Rafał GRABOWSKI[*], **Jolanta IŁOWSKA**[*], **Justyna CHROBAK**[*], **Michał SZMATOŁA**[*],
Jolanta DRABIK[**], **Magdalena TRZOS**[**]

METHODS OF THE MODIFICATION OF VEGETABLE OILS IN ORDER TO OBTAIN BASE OILS

METODY MODYFIKACJI OLEJÓW ROŚLINNYCH W CELU UZYSKANIA BAZY OLEJOWEJ

Key words: vegetable oils, base oil, oxidation, N-hydroxyphthalimide, supercritical carbon dioxide.

Abstract The research results were presented concerning the development of vegetable oil modification in order to obtain a base oil with desired physicochemical properties allowing the use of such oils as the base oil in pro-ecological lubricating agents. The possibilities to modify vegetable oil to obtain base oils with a higher viscosity class were presented. The process consisted of the oxidation of oils with oxygen in the presence of NHPI as a catalyst and with the use of supercritical carbon dioxide. The influence of temperature, catalyst amount, oxygen pressure, and amount of carbon dioxide in the rape-seed oil modification process were studied. As a result of vegetable oil modification, base oils with viscosity values higher than oil without modification were obtained. The significant influence of the conditions of the process carried out in a pure oxygen atmosphere and in supercritical carbon dioxide conditions was found. It was observed that it is possible to control lubricating properties of oil intended as base oil for a lubricating agent, if the process is carried out in an oxygen atmosphere and in the presence of carbon dioxide. A product with purposely changed properties in comparison with the properties of initial oil is the effect of modification.

Słowa kluczowe: oleje roślinne, baza olejowa, utlenianie, N-hydroksyftalimid, nadkrytyczny dwutlenek węgla.

Streszczenie W artykule przedstawiono wyniki badań, których celem było opracowanie nowej metody modyfikacji olejów roślinnych w celu otrzymania bazy olejowej o pożądanych właściwościach fizykochemicznych, które umożliwią zastosowanie tych olejów jako bazy w proekologicznych środkach smarnych. Poszukiwano możliwości modyfikacji oleju roślinnego celem uzyskania baz olejowych o wyższych klasach lepkości. Proces polegał na utlenianiu olejów tlenem w obecności katalizatora i z zastosowaniem nadkrytycznego dwutlenku węgla. Zbadano wpływ temperatury, ilości dodatku katalizatora, stężenia tlenu oraz ilości użytego dwutlenku węgla w procesie modyfikacji oleju rzepakowego. W wyniku modyfikacji olejów roślinnych uzyskano bazy olejowe o wyższych wartościach lepkości niż olej bez modyfikacji. Stwierdzono istotny wpływ warunków procesu prowadzonego wyłącznie w atmosferze tlenu oraz w warunkach nadkrytycznego dwutlenku węgla. Zaobserwowano, że prowadząc proces w atmosferze tlenu i obecności dwutlenku węgla, można sterować właściwościami smarnymi oleju o przeznaczeniu na bazę olejową środka smarnego. Efektem modyfikacji jest produkt o celowo zmienionych właściwościach w porównaniu z właściwościami oleju wyjściowego.

INTRODUCTION

Lubricating agents are materials used to reduce the friction of surfaces in mutual contact and to increase their durability. Depending on components type, they can be divided into lubricating oils and greases [**L. 1–3**]. Greases are produced using a number of base oils which serve as a dispersive phase. They also contain a dispersed phase and additives. Depending on content of several components greases with various consistencies (from very fluid, to soft and even very hard) are produced [**L. 4**]. Depending on the base oil, which is the main component of greases, they can be classified as mineral (originating from petroleum), synthetic (polyalphaolefins, polyalkylene glycols, synthetic esters, silicones, etc.), and pro-ecological, biogreases.

---

[*] Institute of Heavy Organic Synthesis “Blachownia”, ul. Enegetyków 9, 47-225 Kędzierzyn-Koźle, Poland.
[**] Institute for Sustainable Technologies – National Research Institute, ul. K. Pułaskiego 6/10, 26-600 Radom, Poland.

Mineral greases, currently the most commonly used, are a complex mixture of saturated aliphatic hydrocarbons (straight-chained and branched-chained), unsaturated aliphatic hydrocarbons, naphthene hydrocarbons, and aromatic hydrocarbons, containing from 20 to 50 carbons atoms in the molecule. They are quite stable and cheaper than other kinds of lubricating agents. On the other hand, they have poor biodegradability and pose an environmental hazard, because they contain toxic compounds. Therefore, the demand for environmental friendly greases from renewable raw materials, such as vegetable oils, constantly grows [**L. 5–7**].

Regulations for lubricating agents approved for contact with food are very extensive.8 Products used in the food industry should be consistent with HACCP (Hazard Analysis and Critical Control Point) and GMP (Good Manufacturing Practice) regulations. Lubricating oils with H1 food grade are classified as permitted for accidental contact with food. In the case of H2 lubricating agents, they are not approved for accidental contact with food, but still can be used in food industry [**L. 9**]. In Poland, the National Institute for Public Health – State Department for Hygiene (Narodowy Instytut Zdrowia Publicznego – Państwowy Zakład Higieny, NIZP-PZH) is authorized for certification [**L. 10**].

In connection with the search for pro-ecological base oils in the range of realized Smart Growth Operational Program (POIR) project, the authors of this paper developed a method to modify vegetable oils in order to achieve a change in the vegetable oil's properties to improve their usability as base oils for lubricating agents [**L. 11**]. In the above mentioned paper [**L. 11**], the method used for rape-seed oil modification process parameters optimization was presented. The Taguchi approach, used formerly for tailoring of ecological greases, was applied as a part of the presented method [**L. 12, 13**]. In this article, the modification method and the obtained result confirmed the effect of rape-seed oil lubricating properties improvement after the application of the developed method was shown.

MODIFICATION OF VEGETABLE OILS

In order to obtain vegetable base oils of different viscosity grades, the oil oxidation process was applied, which occurs according to free radical chain reaction mechanism, consisting of three stages: initiation, propagation, and termination (**Fig. 1**).

As a result of the oxidation of vegetable oils with oxygen – hydroperoxides, several secondary products are formed [**L. 1, 7, 14**]. Such products can be divided into volatile and non-volatile compounds, high molecular and free fatty acids. Volatile compounds have a negative influence on lubricating properties of modified vegetable oils. They are mainly low-molecular alcohols, which are aldehydes from decomposition of polyunsaturated fatty acids. Non-volatile compounds have a partially beneficial influence on tribological properties of modified vegetable oils. The main products with a beneficial influence are epoxides, because they cause a decrease in viscosity and are relatively resistant to further oxidation, improving lubricating properties. High molecular compounds are formed as a result of cyclization and oligomerization reactions at high temperature, during the final stages of oxidation. These processes lead to an increase in viscosity (positive effect) and to an increase in free acids and polymers (negative effect). Free fatty acids are created through the decomposition of glycerides and cause the increase in tribological properties (anti-wear properties); but, at the same time, they have a lower oxidation stability and cause an increase in the corrosivity of modified oil.

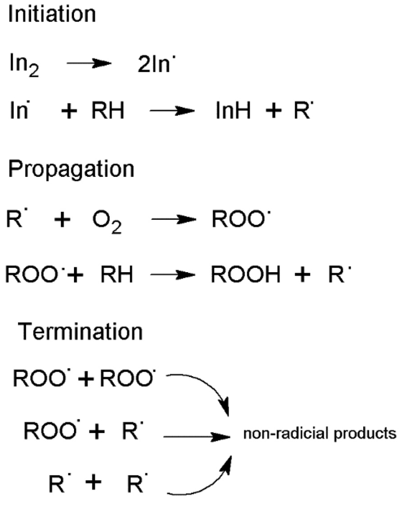

Fig. 1. Mechanism of free radical oxidation
Rys. 1. Mechanizm łańcuchowego utleniania wolnorodnikowego

To suppress the formation of undesired decomposition products, the temperature of the process can be lowered by application of a free radical reaction catalyst. The addition of such compound allows, due to lowering the process temperature, obtaining less undesirable high-molecular compounds and free acids with a synchronous increase in the viscosity and stability of vegetable oil. One of such catalysts is *N*-hydroxyphthalimide (NHPI), which in recent years is the subject of numerous studies on its use as a oxidation processes catalyst [**L. 7, 15**]. The mechanism of its catalytic action consists of creation of a PINO nitroxyl radical in the reaction of NHPI with the peroxyl radical [**L. 16**]. The radical formed in such way reacts with hydrocarbon, leading to the recreation of NHPI and yielding the hydrocarbon radical, which then reacts with oxygen, recreating a peroxyl radical (**Fig. 2**).

Oxidation processes are characterized by incubation time, in which free radicals, necessary for chain reaction, are accumulated. To reduce that time, various initiators of free radical reactions are used. Nitrogen and peroxide are the most often used substances, which are homolytically decomposed

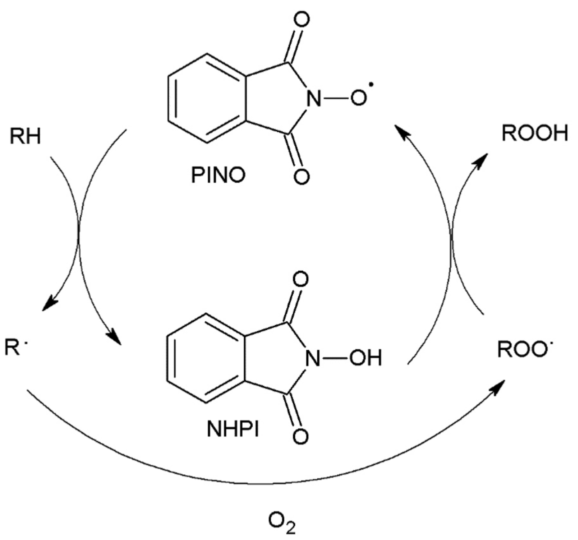

Fig. 2. Principle of NHPI catalytic cycle [L. 7]
Rys. 2. Zasada działania NHPI [**L. 7**]

to free radicals at elevated temperatures. Small additions of these initiators enable significant shortening of incubation time, supplying enough radicals to initiate the radical process. 2,2'-azobis(isobutyronitrile) (AIBN), 1,1'-azobis(cyanocyclohexane) (ACHN), tert-butyl peroxide, dicumyl peroxide are commonly used initiators [**L. 17**].

OIL MODIFICATION METHOD

NHPI, which is intended to improve process kinetics, at the same time keeping the viscosity and stability of obtained oil base, was used in the reaction. The process was carried out without the presence of solvent and in presence of carbon dioxide. Rape-seed oil was used as starting material. The influence of temperature, the amount of catalyst, the pressure of oxygen and solvent on parameters of the modified vegetable oils obtained were tested. To determine the optimal parameters of the process, the DOE approach was used.

The DOE approach enables the optimization of the process, which means being able to determine the optimum values of initial quantities for the assumed goal. The experimental plan and the statistical analysis of obtained results were done in ITeE-PIB in Radom. To optimize the process of oil modification, the Taguchi method was used [**L. 13**].Three project parameters, changed on three levels each, were analysed. The obtained orthogonal table contained 9 planned experiments in oxygen at various temperatures and 9 with the addition of CO_2. For the temperatures, following levels were assumed: 80, 100, 120°C; for NHPI catalyst contribution: 0; 0,5; 0,05% of mass; for oxygen pressure: 0,1; 0,4; 0,6 MPa; for CO_2 experiments: 10, 15, 20 MPa. In the experiments carried out in the presence of carbon dioxide, a constant pressure of oxygen – 2.5 MPa at room temperature was used. Obtained products were tested through the determination of kinematic viscosity, peroxide number (LN), iodine number (LJ), and acid number (LK). The purpose of process parameters optimization was to obtain maximum viscosity values while maintaining possibly low values of acid, peroxide, and iodine numbers.

Unrefined rape-seed oil from the Napus-Oil S.C. was used for modification process, with the following physicochemical properties: 0.900–0.915 g/cm^3 density; 35.19 cSt kinematic viscosity at 40°C; 1.16 meq O_2/kg peroxide number; 97.59 g I_2/100 g iodine number; 203.2 mg KOH/g saponification number; and, 1.04 mg KOH/g acid number. The apparatus used in the test consist of a Büchi limbo pressure reactor and a HPLC pump that was used to dose liquid CO_2. The Büchi limbo reactor is a metal high-pressure reactor that allows operation at a maximum pressure of 350 bar and a temperature of –10 to 350°C. The maximum volume of the reactor is 285 ml.

The rape-seed oil modification process with oxygen in the presence of NHPI was carried out according to the experimental plan (**Table 1**). On the basis of the obtained results, the objective function value was calculated, and its maximum was determined, indicating process parameters for which the maximum viscosity was predicted. The objective function value for all process parameters combinations was calculated

Table 1. Experiments plan for vegetable oils modifications with pure oxygen and oxygen admixed with carbon dioxide
Tabela 1. Plan eksperymentów modyfikacji olejów roślinnych tlenem czystym oraz w obecności dwutlenku węgla

Set no.	Temperature, °C	Catalyst, %	O_2 Pressure, MPa	Σ Pressure in presence of CO_2, MPa
1	80	0	0.1	10
2	80	0.05	0.4	15
3	80	0.5	0.6	20
4	100	0.5	0.4	10
5	100	0	0.6	15
6	100	0.05	0.1	20
7	120	0.05	0.6	10
8	120	0.5	0.1	15
9	120	0	0.4	20

as well, allowing the evaluation of viscosity prediction for all process parameter sets (**Fig. 3**). On the basis of prediction, three various modification processes were chosen to obtain viscosity values most similar to viscosity values of three oil viscosity classes selected for lubricating bases. Selected parameters for three rape-seed oil modification process, as well as predicted viscosity values after such modification are shown in **Table 2**.

Table 2. Statistical analysis results for selected samples of rape-seed oil modification without addition of CO_2 – parameters predicted by the model

Tabela 2. Wyniki analizy statystycznej wybranych prób modyfikacji oleju rzepakowego bez dodatku CO_2 – parametry przewidziane przez model

Predicted viscosity grade	**VG 46**	**VG 68**	**VG 150**
Temperature, °C	100	120	120
O_2 pressure, MPa	0.1	0.1	0.4
Catalyst, %	0.05	0.05	0.05
Predicted viscosity at 40°C, cSt	39.07	69.88	187.71

The obtained results of statistical prediction allowed us to expect that it is possible to obtain rape-seed oil as base oil with a chosen viscosity class (in accordance with ISO) in dependence on process parameters. According to process parameters shown in **Table 2**, the outcome of the modification process carried out as prognosis verification is shown in **Table 3** and on **Figure 3**.

Table 3. Rape-seed oil properties after modification processes without use of solvent – experimental results

Tabela 3. Wyniki eksperymentów potwierdzających poprawność modelu matematycznego modyfikacji oleju rzepakowego

Viscosity class	**VG 46**	**VG 68**	**VG 150**
viscosity at 40°C, cSt	42.00	55.65	110.00
LN, meq O_2/kg	42.13	21.29	28.07
LK, mg KOH/g	2.02	5.33	17.33
LJ, g I_2/100 g	120.52	105.98	78.90

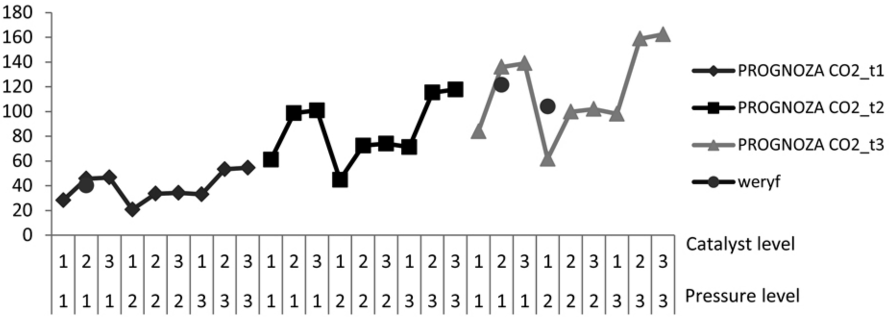

Fig. 3. Prognosis rape-seed oil viscosity values in dependence with modification process parameters without solvent and viscosity values from verification research

Rys. 3. Prognozowane wartości lepkości oleju rzepakowego w zależności od parametrów procesu modyfikacji bez rozpuszczalnika oraz wartości lepkości z badań weryfikacyjnych

As an outcome of the verification process, results with diverse deviations from the prognosis, depending on assumed viscosity class, were obtained. Modified rape-seed oil with a VG 46 viscosity class similar to the predictions was obtained during the experiment. In the case of oil with assumed a VG 68 viscosity class, the obtained value was almost the same as the prediction (insignificantly lower). In the case of oil with a VG 150 viscosity class, the obtained oil had a viscosity lower by a whole class (VG 100). The divergence between prognosis and process verification for oil with forecasted VG 150 viscosity class comes from catalyst decomposition at 120°C, which results in the decrease in system catalytic activity. Additionally, in comparison with 100°C, the number of peroxide group drops, which negatively influences product viscosity.

On the next research stage, the process of rape-seed oil modification with oxygen in the presence of NHPI and carbon dioxide was carries out, according to experimental plan (**Table 1**). In each case, 2.5 MPa of oxygen was used as the initial value of oxidant. Results obtained from the experiments were analysed and the prognosis for oil properties after modification for several process parameters sets were calculated (**Figure 4**). In accordance with planed viscosity classes, three modification parameters sets were selected, which predicted obtaining the proper oil. Selected parameters for three rape-seed oil modification processes and predicted viscosity values after such modification are shown in **Table 4**.

Table 4. Rape-seed oil modification process parameters in presence of CO_2 selected to obtain assumed viscosity classes – parameters predicted by the model

Tabela 4. Parametry procesów modyfikacji oleju rzepakowego w obecności CO_2 wytypowane w celu uzyskania zaplanowanej klasy lepkości

Predicted viscosity grade	VG 46	VG 68	VG 150
Temperature, °C	80	120	120
Σ pressure, MPa	10	15	10
Catalyst, %	0.05	0.00	0.05
Predicted viscosity at 40°C, cSt	45.64	61.6	135.9

The obtained results of statistical prognosis allow us to expect that it is possible to obtain the modification in the presence of carbon dioxide rape-seed oil as an oil base with each of the planned viscosity classes (in accordance with ISO). In dependence with assumed viscosity class in the modification process, parameters should be applied according to **Table 4**. Prognoses verification was carried out and the results are shown in **Table 5** and **Figure 4**.

Table 5. Rape-seed oil properties after modification processes in the presence of CO_2 – experimental results

Tabela 5. Właściwości oleju rzepakowego po procesach modyfikacji oleju rzepakowego w obecności CO_2

Viscosity grade	VG 46	VG 68	VG 150
40°C viscosity, cSt	40.10	104.00	121.40
LN, meq O_2/kg	62.9	10.94	12.07
LK, mg KOH/g	3.04	29.04	28.86
LJ, g I_2/100 g	113.5	77.43	62.06

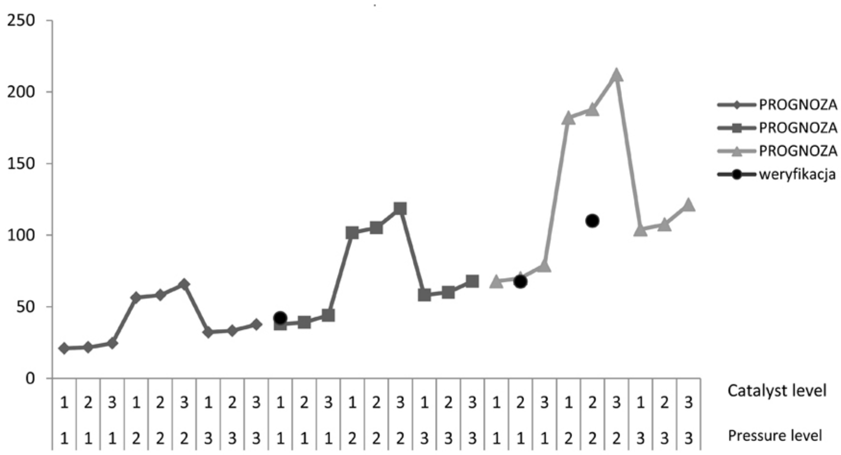

Fig. 4. Prognosis of rape-seed oil viscosity values depending on modification process parameters with use of CO_2, as well as viscosity values from verification research

Rys. 4. Prognozowane wartości lepkości oleju rzepakowego w zależności od parametrów procesu modyfikacji z użyciem CO_2 oraz wartości lepkości z badań weryfikacyjnych

As a result of the experiment, modified rape-seed oil with VG 46 and VG 150 viscosity classes with viscosities different from predictions by about 10% were obtained. In the case of oil with assumed VG 68 viscosity class, the obtained viscosity was by 70% higher than the assumption. The viscosity of oil synthesized in these conditions is higher by a class (VG 100).

While choosing three levels of 100-150-200 bar total pressure, we aimed to determinate optimal pressure for observing the beneficial influence of the solvent. The decrease of viscosity (capacity) of the process in the range between 100 and 150 bar suggest the lack of CO_2, which results with the low density of the reaction mixture and only dilutes the oxygen in the reactor. A pressure increased to 200 bar results with higher viscosity (in comparison to 150 bar), which may suggest that the density of the reaction mixture is higher and that the vegetable oil is completely dissolved in CO_2. Additionally, these results suggest that the carbon dioxide is present in the system in its supercritical state.

In the case of using supercritical CO_2, the modification runs best at 10 MPa and 20 MPa pressure. In the case of 10 MPa it is probably caused by low dilution of oxygen, which results with faster oil modification. In the case of 20 MPa, the influence of the higher density of the reaction medium can be seen (higher amount of CO_2 in the reactor), which leads to better reagents homogenization and enables better contact of oxygen with raw material.

The next stage was the comparison of lubricating properties between R_O2_VG 68 modified rape-seed oil and R_VG 32 pre-modification rape-seed oil. Using an hourly test, the anti-wear properties of studied oils were determined. This test was conducted in the conditions of constant load (P) of a friction couple of 392 N, a constant spindle speed of 500±20 rpm, and a temperature of 20±5°C. After ending the test, the wear diameter (d) on the balls was measured, and the maximum wear load was calculated from the $G_{oz} = 0.52\ P/d^2$ dependence, in which friction couple load (P) and average wear sign diameter (d) were taken under consideration (**Figure 5**).

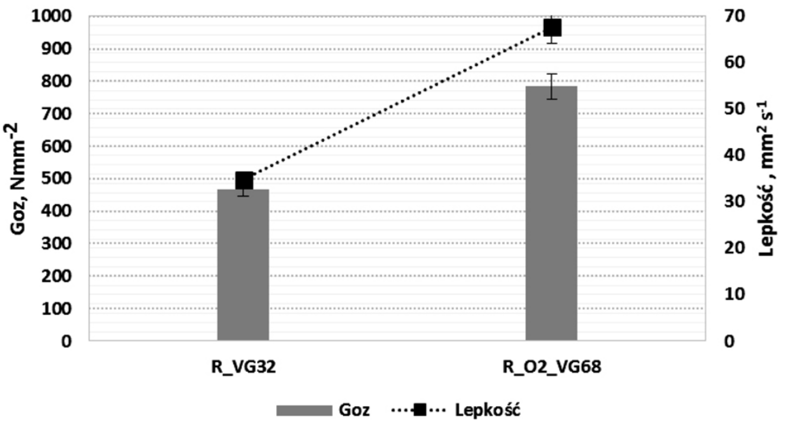

Fig. 5. The influence of rape-seed oil viscosity change on anti-wear properties
Rys. 5. Wpływ zmiany lepkości oleju rzepakowego na właściwości przeciwzużyciowe

According to the prognosis, modification of R_VG 32 rape-seed oil carried out without solvent allowed obtaining R_O2_VG 68 oil with a higher viscosity class. It was observed that the increase of rape-seed oil viscosity, obtained in such conditions, allowed an increase in G_{oz} maximum wear load, which means that the mentioned oil has very good anti-wear properties. It was stated that R_O2_VG68 modified rape-seed oil in comparison to R_VG32 rape-seed oil ensures better protection against wear of lubricated elements of the friction couple.

CONCLUSIONS

To reduce the number of experiments to be conducted, statistical data analysis was used, as well as a mathematical model. Based on the conducted experiments, a simulation was performed. The results corresponding to particular viscosity grades were chosen for verification. In most cases, the verification of the model confirmed its correctness.

The use of the catalyst (N-hydroxyphthalimide) in the vegetable oils modification process enabled the lowering of process temperature. It was possible to obtain similar properties of base oil at a lower temperature than would be possible without a catalyst in the reaction.

CO_2 as solvent in the process diluted the system, leading to milder oil oxidation. The oil obtained in such conditions had a higher peroxide number and a lower viscosity. The use of the solvent also prevented oil degradation to lower molecular organic compounds at higher temperatures. The decrease of viscosity in processes with CO_2 in comparison to the processes carried out in the oxygen is caused by the dilution of the reaction mixture. In the reaction mixtures with CO_2, the oxygen concentration is lower, causing the milder course of process. Therefore the obtained product has a lower viscosity but also a lower degradation degree.

As a result of rape-seed oil modification, base oils for lubricating agents with different viscosity grades (depending on process conditions) were obtained. The primary conditions influencing properties of modified oils were temperature, the presence of a catalyst, and oxygen pressure.

ACKNOWLEDGEMENTS

This research was realized within Smart Growth Operational Programme project, action 4.1.2, titled "Development of the technology of new generation, high quality lubricating agents, guaranteeing food production safety, for the food and agricultural sector," in years 2017-2019, POIR no. 04.01.02-00-0004/16.

REFERENCES

1. Karmakar G., Ghosh P., Sharma B.: Chemically Modifying Vegetable Oils to Prepare Green Lubricants. Lubricants 2017, 5 (4), 44.
2. Ptak S.: Klasyfikacja jakościowa i charakterystyka przemysłowych środków smarowych. 2012, 454–461.
3. Drabik J., Rogoś E., Trzos M., Kozdrach R., Michalski J., Janecki J., Piątkowski M.: Specjalistyczne środki smarowe gwarantujące bezpieczeństwo produkcji żywności. In Innowacje w Przemyśle Chemicznym; 2018.
4. Zajezierska A.: Smary plastyczne – europejskie normy klasyfikacyjne i wymagania jakościowe. 2012, 714–720.
5. Campanella A., Rustoy E., Baldessari A., Baltanás M.A.: Lubricants from Chemically Modified Vegetable Oils. Bioresour. Technol. 2010, 101 (1), 245–254.
6. Sharma U.C., Sachan S., Trivedi R.K.: Viscous Flow Behaviour of Karanja Oil Based Bio-Lubricant Base Oil. J. Oleo Sci. 2018, 67 (1), 105–111.
7. Iłowska J., Chrobak J., Grabowski R., Szmatoła M., Woch J., Szwach I., Drabik J., Trzos M., Kozdrach R., Wrona M.: Designing Lubricating Properties of Vegetable Base Oils. Molecules 2018, 23 (8), 2025.
8. Kropiewnicka-Mielko A.: Smary w przemyśle spożywczym http://glowny-mechanik.pl/2016/06/27/smary-przemysle-spozywczym/ (accessed Oct 2, 2018).
9. Drabik J., Sitkowska R.: Analiza potencjalnego zapotrzebowania na nietoksyczne smary plastyczne z wykorzystaniem procedury badania tendencji rozwoju produktów. Pr. Nauk. Uniw. Ekon. we Wrocławiu 2013, nr 300 Innowacje w zarządzaniu, 39–46.
10. Oleje i smary dla przemysłu spożywczego http://gorner.pl/o-firmie/aktualnosci/oleje-i-smary-dla-przemyslu-spozywczego (accessed Oct 2, 2018).
11. Trzos M., Drabik J., Iłowska J., Grabowski R.: Design of Conditions for the Modification of Oil in the Process of Desing Ecological Lubricants. Tribologia 2018, No. 2, 133–138.
12. Drabik J., Trzos M., Iłowska J., Bereska B.: Kompleksowe smary plastyczne wytwarzane w reaktorze kalorymetrycznym. Cz. 1, Dobór parametrów procesu wytwarzania ze względu na jakość smaru plastycznego. Przem. Chem. 2013, 92 (10), 1846–1849.
13. Karna S.K., Sahai R.: An Overview on Taguchi Method. Int. J. Eng. Math. Sci. 2012, 1 (1), 1–7.
14. Fox N.J., Stachowiak G.W.: Vegetable Oil-Based Lubricants-A Review of Oxidation. Tribol. Int. 2007, 40 (7), 1035–1046.
15. Grabowski R., Orlińska B., Zawadiak J., Iłowska J.N.: Hydroksyftalimid jako potencjalny katalizator przemysłowych procesów utleniania węglowodorów. Przem. Chem. 2014, 4 (93), 495–499.
16. Amorati R., Lucarini M., Mugnaini V., Pedulli G.F., Minisci F., Recupero F., Fontana F., Astolfi P., Greci L.: Hydroxylamines as Oxidation Catalysts: Thermochemical and Kinetic Studies. J. Org. Chem. 2003, 68 (5), 1747–1754.
17. Denisov E., Afanas'ev I., Denisova T., Drozdova T., Trepalin S.: Oxidation and Antioxidants in Organic Chemistry and Biology; Boca Raton: CRC Press, 2005.