAPRO oils as compared with a rape-seed oil BIOMIL PR (typical raffinate), viz.

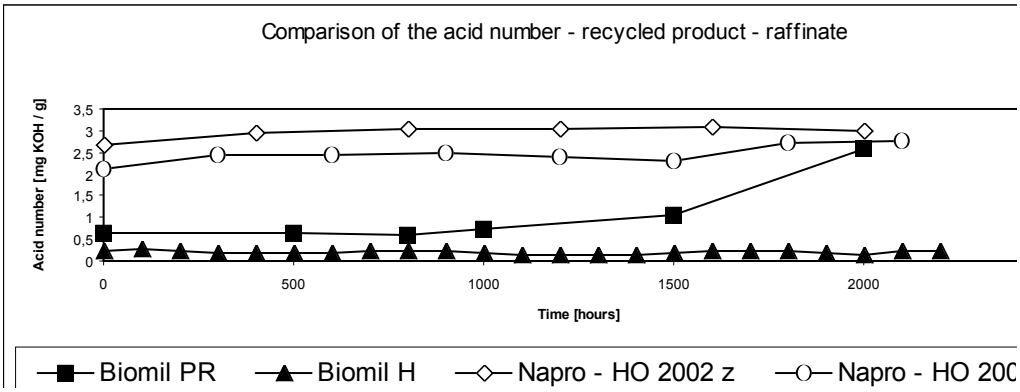


Figure 2. Comparison of the acid number of recycled products and raffinates

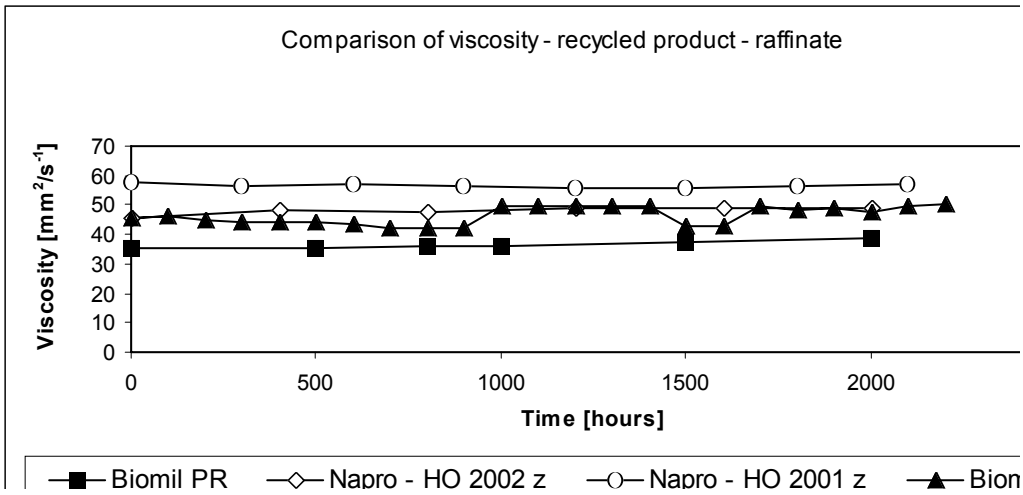


Figure 3. Comparison of the viscosity of recycled products and raffinates

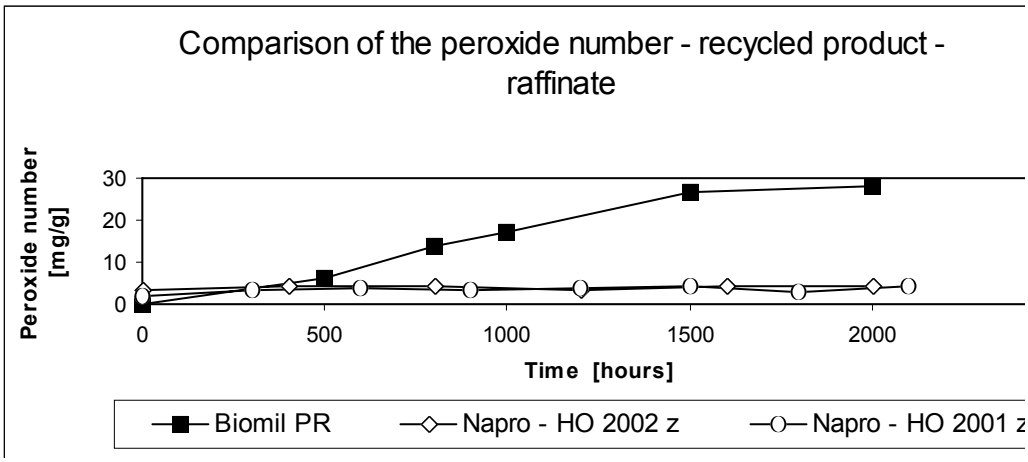


Figure 4. Comparison of the peroxide number of recycled products and raffinates

changes in viscosity (Fig. 2), acid number (Fig. 3) and peroxide number (Fig. 4).

Based on the diagrams it is possible to conclude that in all samples viscosity changes within a tolerable limits up to 1000 service hours, acid number is slightly increased (in recycled products being naturally higher). Noticeable differences occur, however, in peroxide number where thermooxidation instability of raffinates is evident. Thermooxidation stability of recycled products is good being comparable with mineral oils.

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.

To study the problem, it is important to know values of parameters of biodegradable non-additivated oils based on rape seed which went to tests directly from manufacture. BUSCH (1989) gives the following values (Tabs. 1 to 3) which were mostly corroborated by our measurements.

CONCLUSION

The paper deals with a possibility to improve thermooxidation stability of rape-seed oils of HETG type. One of the possibilities which corresponds to the state programme of a useful, economic but above all 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 oils on a rape seed basis. Particularly deep frying oils appear to be suitable. A basic idea consist in an assumption that through thermal load considerable amounts of double bonds decreased the bonds being the basic source of polymerization reactions, in other words thermooxidation instability of oils. After recycling, such an oil (maintaining other important physical and chemical parameters) can be used as a filling of gearboxes or less loaded hydraulic circuits. Service life

Table 1

Chemical parameters	Value	Unit	Standard
Total acid number	1.9 – 2.4	mg KOH.g^{-1}	ASTM D644
Saponification number	168 – 195	mg KOH.g^{-1}	
Neutralization number	0.1 – 0.6	mg KOH.g^{-1}	
Cetane number	44		
Iodine number	95 --105	mg I_2/100g	
Sulphur content	ca 19	ppm	
Impurity content	ca 21	ppm	
Water content	0.1	% weight	
Ash	ca 0.001	% weight	

Table 2

Physical parameters	Value	Unit	Standard
Density	920 – 935	kg.m^{-3}	
Molecule weight	ca 283	g.mol^{-1}	
Viscosity index	210 – 230		DIN ISO 2909
Viscosity 40^{o}C	35 – 38	mm^2.s^{-1}	
Flash point	ca 250	$^{\circ}$C	
Ignition temperature	ca 330	$^{\circ}$C	
Aniline point	9.5		
Flow point	-12	$^{\circ}$C	ASTM D97

Table 3

Technical parameters	Value	Unit	Standard
Corrosive resistance on steel	0 – A		DIN 51518
Corrosive resistance on copper	1		DIN 51759
Compressibility	7		DIN 51381
Demulsification properties	20		DIN 51599
Foam content at 25 max.	90/0	ml	
Foam content at 95 max.	30/0	ml	
FZG test	10 – 12		DIN 51354

tests have showed that NAPRO HO oils are in a good condition after 1500 service hours and the oil can be recommended as a filling for gearboxes. Comparisons with the behaviour of commonly recommended oils show that NAPRO oils rank among types of rape-seed oils with average properties. Thermooxidation stability of the oil has been substantially improved, peroxide number is stable and the origin of hardenable polymerized deposits has not been proved. In the operation of gearboxes, it is suitable to recommend annual terms of exchange.

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