

Małgorzata WRONA, Karolina DZIOSA, Anna MROCZKOWSKA
Institute for Sustainable Technologies – National Research Institute, Radom
malgorzata.wrona@itee.radom.pl, karolina.dziosa@itee.radom.pl,
anna.mroczkowska@itee.radom.pl

INVESTIGATION OF THE CHEMICAL TRANSFORMATIONS OF LUBRICATING OILS MADE USING PLANT MATERIALS

Key words

Natural antioxidants, oil compositions, thermo-oxidative stability.

Abstract

Products of natural origin represent rich source of compounds with antioxidant properties. Investigations concerning chemical composition and possible applications of these products in lubricating materials technology were conducted. The transformations of the compositions based on natural materials arising during the oxidation process were studied. The assessment of the chemical composition of base oils with plant products was carried out by FTIR spectrophotometric method.

Introduction

During typical use, lubricating oils are affected by chemical and thermal extortions. Chemical changes in oils are first of all the result of the destructive processes, including thermo – oxidation [1]. The fundamental problem, associated with usage time, is insufficient thermal and oxidation resistance. To improve the oxidation stability, among other things, suitable additives can be

introduced into a oil bases. Effectiveness of their action is mainly dependent on chemical structure, amount, interaction with oil base and different additives [1,3]. Existing technologies for the production of lubricating oils are based on use synthetic antioxidants, which in most cases are environmentally harmful. Typical additives with antioxidant action are: phenols, zinc dialkyldithiophosphates, aromatic amines, sulphides, dialkyldiaminomethane, zinc, antimony and bismuth dialkyldithiocarbamates. It is necessary to search for other substances, in particular of natural origin, which would increase ecological character of oil products by elimination of harmful metal elements from molecular structures of applied additives. Among unotoxic substances are first of all compounds of natural origin, isolated from vegetable raw materials [4–7]. Compounds with confirmed antioxidant action (and detailed described by biochemical reactions) in vegetable organisms are for example: silymarin, tocopherols, polyphenols, coenzyme Q10. Effectiveness of these compounds was empirically confirmed outside of living organisms also, particularly in cosmetic, pharmaceutical products and food. However, synthetic environment of lubricating oil, in which enzymes, coenzymes and coantioxidants not occurred in natural manner (characteristic for living organisms), fundamentally influences process of structural conversion of natural antioxidant substances, that affects their mechanism of action and effectiveness of inhibition of thermooxidative reactions.

Growth of interest in natural environmental protection problems and continuous technological progress more frequently force on producers of lubricating oils necessity of searching for products with increased ecological values. Therefore, it is reasonable to intensify investigations on use of alternative natural resources, which allows to extend usage time of oil and improve its biodegradability.

In connection with above, the objective of works was to investigate effectiveness of action of antioxidant additives of natural origin, introduced to typical base oils of mineral and synthetic origin.

1. Research methodology

Compositions of vegetable products with base oils with different percentage were examined. In the tests commercial vegetable products were used, i.e. amaranth oil, tea oil (extract), silybum oil, cold pressed oil tea, wheat germ oil. The oil bases were mineral oil SAE 30/95, poly(α)olefin Spectrasyn 6, polyester Priolube 3970. Compositions were prepared by adding selected products in an amount 0.5; 1; 5 and 10% to the base oils.

The thermooxidation stability of the particular composition was determined with PetroOXY test in 110°C temperature. This determination was based on designation of induction time, which is determinate on the base of the oxygen

pressure decrease in the reaction cell. In order to evaluate the thermooxidative degradation of oils, infrared range spectrophotometry method was used. It allowed the analysis of the chemical constitution of the oil components before and after oxidation. Transmission spectra in infrared range were carried out in a FTIR 6200 spectrophotometer equipped with an attachment ATR with a diamond crystal. The process was carried out in spectrum range $4000\text{--}600\text{ cm}^{-1}$, resolution 4 cm^{-1} , the background and measurements: 10 scans. To analyze the composition of the oils a gas chromatograph equipped with mass spectrometer GC/MS Clarus 680 was also used. The oven temperature was programmed for 80°C (2 min), $5^\circ\text{C}/\text{min}$ to 280°C . ZB-5Msi capillary column (30 m x 0.25 mm x 0.2 μm) was used. The carrier gas was helium with purity 99.9999%. The MS detection was conducted in the $m/z = 33$ do $m/z = 500$ u range in electron ionization mode. Chemical compounds were identified by comparing the mass spectrum with data from the NIST database.

2. Test results and their analysis

Figure 1 shows antioxidation activity of selected vegetable products, which was determined by Petrooxy test. It is shown that tested products differed in their antioxidation properties. Values of the induction time those materials ranged from 0.5 h for to 1.8 h for amaranthus oil. It means that wheat germ oil oxidized the fastest and it was the reason why it had the smallest stability while the Amaranthus oil indicated the biggest oxidation resistance.

Analogous tests were made for base oil composition with vegetable products. Values of the induction time tested compositions are shown in Fig. 2–4. Results of tests showed varied antioxidation activity of examined products, which depended of their concentration in base oils. On the basis of the PetroOXY test the best antioxidation properties had composition with mineral oil base with silybum oil. Values of the induction time those composition ranged from 107.8 h to 93.2 h. Addition of 0.5% silybum oil to mineral oil caused a induction time elongation from 93.3 h to 107.8 h, it is about 15.5%. Increasing the concentration of this product to 1 and 5% caused slightly smaller, but equally important, elongation of the induction time appropriately about 12.5% and 9.1%. At the maximum concentration (10%), there was no significant influence of the used product for base oil.

Among determined products there was also protective effect to mineral oil by the amaranthus oil. 1% of amaranthus oil caused a induction time elongation from to 100.2 h (approximately 7.4%), in concentration 5% – to 100.5 h (approximately 7.7%). In concentrations 0.5% and 10% amaranthus oil indicated opposite effect, i.e. prooxidation.

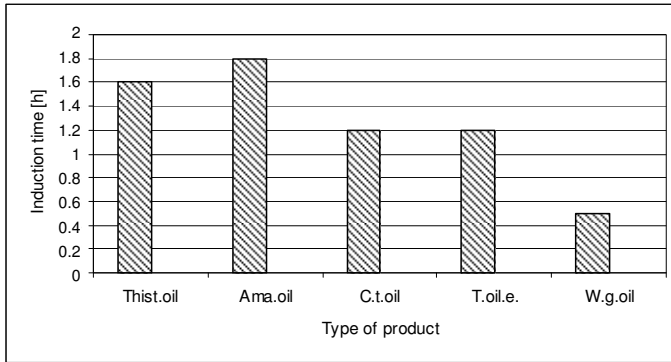


Fig. 1. Statement induction times of the vegetable products

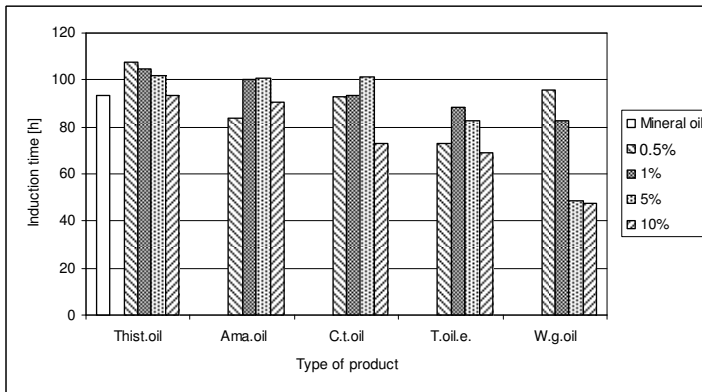


Fig. 2. Influence of the vegetable products for induction time of the mineral oil

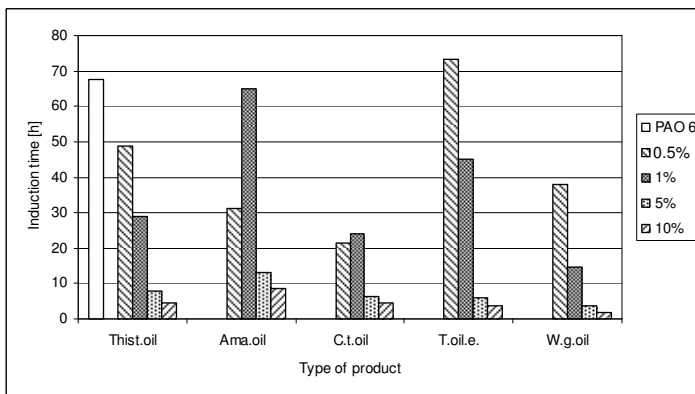


Fig. 3. Influence of the vegetable products for induction time of the PAO 6 oil

Comparing the influence of the tested vegetable materials for base oils stability (Fig. 3, 4) it was found that tea oil (extract) in concentration 0.5% efficiently inhibited polyalphaolefine oil oxidation. The induction time of base oil increased from 67.6 h to 73.3 h (approximately 8.4%). Other products used to protection base oils characterized by lowered antioxidation activity. This can be caused by oxidation of the additive itself, which was introduced into the composition as shown by the decrease in the induction time, with the increase of additive content in the oil.

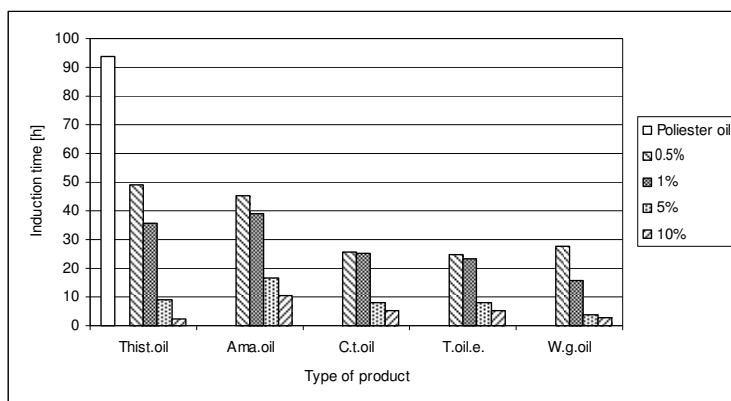


Fig. 4. Influence of the vegetable products for induction time of the polyester oil

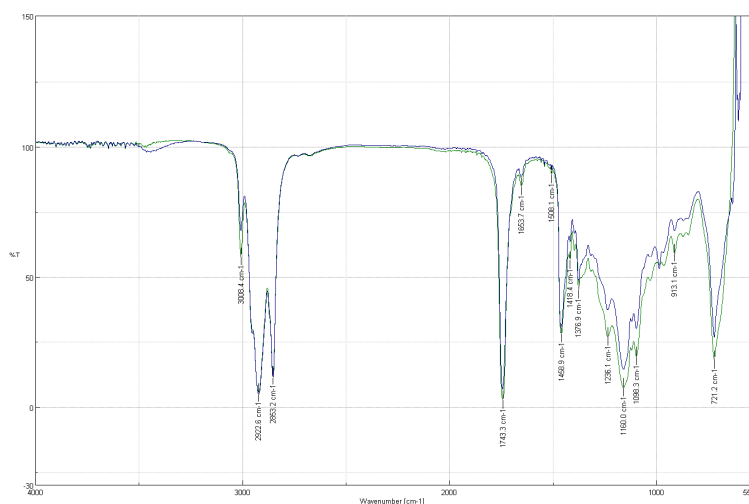


Fig. 5. FTIR spectra of the cold pressed oil tea before (1) and after (2) oxidation

The analysis of the impact of termooxidation process on determined vegetable products and their compositions with base oils was also carried out by spectrophotometer FTIR method. Examples of the infrared spectra are shown in Fig. 5–6. On the IR spectra of the determined vegetable products are visible a strong band of valance vibration from carbonyl group C=O located at 1743 cm^{-1} and band vibration from C-O group located at 1160 cm^{-1} (Fig. 5). Bands located at 1456 cm^{-1} and 720 cm^{-1} derive from deformation vibrations C-H, while band located at 1377 might be assigned to deformation vibrations O-H. In the range of approximately 3100 cm^{-1} to approximately 2860 cm^{-1} are visible signals derive from valance vibrations C-H. Analysis of the determined products after oxidation IR spectra didn't show significant differences in their courses.

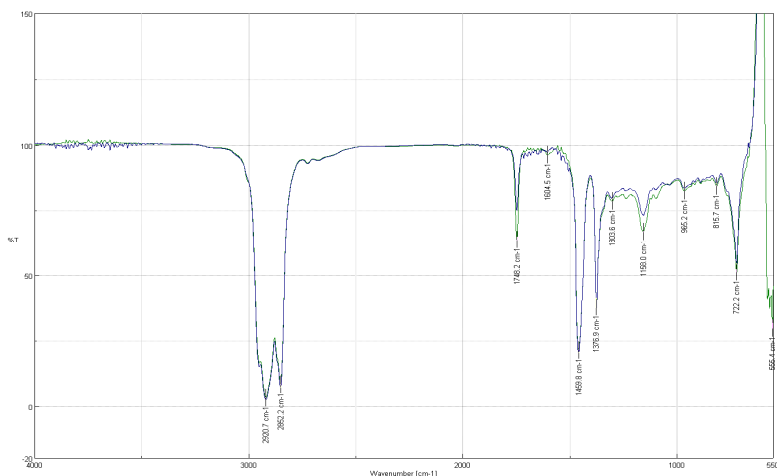


Fig. 6. FTIR spectra of the composition of mineral oil with 5% cold pressed oil tea before (1) and after (2) oxidation

IR spectra of determined oil compositions contained adsorption band characteristic for functional groups of base oils and vegetable materials which are resultant of overlapping bands. In Fig. 5 are showed IR spectra of the polyester oil with vegetable products, confirming the presence of adsorption bands which are typical for this base oil. On the IR spectra of the mineral oil and the polyalphaolefine oil with the addition of those materials there is visible band located at 1750 cm^{-1} which is characteristic for compounds of vegetable origin (Fig. 6). The changes observed in those spectra depend on the quantity of product introduced into the vegetable oil base. The appearance of the bands in the $1700\text{--}1500\text{ cm}^{-1}$ in the spectra of the composition after oxidation may indicate the presence of oxidation products (aldehydes, ketones, carboxylic acids).

Additional information about the vegetable products composition were delivered by the results of GC/MS analysis. In Fig. 7 are shown chromatograms of the before and after termooxidation process.

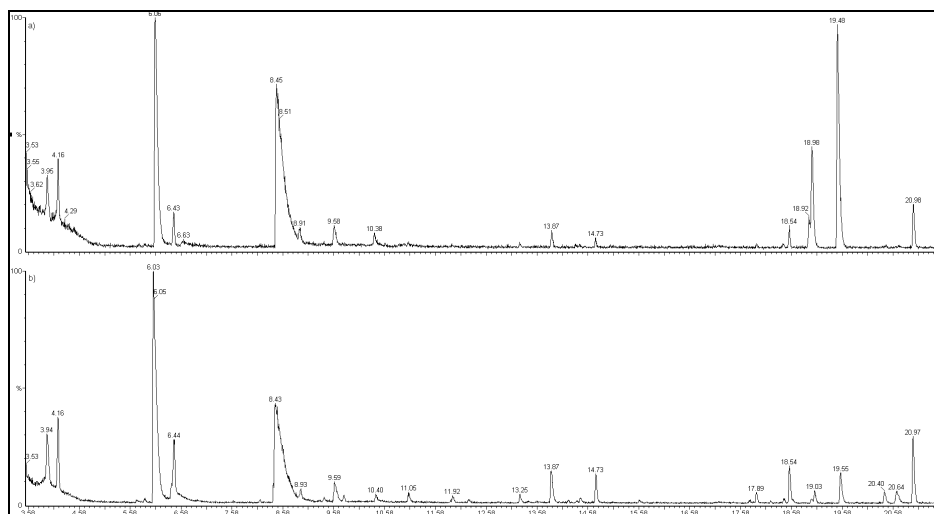


Fig. 7. Statement chromatograms of the tea oil (extract) a) before termooxidation, b) after termooxidation

The analysis of chromatographic investigation results confirms changes in composition of the tea oil (extract) after termooxidation process. In particular, content of the compounds eluted in the retention times 8.45; 18.98; 19.48 decreased, which is observed as a decrease of the appropriate peak height. The content of some of the compounds didn't change after termooxidation process, i.a.: 3-methylbutanal (retention time 3.95), heptan (retention time 4.16), hexanal (retention time 6.06). In the oil after termooxidation process some compounds were detected that were no presence in the oil before oxidation, i.a.: 1-ethyl-2-methylcyclopentane (retention time 11.05), nonanal (retention time 11.92). On the chromatogram of the oil after termooxidation process was also observed a significant increase in the content of substances eluted in retention time 6.4, i.e. 2.4 – dimethylheptan; 14.73 i.e. heptyl propyl ester oxalic acid; 20.98 i.e. 2.4-dodecadial. During the analysis of the chromatograms only peaks with at least 90% of match were considered.

Conclusions

The results indicate new possibilities for the use of plant materials in the production technology of lubricants, positively affecting oxidative stability of

base oils. The use of natural antioxidants as lubricant additives may be advantageous in comparison with synthetic antioxidants because they are generally more environmentally friendly. Based on these results, on mineral oil can conclude that the best antioxidant properties have compositions. In the case of oil PAO6 and oil Priolube decreased induction time tested compositions, which could be caused by direct oxidation addition, using the test Petrooxy. Antioxidant supplements will improve the oxygen consumption of mineral oil. In the case of other oils the additives did not improve the oxidation of properties.

Scientific work executed within the Strategic Project “Innovative Systems of Technical Support for Sustainable Development of Economy” within Innovative Economy Operational Programme.

References

1. Beran E.: Wpływ budowy chemicznej bazowych olejów smarowych na ich biodegradowalność i wybrane właściwości eksploatacyjne. Prace Naukowe Wydziału Chemicznego Politechniki Wrocławskiej. Monografie. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2008.
2. Podniało A.: Paliwa, oleje i smary w ekologicznej eksploatacji. WNT, Warszawa 2009.
3. Surygała J.: Ropa naftowa a środowisko przyrodnicze. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2001.
4. Kaczor E., Molenda J., Sadowski D.: Badanie przydatności sylimaryny jako ekologicznego dodatku przeciwutleniającego do syntetycznych i mineralnych baz olejowych. Mat. Konf. „Nafta i Gaz 2009”, Radom, 07.05.2009, s. 92–98.
5. Kozancev i in.: Stabilizacja oleju rzepakowego oraz jego estrów metyloowych naturalnymi przeciwutleniaczami. Tłuszcze jadalne 2004, 39, 246–251.
6. Małecka M.: Składniki frakcji nieglicerydowej olejów roślinnych jako przeciwutleniacze. Tłuszcze Jadalne 1995, 30, 123–130.
7. Patil A.S., Pattanshetti V.A., Dwivedi M.C.: Functional Fluids and Additives based on Vegetable Oils and Natural Products: A Review of the Potential. Journal of Synthetic Lubrication 1998, 15, 193–212.

Badanie stabilności biododatków antyoksydacyjnych w warunkach przyspieszonego utleniania

Słowa kluczowe

Przeciwutleniacze naturalne, kompozycje olejowe, stabilność termo-oksydacyjna.

Streszczenie

Produkty pochodzenia roślinnego stanowią bogate źródło związków o właściwościach przeciwutleniających. Przeprowadzono badania dotyczące składu i możliwości zastosowań tych produktów w technologii otrzymywania środków smarowych. Zbadano przemiany kompozycji opartych na surowcach naturalnych zachodzące podczas procesu utleniania. Ocenę składu chemicznego badanych kompozycji przeprowadzono metodą spektrofotometrii w podczerwieni FTIR i chromatografii gazowej sprzężonej ze spektrometrią mas GC/MS.