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DESIGN OF CONDITIONS FOR THE MODIFICATION OF OIL IN THE PROCESS OF DESIGNING ECOLOGICAL LUBRICANTS

DOBÓR WARUNKÓW MODYFIKACJI OLEJU W PROCESIE PROJEKTOWANIA SMARÓW EKOLOGICZNYCH

Key words: lubricants, plant oils, oil base modification, process parameters modification.

Abstract The paper presents results of research concerning the oil bases designs that are dedicated to application in lubricants for the food industry. The method of vegetable oil modification was proposed that use supercritical carbon dioxide as a solvent. This resulted in a milder course of oil oxidation. In order to minimize the number of necessary experiments, the Taguchi approach to experiments planning was used. As part of the research, the properties of vegetable oils, inedible (*Crambe Abyssinica oil*) one and edible (*Brassica Campestris* (*Rapeseed*) *oil*) after modification, were compared. The optimal, due to the adopted criteria, values of oil modification process parameters were determined for each of the oils. Analyses and comparisons of processes for obtaining an oil base suitable for the planned use in ecological lubricants have been made.
Under optimized conditions, the modified oils obtained a needed appropriate viscosity class.

Słowa kluczowe: środki smarowe, oleje roślinne, modyfikacja bazy olejowej, optymalizacja parametrów procesu.

Streszczenie W artykule przedstawiono wyniki badań dotyczące uzyskania roślinnej bazy olejowej odpowiedniej do zastosowania w smarach przeznaczonych do przemysłu spożywczego. Zaproponowano modyfikację oleju roślinnego z użyciem w procesie nadkrytycznego dwutlenku węgla jako rozpuszczalnika. Spowodowało to łagodniejszy przebieg utleniania oleju. W celu zminimalizowania liczby niezbędnych doświadczeń zastosowano planowanie eksperymentu z wykorzystaniem podejścia Taguchiego. W ramach przeprowadzonych badań porównano właściwości olejów roślinnych: niejadalnego (abisyńskiego) i jadalnego (rzepakowego) po modyfikacji. Wyznaczono dla każdego z nich optymalne, ze względu na przyjęte kryteria, wartości parametrów procesu modyfikacji oleju. Dokonano analiz i porównań procesów uzyskania bazy olejowej odpowiedniej do planowanego zastosowania w smarach ekologicznych.
W zoptymalizowanych warunkach zmodyfikowane oleje uzyskały wyższą liczbę nadtlenową i odpowiednią klasę lepkości.

INTRODUCTION

Lubricants are indispensable elements of the machines and industrial equipment for appropriate work. Their high quality is significantly determined by the achievement of planned production outputs. Lubricants are indispensable elements for the proper work of numerous machines and industrial equipment. Their high quality largely determines the achievement of planned production outputs. The selection of lubricants should be characterised by needed useful properties. Depending on the purpose of the lubricants, they should have the required functional properties. Researchers are looking for ways to improve lubricating properties, e.g., by using appropriate additives [**L. 1–3**], and there are many areas in which the lubricant should meet ever more stringent ecological requirements. The authors of this paper have conducted, among others, research on the application of ecological grease as an additive into a composite in order to the improvement of its friction collaboration in a friction couple [**L. 4**]. The results confirmed the validity of the modification of the composite. Due to ecological requirements, oil bases are sought that are alternatives to mineral oils. The plant oils are characterized by

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practically full biodegradability, and they are not-toxic; however, their broad application as bases oils is limited by weak oxidation stability and often insufficient lubrication properties needed in an application area. Because of that, intensive investigations are conducted to develop new lubricants that meet these requirements [**L. 5–6**].

Unmodified vegetable oils as oil bases are used only in applications with low thermal loads due to limited thermal and oxidative stability. In designing organic lubricants based on vegetable oils, an important problem is proper preparation and modification of the base oil in order to obtain its properties required for the planned application, including, for example, viscosity at operating temperatures, and oxidative and thermal stability [**L. 10**]. Shixing Cui et. al. developed a new biological base oil. The properties of new lubricant modified with trimethylchlorosilane, such as the flash point and viscosity index, are a significant improvement over 150 N mineral oil [**L. 11**]. Young W et. al have proven that, after chemical modification, the wear resistance and extreme pressures of methyl oleate have been significantly improved [**L. 12**]. In the literature on the subject, there are practically no reports on the optimization of the base oil modification process in order to improve its lubricating properties. This article presents a proposal for chemical modification of oil in processes using a catalyst, including this process optimization. The experiment plan was built according to the Taguchi approach.

METHOD OF OIL MODIFICATION

As part of the research, modification of oil bases involving the oxidation of vegetable oil with oxygen in the presence of a catalyst was carried out.

The high temperature that is being used in the process, apart from a positive effect such as stability and viscosity raise, causes unfavourable degradation of vegetable oils. Therefore, temperature lowering is needed, which is possible with the use of an oxidation reaction catalyst. For the comparison of different oil modification effects, two kinds of processes were carried out, namely, with and without compressed CO_2 as a solvent [**L. 13, 14**]. Two different oils were tested: (*Brassica Campestris* (*Rapeseed oil*) edible one and (*Crambe Abyssinica*) inedible. For the modification of vegetable oils, an apparatus consisting of the following was used: a Buchi "limbo" pressure reactor, a Blue Shadow dosing pump, and a Julabo thermostat. The desired amount of oxygen or CO_2 was introduced into the reactor, and temperature and pressure were controlled during the process. If necessary, the pressure in the reactor was adjusted by adding oxygen (for the process without solvent) or CO_2 (for the process with solvent). The products obtained were examined, inter alia, by determining the kinematic viscosity and peroxide number. The use of supercritical carbon dioxide as a solvent caused a dilution of the system, which leads to a milder oil oxidation. Under these conditions, a modified oil with a higher peroxygen number and lower viscosity was obtained. The use of a solvent also allows preventing oil degradation at higher temperatures to low molecular weight organic compounds.

EXPERIMENT DESIGNING

In the studies that aim at the influence of an estimation of technological process parameters on properties of modified oil, we considered the influence of temperature, pressure, and the percentage content of catalyst. For each of modification parameters, three levels (**Table 1**) of values were investigated. In the oil modification processes, the changes of parameter levels and their influence on oil viscosity were investigated. In particular, viscosity was analysed as one of the basic rheological parameter significant for lubrication properties of grease. The experiments were designed to minimize the number of parameter combinations to study their effect on viscosity.

Table 1. Values of oils modification processes parameters
Tabela 1. Wartości parametrów procesów modyfikacji olejów

	Processes without solvent			Processes with solvent		
Parameter level	Temperature °C	Pressure 10^5 ps	Catalyst %, g/g	Temperature °C	Pressure 10^5 ps	Catalyst %, g/g
1	80	1	0	80	100	0
2	100	4	0.05	100	150	0.05
3	120	6	0.5	120	200	0.5

One of the most important goals of planning an experiment is to get as much information as possible with as few experiments as possible. In the presented studies, concerning the effect of technological conditions on the properties of oils, an optimization experiment was planned, because the goal was to obtain optimal properties due to the planned application of grease.

The Taguchi method was used. In accordance with the orthogonal array, nine layouts for the experiments without solvent and nine for the experiments in an atmosphere of carbon dioxide were planned (**Tab. 2**).

Table 2. Orthogonal table of experiment plan
Tabela 2. Tabela ortogonalna planu eksperymentu

Test number	Parameter level		
	temperature	pressure	catalyst
1	1	1	1
2	1	2	2
3	1	3	3
4	2	2	3
5	2	3	1
6	2	1	2
7	3	3	2
8	3	1	3
9	3	2	1

As a result, the experiments were carried out in accordance with the optimization plan, and values were obtained that specify the properties of the studied modified oils. Then they were analysed in accordance with the Taguchiego approach. Analyses of the ETA functions, which represent the signal-to-noise ratio, were carried out. We looked at the Eta function that describes the oil viscosity. Because, due to the planned use, it was essential to estimate the process parameters to ensure getting as high viscosity of oil as possible, and "the bigger the better" criterion was used. The Eta function, in accordance with the method used, is a logarithmic function constructed on the basis of maxima determined value for each parameter that is the best for the analysed object of research.

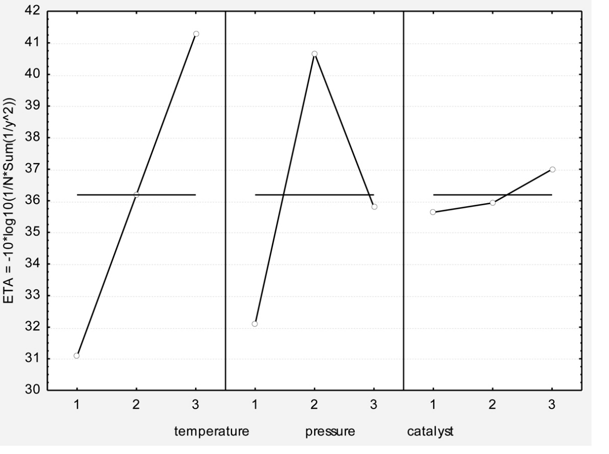

Fig. 1. Eta function values for the viscosity of oil modified under different process conditions without using a solvent
Rys. 1. Wartości funkcji Eta dla lepkości oleju modyfikowanego w różnych warunkach procesu bez użycia rozpuszczalnika

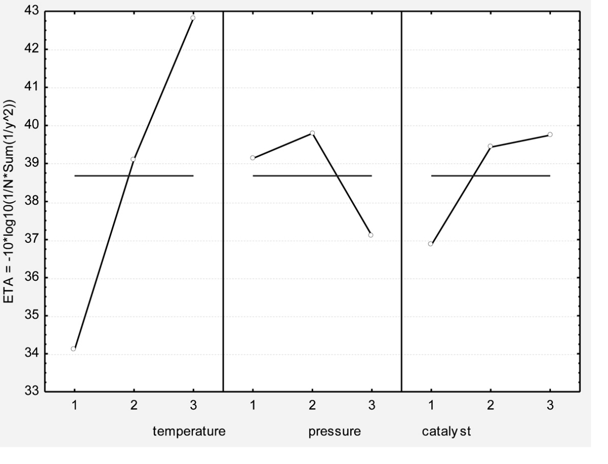

Fig. 2. Eta function values for viscosity of the edible oil modified under various conditions of the process with the use of CO_2 as a solvent
Rys. 2. Wartości funkcji Eta dla lepkości oleju jadalnego modyfikowanego w różnych warunkach procesu z użyciem CO_2 jako rozpuszczalnika

RESULTS DISCUSSION

Edible oil (*Brassica Campestris* (*Rapeseed*) *oil*)

The graphs in **Figs. 1** and **2** present the values of the Eta function for the criterion "the greater the better" for viscosity. Oil modification was carried out in the atmosphere without solvent, **Fig. 1**, and in an atmosphere of carbon dioxide, **Fig. 2**.

The optimum value ETA = 46.53 was obtained for the following parameters: temperature = 3, pressure = 2, and catalyst = 3. However, the catalyst content is insignificant and practically does not affect the viscosity change of the modified oil.

In the case of oil modification in the atmosphere of CO_2 to obtain the maximum viscosity, the temperature is practically the most important, and its effect is four times higher than the other variables. The optimal value of ETA is 45.

In both cases, the use of CO_2 and O_2 atmosphere, the set of optimal parameters is the same, i.e. temperature = 3, pressure = 2, and catalyst = 3. However, it can be assumed that the change in the catalyst content does not practically change when using the atmosphere without solvent; whereas, when using CO_2, levels of catalyst 2 and 3 practically make an identical contribution to improving viscosity.

The predicted viscosity values for all possible combinations of oil modification process parameters are presented on the basis of calculations using the results of the conducted tests. The calculations were made with the use of the marginal averages and the ratings of parameters according to the Taguchi approach. The predicted values, depending on modification process parameters for both processes, with and without the use of a solvent, are presented in **Fig. 3**.

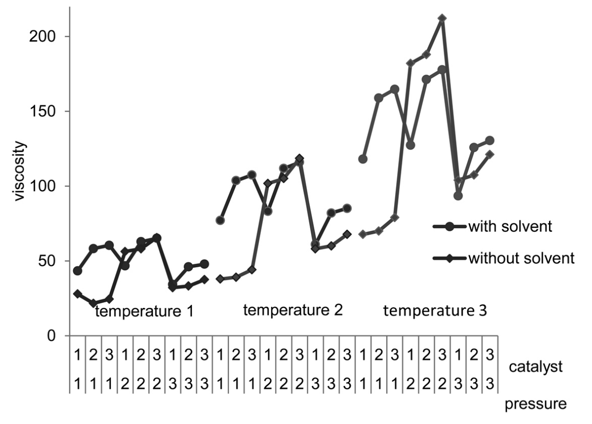

Fig. 3. Predicted viscosity values of edible oil after modification at various parameters

Rys. 3. Prognozowane wartości lepkości oleju jadalnego po modyfikacji przy różnych parametrach procesu

Based on the analysis of the results and the predicted viscosity values, it was shown that the modification of the edible oil at the highest temperature used and at the second pressure level allows obtaining the oil with the most favourable characteristics, due to the planned application. In the case of the modified (without solvent) oil, the use of a catalyst does not practically affect the viscosity change; whereas, in the atmosphere of carbon dioxide, the lack of catalyst significantly reduces the viscosity. In this case, it is sufficient to add a small amount of catalyst, and the second level is enough, because further increasing the catalyst content does not significantly improve the viscosity.

Inedible oil (*Crambe Abyssinica oil*)

Analogous to the edible oil, the tests were carried out for non-edible oil.

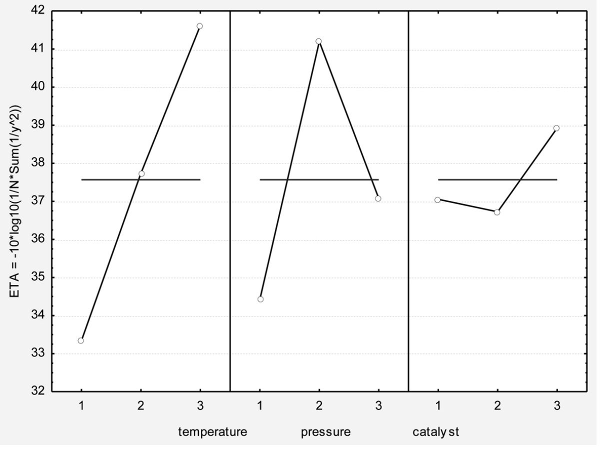

Fig. 4. Eta function values for viscosity measurements of inedible oil modified under different conditions of the process without solvent

Rys. 4. Wartości funkcji Eta dla pomiarów lepkości w różnych warunkach procesu modyfikacji oleju niejadalnego bez zastosowania rozpuszczalnika

Figure 4 shows a graph of extreme mean functions of Eta for inedible oil modified without solvent, and **Fig. 5** presents graphs for inedible oil modified with the use of carbon dioxide.

The optimum value of the Eta function, similarly to that for edible oil, was obtained for the following levels: temperature = 3, pressure = 2, and catalyst = 3. The catalyst process input variable, compared to the others, is practically negligible for maximizing oil viscosity.

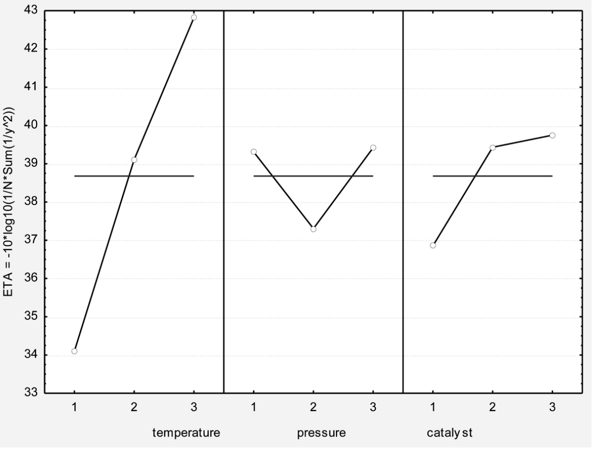

Fig. 5. Eta function values for viscosity of the inedible oil modified under various conditions of the process with the use of CO_2 as a solvent

Rys. 5. Wartości funkcji Eta dla pomiarów lepkości w różnych warunkach procesu modyfikacji oleju niejadalnego w atmosferze CO_2

In the case of searching for the maximum viscosity value of inedible oil, in processes without solvent, the higher values are achieved when the temperature is higher. The pressure value is of lesser significance. Due to the maximum of the objective function, the best value of pressure is 4 · 105 Ps. The use of a catalyst is practically irrelevant. The Eta value under optimal conditions, is 46.6. Similarly, in the case of the modification of inedible oil in the atmosphere of carbon dioxide, the temperature has the biggest influence on the viscosity, and the influence of the other two parameters is of little significance. The Eta value under optimal conditions is 45.

The calculated viscosity predictions for the analysed levels of input variables (temperature, pressure, catalyst) for the studied processes, with and without solvent, are shown in **Fig. 6**.

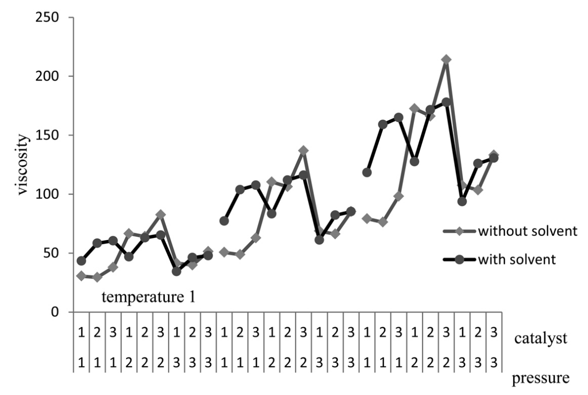

Fig. 6. Predicted viscosity values of inedible oil after modification at various process parameters

Rys. 6. Prognozowane wartości lepkości oleju niejadalnego po modyfikacji z różnymi ustawieniami parametrów procesu

COMPARISON OF MODIFIED EDIBLE AND INEDIBLE OIL

The research results, presented in **Figures 3** and **6**, have shown that the course of viscosity changes, considered under various modification conditions for both kinds of oils, is very similar. For both oils, the most important is the temperature, Level 2 of pressure is the best to achieve the highest viscosity values, and the Level 2 of the catalyst is sufficient, especially when modifying the oil in a carbon dioxide.

The presented changes in viscosity illustrate the decisive influence of the process temperature on viscosity values. When not using a solvent, a significant decrease in oil viscosity when the optimum pressure level is changed is observed. That change is definitely milder when using a carbon dioxide atmosphere.

Similarly to the edible oil, the modification temperature also has the biggest influence on the change of viscosity in the case of inedible oil. For this oil, when the solvent is not used, a significant decrease in viscosity is also observed when the pressure level changes from the optimal value.

The analyses carried out showed that, in the case of both kinds of oils, the nature of changes in viscosity, depending on the process parameters, is practically the same. It differs significantly, depending on that if a solvent is used or not. The highest viscosity values can be obtained using a temperature at Level 3 and a pressure at Level 2, and the importance of the catalyst is small, it can be assumed that its value at Level 2 is sufficient.

The studies carried out to verify the forecasts have shown that, in the case of inedible oil, the prediction error, calculated as the ratio of a difference between the prediction and the measurement result, did not exceed 20% and ranged from 10% to 18%. For edible oil, the prediction errors were much higher and reached even 40%, and they changed from 25% to 41%.

CONCLUSION

As a result of the tests carried out in accordance with the plan of the experiment for the modification of edible and inedible oil, a base was obtained for lubricants with different needed viscosity classes dependent on the process parameters. The main factor affecting the properties of the modified oils was temperature. The presence of a catalyst and oxygen pressure were of less importance.

The application of the optimization plan allowed the determination of the best, due to the assumed objective functions, values of the oil modification process parameters, while limiting the number of necessary tests.

The effect of oil modification is a product with altered properties compared to the properties of the starting oil. An important modified property of the oil was viscosity, which determines the class of lubricants.

The oil base produced has the properties required in accordance with the assumptions set for the oil base of the designing lubricant.

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