# PROBLEMY EKSPLOATACJI

# MAINTENANCE PROBLEMS

no 2/2015

INSTITUTE
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NATIONAL RESEARCH INSTITUTE

## Problemy Eksploatacji – Maintenance Problems

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INNOVATIVE ECONOMY
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# NON-TOXIC PLASTIC LUBRICANT FOR THE FOOD INDUSTRY

**Key words**

Base oils, non-toxic plastic lubricants, lubricating properties, oxidising stability.

## Abstract

The implementation of mandatory quality management systems in the food industry generates the need to develop lubricating products with appropriate performance properties that are safe for the ecosystem. When designing specialized lubricants, special attention was given to the selection of components, taking into account, in addition to their functional properties, their ecological properties. This article presents a description of a lubricant based on non-toxic ingredients. The main components of the lubricant are synthetic oil and a thickener with certified components. The lubricant performance properties and its oxidising stability were examined.

As a result, a comprehensive lubricant was developed, characterised by performance durability. The designed lubricant has a health clearance certificate of the National Institute of Hygiene and is permitted in the food industry. The

developed product is intended for industrial use as a typical bearing lubricant, wherever it is required to use certified lubricant.

## Introduction

The implementation of mandatory quality management systems in the food industry forces the development of the appropriate lubricants with appropriate lubricating properties and non-toxicity [1, 2, 3]. At present, all processing plants producing food, including small and medium-sized enterprises in the food industry adapt their production conditions to the requirements set by the EU directives relating to the safety and hygiene of food production [4] and follow the requirements of machine maintenance in regards to only using certified lubricants [5]. The diversity and specificity of the production in the food industry translates directly into an increased demand for specialized lubricants, which are used wherever there is a risk of food contamination [3].

In addition, the environmental policy pursued by the European Community is committed to the implementation of the certification scheme, which aims to promote those products in the Common Market that have the least adverse impact on the environment [6]. To reduce the harmful effects on the environment of the lubricants, special attention should be paid in their design process to the choice of their components in regards to their non-toxicity and biodegradability, in addition to their performance properties [2, 7].

The increasing demand for specialized lubricating materials for use in machine bearings working in the food industry in a wide range of rotation and loads determined the undertaking of this research in the development of synthetic oil based, non-toxic and biodegradable lubricants [2]. The key issue in the production of non-toxic lubricant is a selection of the main ingredient, which is the oil base. Positive results [2, 9, 10] during the manufacture of plastic lubricants were obtained by using highly refined petroleum oils and synthetic oils from Group IV and V [8] characterised by being less harmful to the ecosystem than other petroleum oils.

The manufacture of lubricants for the food industry included the appropriate requirements for oil bases, thickeners, and additives [9, 10]. The process [11] demonstrated the validity of the application of statistical analysis methods for experimental data in modelling performance properties based on experimental tests results and, in particular, thermal analysis and tribological testing.

In accordance with oil classification of the American Petroleum Institute API [8], which divides oils into five groups depending on their composition, physicochemical properties, and production technology, the selected base oils for the non-toxic plastic lubricants were synthetic oils [2]. In order to produce plastic lubricants with good structural and mechanical stability, and enhanced lubricating properties, a method of in-situ production was developed for manufacturing complex lubricant in a calorimetric reactor [10]. The production of the lubricant using the *in-situ* method consisted in a synthesis of the thickener directly in the base oil and its dispersal in it. Using complex soap as a thickener provides performance enhancement for the lubricant in comparison to the lubricants where simple soap was used as a thickener. Complex thickeners have a very complex structure and usually are in the form of two acids of different chain length and with the type of the introduced action into the soap molecule, which affects the type of the thickener [10, 11].

The aim of the study was to investigate the influence of the composition of the complex thickener on the oxidising stability of lubricants and their lubricating properties determined in boundary and seizure conditions. Achieving this aim required testing for the oxidation of the produced lubricants using thermal analysis methods and friction tests.

## 1. Materials and test methods

The objects of research were plastic lubricants that were synthesised in a base oil with a complex thickener participation produced by the *in-situ* method with lithium soaps of mono-(MK) and dicarboxylate (DK) acids, with different MK:DK molar ratios [2, 10]. The process consisted in the synthesis of thickener (lithium soaps: 12-hydroxystearic and adipic acids) in oil, which forms the base of the plastic lubricant. Synthetic oil PAO8 – poly-alpha-olefin was used as the base oil. The manufactured lubricants with variable mono-(MK) and dicarboxylate (DK) acids' ratios are indicated as follows: SM A1/0.5 (MK:DK 1:0.5), SM A2/0.6 (MK:DK 1:0.6), SM A3/0.75 (MK DK 1:0.75).

After the plastic lubricant was produced by the in-situ method, based on a complex thickener with varying molar ratios of carboxylic acids, the structures of the produced lubricants were examined using spectral analysis.

Oxidising stability of complex greases was examined using the *Petrooxy* method by determining oxidation induction time. The tests were conducted in isothermal conditions at 140°C and with continuous flow of oxygen.

The parameters used for the basis of the evaluation of lubricating properties were the value of boundary load wear $G_{oz/40}$ and the diameter of the wear trace "d" after an hour test was carried out at a constant load on the node of 3924 N. The obtained value of the wear load ($G_{oz}$) describes the anti-wear properties of the lubricant in the conditions of boundary lubrication and indicates the stability of the boundary film. The lubricating properties in scuffing was determined by scuffing load $P_t$ and threshold seizing pressure $p_{oz}$ indicating the effectiveness of the lubricant in the conditions of extreme force.

## 2. Test results

When choosing the oil base made for the complex plastic lubricants, the lubricating properties of the oil were taken into consideration, since they are an essential component of the lubricant (Fig. 1). The lubricating characteristics of the oils from the hydrocarbon group confirmed the highest efficiency in anti-wear performance of the PAO8 oil in boundary lubricating conditions, which was the basis for the selection of this oil as base oil for the production of complex plastic lubricants.

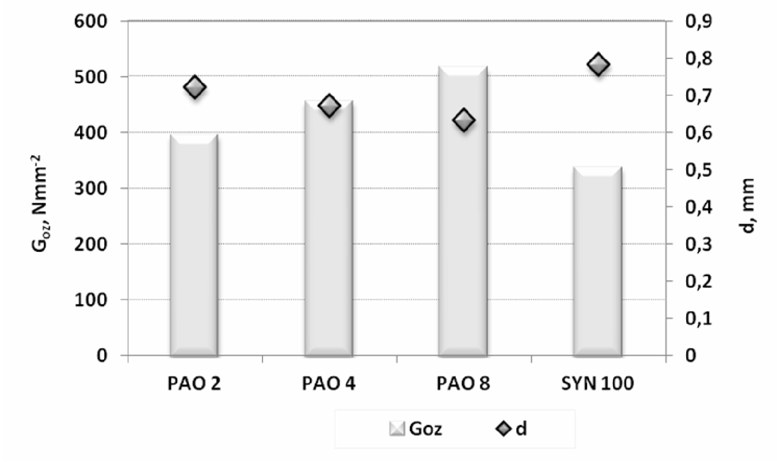


Fig. 1. A comparison of anti-wear properties of synthetic hydrocarbon oil bases – poly-alpha-olefins type (PAO2, PAO4, PAO8, Syn 100)

To monitor the process of in-situ a complex thickener and plastic lubricant production, an infrared spectral analysis method of FT-IR was applied. The FT-IR method is based on the analysis of the characteristic absorption bands of free carboxylic acid (RCOOH) and absorption bands of lithium salts produced in the reaction of the acids with lithium hydroxide (RCOO $Li^+$). The reaction of mono- and dicarboxylate acids with lithium hydroxide results in absorption bands in the 1580 and 1560 $cm^{-1}$ range corresponding to the vibrations of the Group C = O and absorption band ca. 1405 $cm^{-1}$ that come from the C-O group, which was confirmed by the formation of lithium salts (RCOO $Li^+$) by the dicarboxylate acids. The production of complex thickeners was confirmed by the analysis of the change of the intensity of characteristic absorption bands assigned carboxylate ion $COO^-$ in the spectral area of 1580–1560 $cm^{-1}$ (Fig. 2).

Based on the analysis, it was found that the structure of the lubricants (SM A1/A2/SM 0.5, 0.6, SM A3/0.75) produced with variable MK:DK ratios show variation in the intensity of absorption bands of carboxylate groups, with a maximum for these bands obtained for the MK:DK molar ratio of 1:0.5. In view of this difference, the impact on the stability of oxidising and tribological characteristics of the manufactured lubricants was assessed.

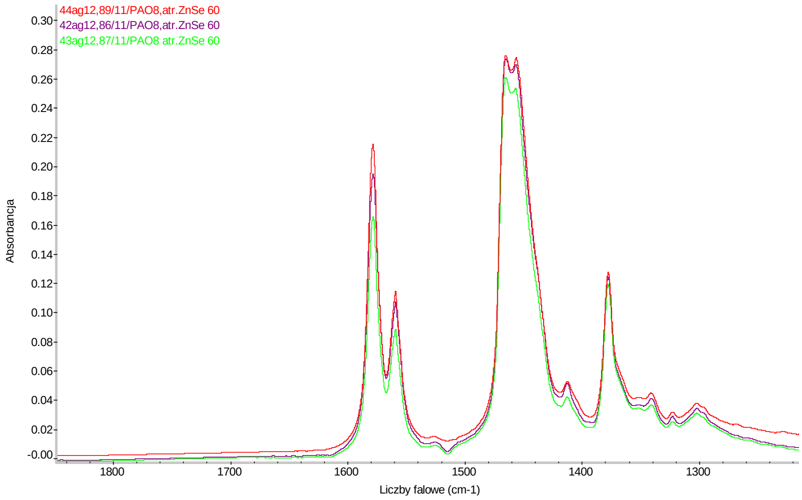


Fig. 2. A fragment of the FT-IR (ATR) spectrum obtained from oil based hydrocarbon lubricant PAO8 with different acid ratios of MK:DK, SM A1/0.5 (1: 0.5), SM A2/0.6 (1-0.6), SM (A3)/0.75 (0.75-1)

The stability of oxidation in the lubricants was assessed on the basis of accelerated oxidation test by the Pertooxy method, by determining, based on the obtained graphs, the pressure drop as a function of oxidation time (Fig. 3a) in the time of oxidation induction (Fig. 3b), which indicates the resistance to the process of oxidation of the tested lubricants.

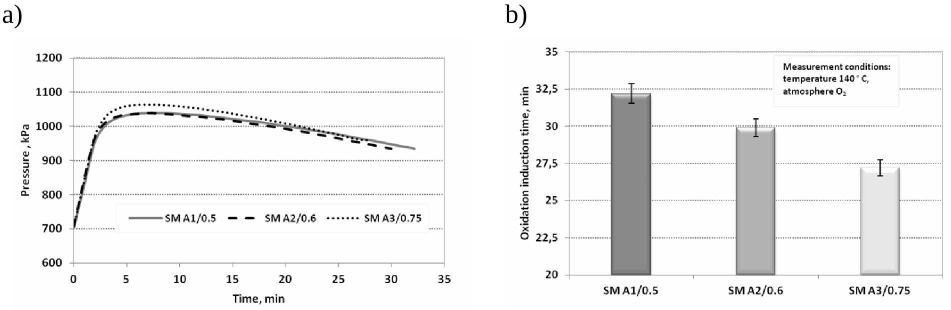


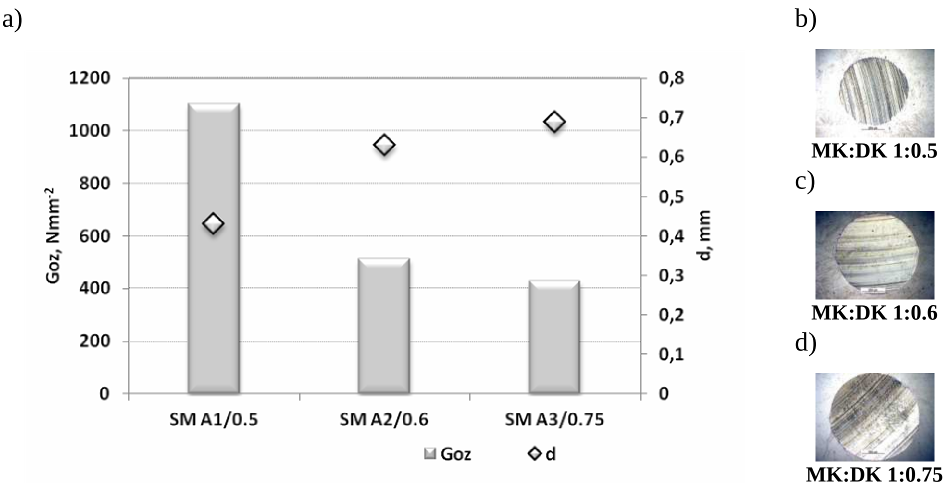
Fig. 3. The influence of thickener component ratios (MK:DK) on the stability of the oxidation of complex plastic lubricants (SM A1/A2/SM 0.5, 0.6, SM A3/0.75) using the Petrooxy method: a) pressure drop graph as a function of time of oxidation, b) oxidation induction time

The conducted experiments indicate that the SM A1/5 lubricant with the lowest dicarboxylic acid content in the complex thickener (1–0.5) is characterized by the highest oxidising stability, which indicates its best resistance to oxidation processes compared to other lubricants. The content of the dicarboxylic acid DK in the thickener has a significant impact on the effect of slowing down the oxidation process; in this case, the lower its contents, the longer oxidation induction time was observed.

In tribological experiments, the effectiveness of the anti-wear properties of the manufactured plastic lubricants was tested by specifying the maximum wear load (Fig. 4) and anti-seizing properties in scoring conditions (Fig. 5).

During the wear test, a reduction was observed in the resistance to wear of a steel friction node lubricated with the SM A3/0.75 complex lubricant, manufactured based on the thickener with the maximum content of dicarboxylic acid, which resulted in a significant reduction in the maximum wear load (Figures 4a, 4d).

When the contents of this acid in the thickener were reduced, the obtained lubricant SM A1/0.5 produced a more stable boundary layer. As a result, the resistance to wear doubled in the friction node (Figs. 4a, 4b).



**MK:DK 1:0.5**

**MK:DK 1:0.6**

**MK:DK 1:0.75**

Fig. 4. The influence of molar ratio of carboxyl acids MK:DK in the thickener on the maximum wear load Goz and diameter of a the wear trace in a given complex lubrication composition. Optical microscope image of friction traces on a ball for the lubrication composition: b) SM A1/5, c) SM A2/0.6, d) SM A3/0.75

The test conducted in seizing conditions confirmed the effect of the MK:DK ratio on the course of changes in friction moment as a function of the load increase (Fig. 5). Depending on the content of dicarboxylic acid DK in the thickener, it was observed that each of the tested lubricants shows a different course of the frictional moment, which in turn leads to seizing in different conditions.

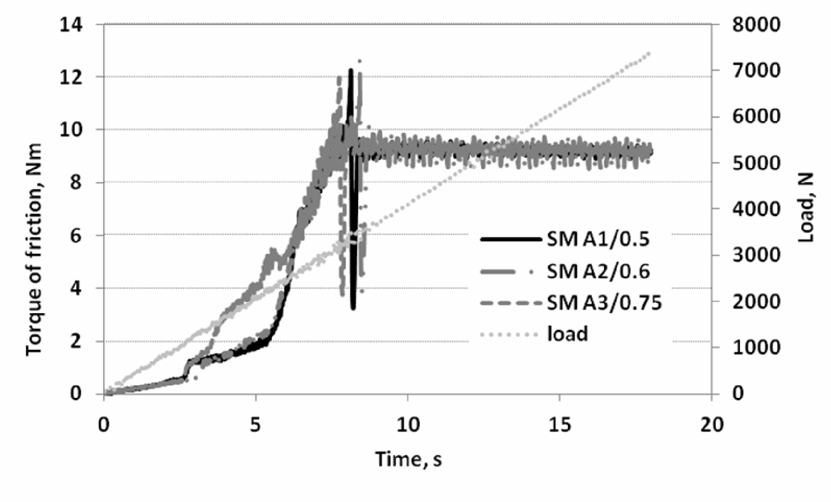


Fig. 5. Changes in the friction moment with a linearly increasing load for plastic lubricants SM A1/A2/SM 0.5, 0.6, SM A3/0.75

Based on the results obtained under the seizing conditions, it can be concluded that the boundary layer created with lubricant SM A1/0.5 and SM A2/0.6 lasts longer than in the case of lubricant SM A3/0.75. In the case of SM A3/0.75 lubricant, a large increase was observed in the frictional moment after crossing the seizing load threshold, while at the same time, the diameter of the scar increased, which indicates the loss of the lubricating properties of the tested lubricant. However, in SM A1/0.5 and SM A2/0.6 lubricants containing less dicarboxylic acid in the complex thickener, the resistance of the node to seizing clearly increases, which indicates an increase load capacity of the lubricating film. After analysing the results, it was concluded that the molar ratio of mono- and dicarboxylic acids, used in the manufacture of a thickener complex significantly affects the evaluated properties.

## Conclusions

The production of the lubricant using the *in-situ* method consisted in a synthesis of the thickener directly in the base oil and its dispersion in it. Physicochemical and lubricant properties were modified by the selection of the components that make up the complex thickener.

The research using methods of thermal analysis confirmed the resistance of complex lubricant to the oxidation process. The friction tests have confirmed a significant impact of the molar ratio of mono-and dicarboxylic acids (MK:DK) in the thickener on the anti-wear and antiseizing effectiveness of complex lubricants.

Plastic lubricants for machines and equipment used in the food industry should provide the required level of performance properties, while meeting the requirements of safety and health for food production. The development of a complex lubricant based on non-toxic components guaranteed producing a lubricant that meets the requirements of the food industry, while meeting performance requirements. The designed lubricant has a health clearance certificate of the National Institute of Hygiene HŻ/D/1192/2013 and is permitted for industrial use as a typical bearing lubricant, wherever it is required to use a certified lubricant.

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## Nietoksyczny smar plastyczny dla przemysłu spożywczego

### Słowa kluczowe

Oleje bazowe, nietoksyczne smary plastyczne, właściwości smarne, stabilność oksydacyjna.

### Streszczenie

Wprowadzanie w przemyśle spożywczym obligatoryjnych systemów zarządzania jakością generuje potrzebę opracowania materiałów smarowych o odpowiednich właściwościach eksploatacyjnych oraz bezpiecznych dla ekosystemu. Podczas komponowania specjalistycznych materiałów smarowych zwrócono szczególną uwagę na dobór komponentów, uwzględniając oprócz ich właściwości funkcjonalnych również właściwości ekologiczne. W artykule przedstawiono charakterystykę smaru plastycznego wytworzonego na bazie nietoksycznych składników. Głównymi składnikami smaru są: olej syntetyczny oraz atestowane komponenty zagęszczacza. Zbadano i oceniono właściwości smarne oraz stabilność oksydacyjną wytworzonego smaru.

W efekcie opracowano kompleksowy smar plastyczny charakteryzujący się wysoką trwałością użytkową. Wytworzony smar posiada atest Jakości Zdrowotnej PZH, dopuszczający stosowanie go w przemyśle spożywczym. Opracowany produkt przeznaczony jest do zastosowań przemysłowych jako typowy smar łożyskowy wszędzie tam, gdzie wymagane jest stosowanie certyfikowanych smarów plastycznych.

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# A METHOD FOR MANUFACTURING OF CONSUMER PRODUCTS FROM RECYCLED RAW MATERIALS

**Key words**

Materials recycling, textile wastes, secondary raw materials, fabrics.

## Abstract

Waste management is one of the most important branches of environmental protection. In the European Union, one of the most important legal acts regards the document on community strategy in the field of waste management, with its emphasis on waste prevention, recycling and re-use of waste in the form of useful products. The article presents models of non-woven utility products derived from raw materials from recycling. The study aimed to obtain useful products made from non-woven textile waste. Indicated are methods for grinding and fiberisation of worn textile to form secondary fibres and possible techniques to be applied in their processing. The end result is to present examples of raw products in the three groups of assortment: “A” with a predominance of natural fibre up to 85%, “B” – a mixture of fibres of PE and PP, and “C” – a mixture of synthetic fibres. In each of these groups, using the proper technique, the examples of commercial, technical, and living products

were manufactured, which may be the subject of trade. Developed solutions will be put into production by a company interested in the results of this work after market research.

## Introduction

Growth in the EU is still accompanied by increasing amounts of waste, causing unnecessary losses of materials and energy, environmental damage, and adverse effects on the health and quality of life. One of the strategic objectives of the EU is to reduce these negative impacts by turning the EU community into a society using recycling and being resource efficient. Waste management is already governed by a comprehensive set of rules, but there are still opportunities for further improving the management of some major waste streams [1].

Textile waste represent, on average, approx. 3% of household waste, which is approx. 250 thousand tons of textile waste annually produced in Poland. Only approx. 10% of that is subjected to material recycling and at least 50% is suitable for processing. For comparison, in the UK, households annually produce approx. 1 million tonnes of textile waste, and 25% of the mass of waste is recycled. Textile waste is generated mostly in households, and this is approx. 8–9%. With the undertaken projects in waste management and the target consumption of textiles per capita per year, it is assumed that the recycling of the textile weight placed on the market should be at the level of 55%. This will be similar to the present state of textiles placed on the market, i.e., approx. 250 thousand tons per year [2].

In the last few years in Poland, there was a large import of used clothing from Western Europe, which is sold in an extensive network of retail outlets throughout the country, and we also now have a huge influx of cheap textiles from the Far East, mainly from China. Because of the shorter lifespan of these goods, the textile waste problem will be more serious than it is today [3].

Considering the overall balance of post-consumer textile waste, it is necessary to take into account the textiles from exploited vehicles. It is assumed that, on average, one car is approx. 15 kg of textiles for various purposes, and in accordance with the requirements of the European Commission Directive it is required, since the 1st of January 2006, to recycle 80% of recyclable materials from the liquidated cars.

Because waste management is one of the branches of the textile industry in the field of environmental protection, it is necessary to prevent waste through the use of low-waste technology for textile production, the introduction of cleaner production, and the development of recycling methods aimed to obtain raw materials for re-use in different processing technologies [3].

In the European Union, among the most important acts is the document titled "Communication from the Commission to the Council and the European Parliament on a Community Strategy in the field of waste management". These are guidelines for the Union's policies with an emphasis on waste prevention, recycling and reuse of waste, and the safe disposal of residues not recyclable.

The next few years will be a period of further demand for textile products, with a reduction of the lifetime of the products by at least 20%, and a further increase in the share of synthetic fibres. These are the next challenges for effective relief of the environment and obtaining valuable raw textile material for re-use.

These research problems, including recycling field and particularly textile recycling, were included in the research priorities of the Strategic Project *Innovative technical support for sustainable economic development* implemented by the Institute for Sustainable Technologies, National Research Institute in Radom. This is a proof that the subject of textile recycling is an object of technology and implementation research aimed at increasing textile recyclables for reuse.

## 1. Segregation of post-consumer textile products for material recycling

The most important issue, which, when properly solved, determines the ability to recycle all waste material is their segregation by appropriate groups, specific criteria, and procedure. Postconsumer products supplied as complete, used household objects (Fig. 1) have been categorised in three groups in terms of the percentage of the highest quantity of certain raw materials.

Fig. 1. Provided postconsumer products

The "A" group includes postconsumer products with a high share in its composition of natural materials, i.e. wool, cotton, and artificial materials with natural origin, such as viscose. The average share of these commodities in the group was 88%.

The “B” group includes postconsumer products with a high proportion of synthetic polyester (PES) and polypropylene (PP) fibres. The average share of these commodities in the group was 82%.

The “C” group included all other postconsumer products where their fibre composition was dominated by synthetic fibres (approx. 60%).

## 2. Technological recycling attempts for particular groups of waste and equipment for the production of finished usable products

In order to obtain the raw material for further processing of textile waste, it is necessary to grind it into the appropriate fraction. Each group of waste has undergone a process of shredding and defiberisation on industrial devices, such as cutters, choppers, and defibrators. The pregrinding process by cutting was performed using a guillotine cutter and rotary cutter (Figs. 2, 3).

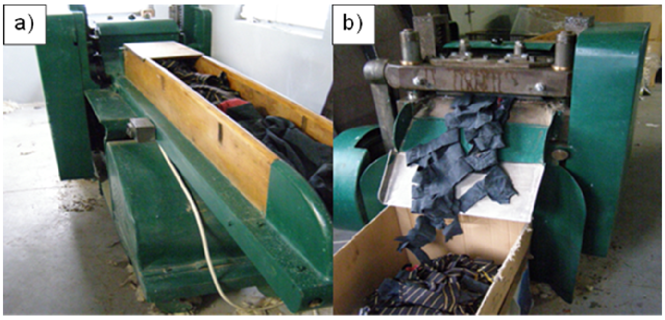

Fig. 2. Guillotine cutter: a) input, b) output

Fig. 3. Rotary cutter: a) input, b) output

After the grinding process, the next stage of textile material recycling of post-consumer products is defibrating, which was performed on two types of devices on which different degrees of defibrate materials can be achieved. The first device that was used for this purpose was defibrator (Fig. 4).

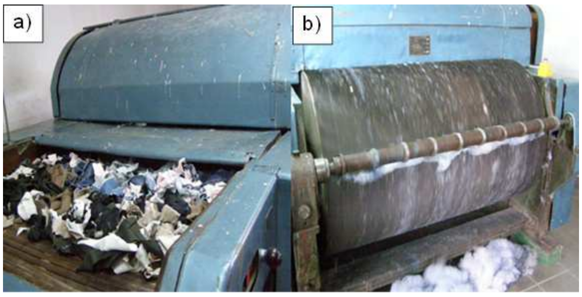

Fig. 4. Defibrator: a) input, b) output

The second device is a six-drum chopper shown in Figure 5.

Fig. 5. Six-drum chopper

As a result of technological trials, secondary fibres were obtained in the three groups of products, all of which were prepared sample products that could be marketed.

With post-consumer products in the "A" group, secondary fibres were obtained with its composition containing natural fibres, i.e. wool, cotton, and natural fibres such as viscose. Figure 6 shows the form of raw material obtained after the defibration process called "selected plunk", which may be a commercial product.

Useful products obtained from recycled fibre in the "A" group were prepared by two mechanical manufacturing techniques – sewing and needling. The sewing technique allows obtaining household products, e.g., woven material, cloth, packaging, etc. (Fig. 7). It is based on stitching of a moulded layer of raw material with yarn using special needles on a piercing machine.

Fig. 6. Six-drum chopper

Fig. 7. Clothes from stitched weave

Needling consists in mutual interlinking of the moulded layer of raw material in a uniform, stable product with the use of needles with special notches, fixed in the board of needling machine. This technique was used to produce, from waste products, the raw materials of agronomic types, such as shielding mats, anti-weed mats, veneers enriched with fertilizer made from fabaceae. The obtained consumer products are shown in Figures 8, 9, and 10.

Fig. 8. Non-woven reinforced fabric with grass seed for strengthening slopes and embankments

Fig. 9. Non-woven agronomic fabric to control the growth of weeds

Fig. 10. Agronomic fabric for cultivation with fertilizer made from *fabaceae*

In the post-consumer waste products from group “B”, secondary fibres were obtained by grinding and defibrating with a high proportion of synthetic polyester fibres (PES) and polypropylene (PP). With this type of fibre, one can produce both household products for thermal insulation materials (warmers, duvet insert) and technical fabrics, such as drainage and road components.

Nonwoven materials are obtained with simplified fleece moulding, as used for blanket inserts, where a loose and airy texture is obtained to a predetermined thickness to achieve a stable structure of the given parameters. The resulting samples of insulating nonwovens of different thicknesses are shown in Figures 11 and 12.

Fig. 11. Thick warmer

Fig. 12. Thin warmer

Another consumer product obtained from recycled fibres derived from post-consumer products in the "B" group is the "technical nonwoven", which was prepared with mechanical consolidation of a fleece layer by needling on a needling machine to obtain a product with stable parameters for the surface weight and thickness. This non-woven material is generally intended for drainage, as a lining for ditches, and mostly as a reinforcing material, stabilizing land for the construction of roads, both access roads and highways. Examples of manufactured consumer products in the form of technical nonwovens are shown in Figures 13 and 14.

Fig. 13. Drainage fabric

Fig. 14. Road-construction fabric

Post-consumer products, qualified for the final "C" group, were secondary fibres obtained mostly as a mix of different types of fibres. Such a mixture of fibres has commonly been called "synthetic plunk".

From the plunk, two consumer products were obtained. The first is a felt that is often used in furniture manufacturing, which is manufactured with the mechanical needling technique (Fig. 15).

Fig. 15. Furniture fabric – felt type

The second product obtained is "synthetic plunk", which is also used in furniture manufacturing, which is produced by needling and thermally stabilising established technical parameters.

The thermal stabilization technique is conducted on a needled fabric by subjecting it to a temperature and pressure in a calender machine. The figure below presents the device producing the finished product in the form of a furniture fabric with given parameters (Fig. 16).

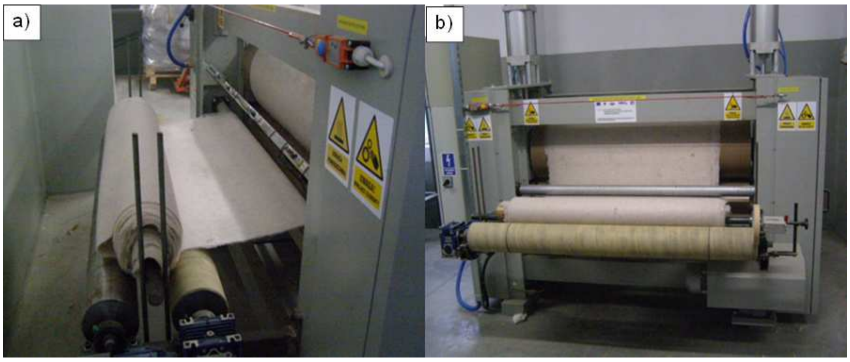

Fig. 16. Thermal stabilization process of furniture fabric: a) infeed of a fabric, b) the output of the finished product

The thermal stabilization process allows one to obtain the finished product with a predetermined thickness, density, and rigidity characteristics, which is of particular importance in the application of these products. Presented below is furniture fabric derived from the processing of reclaimed synthetic plunk of varying density, stiffness, and thickness (Figs. 17–20).

Fig. 17. Thick furniture fabric

Fig. 18. Thin furniture fabric

Fig. 19. Stiff furniture fabric

Fig. 20. Comparison of thickness of fabrics

## Conclusions

From post-consumer products received from the client, as part of the material recycling, one can produce finished consumer products for both household and technical appliances. A higher economic effect can be achieved by the selection of used materials in terms of raw materials. Waste selection is essential in processing materials for recycling into the form of finished products of a certain application and purpose. The article presents examples of a selection for the three groups of raw material products for recycling. With the obtained secondary fibre a total of 15 examples of products (several in each group) were produced to be used in the economy.

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## Metodyka wytwarzania wyrobów użytkowych z surowców wtórnych z recyklingu materiałowego

### Słowa kluczowe

Odpady tekstylne, recykling materiałowy, wyroby użytkowe z surowców wtórnych.

### Streszczenie

Gospodarka odpadami jest jedną z najważniejszych gałęzi ochrony środowiska. W Unii Europejskiej jednym z najważniejszych aktów prawnych jest dokument dot. strategii Wspólnoty w dziedzinie gospodarki odpadami, kładący nacisk na zapobieganie powstawaniu odpadów poprzez recykling i powtórne wykorzystanie odpadów w postaci wyrobów użytecznych. W artykule zostały przedstawione wzory włókninowych wyrobów użytkowych otrzymanych z surowców pochodzących z recyklingu materiałowego. Badania miały na celu uzyskanie pełnowartościowych włókninowych wyrobów wytworzonych z odpadów tekstylnych. Wskazano metody rozdrabniania i rozwłókniania zużytków tekstylnych do postaci włókien wtórnych oraz techniki możliwe do zastosowania w ich przerobie. Wynikiem końcowym jest zaprezentowanie wzorów wyrobów w trzech surowcowych grupach asortymentowych: "A" z przewagą włókien naturalnych do 85%, "B" z mieszanki włókien PE i PP oraz "C" z mieszanki włókien syntetycznych.

W każdej z tych grup, przy zastosowaniu odpowiedniej techniki, wytworzono wzory wyrobów komercyjnych, technicznych i bytowych, które mogą być przedmiotem obrotu handlowego. Opracowane rozwiązania zostaną wdrożone do produkcji przez zainteresowane wynikami tych prac przedsiębiorstwo po wcześniejszym dokonaniu marketingowego rozpoznania rynku zbytu dla opracowanych wzorów wyrobów.

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# PROMOTION OF THE BEST AVAILABLE TECHNIQUES AND POSITIVE ECOLOGICAL SOLUTIONS FOR LEATHER INDUSTRY IN THE LIGHT OF EFFORTS CARRIED ON WITHIN LIFE+ PROGRAMME

**Key words**

Carbon footprint, BAT, leather industry, $CO_2$, Kyoto protocol.

## Abstract

An effect on the environment and its protection play increasing importance in industrial activity. The leather industry has been trying for years to accommodate to increasing demands. The best examples are modernisations in tanneries, which notably have reduced the emissions. Nowadays, the producers must face up to new challenges. There is an increasing pressure to reduce the amount of greenhouse gases emitted by industry. The European Union has also started the promotion of the best available techniques (BAT) and reduction of "$CO_2$ footprint" by financing several projects. Within the footwear sector, examples of such projects are "ShoeBAT" and "$CO_2$Shoe" are carried on within LIFE+ programme. Beside of development of a tool for the calculation of the enterprise's effect on environment and providing the entrepreneurs with new knowledge on low emission techniques, in these projects there are gathered and analysed data related to the perception of environment protection issues by

entrepreneurs of leather industry from such countries as Poland, Spain, Portugal, Italy, and Belgium.

So far, research allowed us to draw the following conclusions:

1. Knowledge on BAT and problematics of greenhouse gases emissions is low among entrepreneurs of leather industry.
2. In majority of enterprises (tanning sector in particular), there are exploited obsolete techniques and processes which constitute a threat for environment. Some of the enterprises do not respect the relevant legislation, using inadequate techniques and/or not monitor the emissions.

The obtained image of knowledge on carbon footprint and BAT and the ecological awareness of leather sector entrepreneurs will be confronted with results of the planned questionnaire surveys that will allow evaluating the effectiveness of promotion tools developed within LIFE+ programme.

## Introduction

The leather industry is commonly considered as environmentally unfriendly. In spite of continuous modernisation of tanning technologies and growing pressure towards the reduction of the effect on environment, the leather sector is treated as an unavoidable and the neighbourhood of the production plant is often perceived by local residents as an unwanted factor, which diminish a quality of life and reduces the prices of real estates.

On the other hand, in European Union tanneries (Spanish and Italian in particular), there has been significant technological progress achieved, which aims to accomplish ecological sustainability. Positive ecological modernisations have been made as the foremost activities to guarantee conformity with the demands of local societies. An active cooperation with all actors of the supply chain allowed achieving notable successes in the field of environmental protection. These changes include the following:

- Reduced water consumption,
- The substitution of hazardous chemical agents with less harmful ones,
- More efficient wastewater treatment,
- The reduction of generation and better reuse of biological wastes,
- Waste recycling, and
- Incineration and energy recovery from wastes.

The analysis of our leather sector indicates that further technological development is necessary. This development must harmonize with international standards as well as with the improvement of the ecological image of the whole sector. To achieve this aim, the priorities of changes and identified technologies have been outlined, which will significantly reduce the effect on environment. Additionally, the implementation of these technologies may bring notable financial benefits for entrepreneurs. However, usually the investments require significant financial expenses; moreover, the quality of the final product is often affected. In the ShoeBAT project, realised within a LIFE+ programme of European Union, data has been gathered on various best available technologies (BAT) in the leather sector, including implementation examples, advantages, and disadvantages of every solution.

One should highlight that Europe plays a significant role in international leather trading. Italy and Spain, the main European footwear producers, account for 20% [19] of the global leather footwear exports, with the European leather sector representing 23% of tanned leather produced worldwide [19]. On the one hand, the European footwear industry consists of a large number of small enterprises. However, there are differences between member states: French and German enterprises employ on average about 100 workers, while Spanish and Italian only 15. The other Member States are placed between these two extremes. For such small companies, it is very difficult to access to the most environmentally friendly techniques; therefore, the ShoeBAT project is primarily addressed to these SME companies. One should also stress that, despite of small size of leather companies, in total, the leather sector gives employment to huge number of workers. In 2009, the footwear sector covered 26,100 enterprises (including components suppliers), generating a turnover of €22 billion and a production added value of €20 billion, and directly employing 291,000 people [20].

## 1. Best available techniques for tanneries

In the project, the most important considered BATs mentioned in BREF document [1], which is a catalogue of commonly accepted as the best available technologies in the EU, were considered. Below we present a review of several BATs, including their advantages, disadvantages, and example applications.

### 1.1. Chromium-free tanning

At the moment, the most dominant method used in tanneries is processing leather with chromium salts. These chemical agents are considered as hazardous (EU Directive no. 2002/95/WE). Even small quantities of hexavalent chromium may negatively affect human health. Contact with contaminated substances is associated with occurrence of allergic symptoms. Hexavalent chromium penetrates cell membranes. When it enters the cell's interior it is reduced to trivalent, which releases electrons damaging the cell's membrane. Then it participates in the formation of the complex compounds, first of all with DNA, which leads to its deterioration and consecutively the occurrence of cancer [2].

Admittedly, restrictive legislation practically has completely eliminated CrVI; however, at the moment also CrIII is considered to be potentially dangerous. Additionally, there is always a risk of transformation of “harmless” CrIII into harmful CrVI [3]. The alternative for chromium technologies have been known for ages and had been used long before the chromium salt solution had been developed. Vegetable tanning methods are the foremost technologies. In comparison to the chromium technology, the vegetable method is inferior in many aspects. First of all, the rheology parameters of the product are affected. Therefore, research to substitute chromium with other substances continues to take place, for example, titanium.

Titanium has a proven usefulness for the production of leathers. It is a non-toxic metal that has several advantages. Titanium is biocompatible, inert, gives no allergic response.

Titanium bounds with leather’s collagen in an analogical way to chromium. An unquestionable advantage is that titanium facilitates production of leathers in a wider range of colours. It is deprived of the chromium-tanning disadvantage – the occurrence of a blue tint, whereas titanium tanned leathers are characterized by a yellowish tone, which allows the tanners to obtain pale colours. The application of the technology does not require any additional costs; however, it also brings no significant savings and the main advantage is diminishing the effect on the environment (elimination of chromium, less chlorides and sulphates, grease and oils needed for baths) [4].

Titan tanning technology has been introduced in several tanneries, for example, in INCUSA Tannery in Spain.

The other tanning technology, which may be used instead of chromium salts, is tanning with oxazolidine compounds. Oxazolidines are saturated heterocyclic compounds prepared by reacting primary amino alcohols with formaldehyde. Monocyclic or bicyclic oxazolidine ring structures are formed, depending on the choice of starting chemicals [5]. Thanks to this technology, it is possible to obtain more biodegradable leathers with an appearance and properties suitable for the manufacture of shoes and other leather goods.

In relations to the effect on environment, the parameters of produced effluents are comparable with chromium tanning, but performed analyses have proven better biodegradability. Moreover, there is higher probability that chromium-free effluents may be reused, for example, in agriculture.

Regarding the proportion of oxazolidine used (3 or 5%), no differences were found in the leathers, which promotes the economic viability of the technology, since the higher oxazolidyne cost compared to chromium salts (2.5÷3 €/kg for oxazolidine versus 1 €/kg for chromium salts) is compensated by the lower dosage (3% of oxazolidine versus 8% of chromium salts).

Despite of numerous research projects that confirm the high quality of oxazolidine-tanned products, as well as the fact that ready-to-use formulas are available on the market (MP Angus Company), the tanneries approach with fear to the implementation of this technology and one should assume that the chromium tanning will still dominate in the future. Therefore, the eco-friendly technologies for tanneries using chromium are of importance. An example of such a technology is the separation of chromium salts from the aqueous effluent stream by precipitation, with dewatering of the precipitate. The precipitated chromium may be used as a partial substitute for fresh chromium salts or the chromium sludge may be used as a raw material by another industry. From the chemical point of view, chromium recovery is a simple process, but it needs strict analytical control and requires special equipment such as the following:

- A separate tank for collecting spent chromium tanning liquors;
- Material to analyse the chromium content, acidity, and alkalinity;
- A tank with stirrer and pH control for adding the right amount of alkali for the precipitation;
- A sedimentation tank for chromium hydroxide settling;
- A filter press or centrifuge for the chromium hydroxide sludge; and,
- A tank with stirrer and heating equipment for the re-solution of the chromium hydroxide by concentrated sulphuric acid.

In the case of double precipitation, the use of fossil flour to absorb fats and other chemicals present in the spent chromium tanning liquors is necessary – more filter presses, more chemicals, more time is required, and consecutively the higher costs are involved.

The liquors containing chromium are collected in a special tank, after which the chromium is precipitated by addition of an alkali. The precipitated chromium is separated from the supernatant, after which the chromium sludge is dissolved in concentrated sulphuric acid (for 1 kg $Cr_2O_3$ as precipitate about 1.9 kg $H_2SO_4$ is required). The supernatant is generally discharged to the effluent. Any alkali will precipitate chromium, but the stronger the alkali, the faster the rate of coagulation. Below we present several options:

- Sodium hydroxide or sodium carbonate will lead to a fast precipitation and voluminous sludge;
- Fast precipitation with additional agents (polyelectrolytes) to facilitate coagulation has the advantage that only simple dewatering is necessary;
- Slow precipitation, e.g. magnesium oxide, gives a denser sludge, which allows for decanting. (Another advantage of the use of MgO is that any excess addition will not cause the pH to rise beyond 10, so that any sludge redissolving at higher pH levels is avoided.)

Based on reports, the recovery processes are quite efficient (even 99.9%). The recovered chromium sulphate solution can be recycled into the tanning process by replacing up to 35% of the “virgin” chromium salt. Italy and Portugal each have one common chromium-recycling unit. The plant in Italy was designed to receive 400–500 $m^3$ exhausted floats per day from about 250 operators and produces 2000 kg $Cr_2O_3$ per day. The tanneries mostly use a mixture of 1 part recycled to 2 parts fresh chromium salts. The primary driver for establishing this plant was economics, because energy is saved because neutralization and filtration take place without the need of heating. Of course, environmental reasons were also taken into account; however, one should remember that chromium recovery requires the use of alkali, acids, and auxiliaries. Consequently, the quantity of neutral salts discharged to the effluents is increased. The effect on quality is insignificant. Chromium recycling also has the disadvantage that a slight change in the colour may occur, since organic compounds can produce a greyish tint. If the achieved quality of the final product is negatively affected by the use of recovered chromium, the chromium can be used for tanning of split. The disadvantages are not as severe as in recycling the liquors, because the concentration of organic compounds, which is usually low, does not disturb the precipitation process. Chromium recovered in this way resembles, in a higher degree, the quality of fresh chromium; therefore, this technique of chromium precipitation tends to be favoured over direct chromium recycling.

The technique can be implemented both in new and existing plants. It is independent of any local conditions and can be introduced in any tannery using chromium as a tanning agent. In practice, it has been applied in larger tanneries or in common effluent treatment plants. It is not appropriate for treating effluents from high-exhaustion chromium tanning.

The advantage of slow precipitation is that no investment in filtering equipment has to be made. However, it should be stressed that slow precipitation may not always be technically possible, as fat and protein impurities may interfere with the settling of the precipitated chromium. In consequence, the economic feasibility will depend on the exhaustion rate of the chromium-tanning agent and the quantity of chromium liquors generated. In general, the lower the exhaustion rate during tanning and the higher the volume of the floats, the higher the economic feasibility [13, 15].

Data from 2004 indicates that the investment cost for a chromium treatment plant for the treatment of 100 m³ water containing chromium is approximately 350 000–450 000 EUR.

Several central chromium recovery installations have been constructed in European tannery conglomerations in order to benefit from economies of scale, e.g. Consorzio Recupero Cromo SpA, in Italy. Some individual tanneries have also been able to implement chromium recovery on site, e.g. in Germany (e.g. Bader and Gmelich) [16], and Italy and Sweden (Elmo Sweden AB) [14].

### 1.2. Replacement of hazardous chemical substances with environmentally friendly

Chromium salts are not the only substances that are harmful for environment. In various stages of production, there is a need to use chemicals, and an opportunity to introduce BAT.

Such a production stage is finishing. To achieve an attractive and desirable effect, leather is treated with various chemical substances, dyes foremost. Some dyes and pigments (particularly yellow, orange, green) contain heavy metals, such a cadmium, lead, chromium (VI)), which should be replaced by compounds based on organic substances. Unfortunately, organic pigments are less effective in concealing leathers' defects than "metallic" pigments; therefore, applicability of "organic" pigments is limited to high quality, spot- and scar less leathers. This limitation also affects the cost-benefit ratio since, despite of the fact that changes in production cost resulting from slightly higher price of "organic" pigments is insignificant, due to necessity to use high quality leathers, the final price is notably higher. Despite of this disadvantage, the technology has been implemented in several tanneries – in Spain it is used in 95% of the plants.

Another processing stage where the BAT may be introduced is the degreasing stage. There is an option to replace halogenated organic compounds either by non-halogenated solvents or by changing over to an aqueous degreasing system. The linear alkyl polyglycol ethers, carboxylates, alkyl ether sulphates, and alkyl sulphate can be applied.

In the stage of aqueous degreasing of sheepskins, there is a possibility to use of linear alcohol ethoxylates instead of alkylphenol ethoxylates. Surfactants are used in many different processes throughout the tannery, e.g. soaking, liming, degreasing of sheepskins, tanning, and dyeing. Nonylphenol ethoxylate (NPE) surfactants were used in the leather industry in the past. NPEs can be degraded to smaller chain NPEs and nonylphenol, both of which are toxic. The European Union carried out an extensive risk assessment of nonylphenol that concluded that nonylphenol displays an endocrine-disrupting activity. The use of NPE in leather processing is now restricted under the REACH regulation. Its use is banned, unless there are adopted such measures which prevent release to waste water or there are employed systems with special treatment where the process water is pre-treated to remove the organic fraction completely prior to biological waste water treatment (degreasing of sheepskins) as it is specified in point 46 of Annex XVII of the regulation [11]. In sheepskin processing, a closed loop cycle is adopted in order to avoid discharges of octylphenol and nonylphenol ethoxylates. The main alternatives in the degreasing of sheepskins are linear alcohol ethoxylates with different chain lengths and ethoxylation degrees. The efficacy of C10 linear alcohol ethoxylate as a degreasing agent is comparable to that of NPE. In this application, a nanophase with very low surface energy is formed that is converted into a macroemulsion. A process for the recovery of the surfactant and fat by solvent distillation using heptane and ethanol has been demonstrated on a pilot scale [17]. The best recovery rate found was 75%. Each one of the aliphatic ethoxylated alcohols has distinct properties, so that the process design differs depending on the material chosen; therefore, the process requires more attention than realized with "standard" methods. On the other hand, an advantage of the technology from the point of view of the producer is the lack of the necessity of preliminary purification of effluents before the biological purification.

The other substances containing halogenated compounds are flame retardants. Actually, firm leather with a dense fibre interweaving is itself more flame resistant than other leather types [8]. Therefore, flame resistance is possible by applying appropriate syntans and the addition of melamine resins in the retanning process, as well as by selecting suitable fatliquors. Furthermore, the application of, e.g. ammonium bromide, leads to a flame-retardant effect that is sufficient for some applications. As an alternative to brominated flame-retardants, phosphorus compounds, such as ammonium polyphosphate, may be applied. Additionally, silicon polymer products used in finishing can give some fire resistance, in that they burn to leave a residue of silica ($SiO_2$) which protects the leather. The advantage of the technique is that it can be applied to both new and existing installations. Unfortunately, for some types of leather, the affinity to the leather is insufficient. The flame proofing of some types of waterproof leather may still require the use of halogenated chemicals. The technology has been introduced in large number of installations in Europe.

### 1.3. Reduction of water consumption

The tanning sector is commonly considered as water consuming, so it is not a surprise that tanneries are looking for solutions reducing water input. Of course, the concern for environment is not a sole reason. The cost of water and resulting management of wastewater is, at the moment, one of the most notable component of costs. One should stress that the majority of Polish and European tanneries, even those that represent an “average” level, have achieved significant success in this field. According to criteria related to the “ecolabel” award, the following limits to water consumption for the tanning of hide and skin shall not be exceeded [6]:

- Hides: 35 $m^3$/t,
- Skins: 55 $m^3$/t.

Based on IPS’s knowledge, most Polish tanneries meet these requirements. Regarding the other countries, a water consumption of approximately 12–25 $m^3$/t (for bovine hides) can be achieved if the tannery operates efficient technical control and good housekeeping. The economic feasibility of a change in consumption to this level depends greatly on the cost of consumed water. In Germany, some tanneries use 15–20 $m^3$/t. A tannery in the Netherlands, processing bovine hides, uses about 20 $m^3$/t.

The way that is possible to reduce the amount of water consumption is to adopt various technologies, for example, purifying and storage of wastes used at the initial stages of production. For the purpose of the secondary use, post-tanning and post-dyeing water is purified in a sedimentation tank and used for soaking in the liming drum and as post-liming washes. Acidic effluents are purified mechanically and then alkalized and sedimented with the addition of polyelectrolytes and metal salts. The obtained purified water is used for soaking in the first rinse stage after liming. Water from the second soaking after liming should be collected and sedimented and may be used for the first soaking. Due to high sulphide and organic contamination, the first rinse requires the treatment to be purified. This technique provides savings equal to 20% of total water consumption. On the other hand, the side effects include a build-up of the salt content, an increase in temperature, as well as problems arising during biological treatment of the effluents. One should also take into account higher energy consumption and a more complicated production scheme, which consecutively may require increased employment. However, calculations based on data obtained in the reference company with 90 employees (Josef Heinen GmbH & Co. Kg, Wegberg) assume that average savings are 40 000 EUR per year and there was no reported any deterioration of quality [9]. It was achieved at the investment cost of 298 000 EUR.

In Poland, the sensible solution seems to be the management of rainwater. The amount of rainwater that falls onto a tannery site will vary according to the weather pattern for the locality. It is good practice for rainwater falling on the roofs of the buildings to be collected separately from the process effluent so as to reduce the volume of water requiring treatment. It may be useful to store it for use both in process operations as well as for general use (cleaning).

A further reduction in water consumption can be obtained if rainwater falling onto all area of the tannery is also diverted away from the process effluent stream. Rainwater from paved yard areas in which spills of process substances (chemicals) are present is collected as a process effluent; therefore, it is recommended to design operations so that the yard area used is as small as possible, so as to minimize the amount of rainwater collected [7].

The other question is cost-benefit ratio of the investment. In Poland, on average, there is reported 600 mm of rainwater per year. So it is possible to gather (theoretically) 6 000 $m^3$ per hectare, which (based on ecolabels criteria) is enough to process about 171 tonnes of hides. The rates for delivery of water and collection of sewage vary in various areas of Poland, but, for the assumed cost of 15 PLN, the potential saving are 90 000 PLN.

### 1.4. Reduction of chemical content

Regardless the efforts to substitute the hazardous agents with harmless ones, there is always a necessity to use agents that are a potential burden for the environment.

It is possible to achieve by the rearrangement of production stages. An example of such an approach is to split leather in the earlier stage of production to reduce the amount of leather to be treated with tanning agents (obtained wastes are not subjected to the further treatment). Savings in chemicals per square meter of the final product during the stage between liming and shaving are directly proportional to the weight of wastes generated in the lime splitting; moreover, eventual non-tanned wastes are less harmful to the environment and, in comparison to the tanned leather, comparatively well biodegradable. The technology's inconvenience is the fact that leather split after liming may require more shavings after tanning since splitting after liming is less precise. It may lead to the generation of more wastes. Therefore, in applications where more uniform and exact thickness is required, the after liming splitting is unavoidable. Moreover, in the case of extremely thin leather, after liming splitting may result in diminished efficiency of the splitting process. In such cases, after tanning splitting may be a recommended solution, since the split leather may be used in further processes [13].

Theoretically, this technology may be used in old and new installations, but it requires purchase or modification of splitting machines. Machines used in after liming splitting and post tanning splitting are generally identical; however, it is necessary to introduce some modifications, more precisely, there are required rollers of different hardness and roughness, due to these disadvantages, a single machine cannot be used for both methods of splitting simultaneously. Investment costs include about 140 000 EUR per new splitting machine. In case of a used machine, the cost may be significantly reduced.

The other option to reduce chemical agent consumption is to use "intelligent" chemicals. An example of such a solution is to carry out dehairing by dissolving the hair root rather than the whole hair. Consecutively, the concentration of hair breakdown products in the effluent is reduced. The hair comes out of the follicle without being macerated and its structure is preserved. The obtained hair may be managed by various methods. Although it is difficult to find an economic outlet, hair can be reused as filling material or as a fertiliser (low rate of releasing nitrogen). An example plant in Sweden has implemented hair-saving since the end of 1998 for all production. The generated hair is used by local farmers as a fertilizer [10].

Generally, sheep wool and goat hair are easier to sell. The biggest advantage is that hair is not included in liquid effluents. Hair has a very high organic load; therefore, its presence in effluents would result in high production of sludge. Additionally, there is a lower volume of sludge for disposal or treatment (The volume of sludge is reduced by 15–30%, there are also reports that there may be obtained a reduction of the amount of sludge dry matter to 100–110 kg per tonne raw hide). Moreover, a saving on wastewater treatment chemicals is achieved.

The hair-save dehairing techniques are based on the different chemical behaviour between the proteins keratin and collagen. Collagen is the leather-making protein of the hide while keratin is the insoluble protein, stabilised through disulphide (-S-S-) bonds. The resistance of keratin to chemical degradation can be substantially increased by treatment with alkali (but without sulphides). The alkali transforms the sulphur cross-links into different, highly resistant thioester bonds. Mature keratin is much more easily immunised than immature keratin. This increases the difference in degradability between hair and hair roots; thus simplifying the hair-save dehairing technique. Immunisation can be achieved by using sodium hydroxide, lime, or calcium hydroxide and usually takes 1–1.5 hours. Several commercial hair-save techniques are available on the market. One should admit these solutions are not suitable for all types of raw hides and leather products. In Italy, this technique is applied to bovine hides for footwear, leather goods, and upholstery, but not to bovine leather used for the production of sole leather or to goatskin.

A hair-save technology for sheepskins, called painting, consists of the application of a semifluid paste on the flesh side of the skin, composed of an inert material (kaolin or other) containing sulphide and lime. The treatment is carried out in a warm environment (max. 30°C) and takes several hours [18].

Modern hair-save dehairing techniques include special equipment for recirculating the float and separating the hair. Hair separation is preferably carried out simultaneously with hair loosening, so as to minimise the degradation of the hair [13].

The technique requires capital investment for existing tanneries. The basic investment includes cost for a drum (wooden, size 4 × 4 metres) equipped with a system for recycling water and with a filter for hair removal is around EUR 100 000–130 000. Besides this cost, there will be costs for the reinforcement or construction of appropriate concrete foundations. An existing drum can be rebuilt introducing channels and washing systems to recycle the float in order to separate the hair. The cost is estimated at EUR 5000–10 000.

Examples of tanneries that introduced this BAT are Elmo Sweden AB, Rino Mastrotto Group – Division Calbe (Italy), Lapuan Nahka (Finland) [14].

During deliming, there is eliminated the alkalinity caused by lime on the collagen. Ammonium salts (NH4Cl) are usually used for this process. At the moment, it is recommended to replace it by weak organic acids. Examples of such substances are Magnesium lactate, organic acids such as lactic acid, formic acid and acetic acids, or esters of organic acids. Environmental benefits that can be achieved using this technique are reduction of nitrogen in the effluents and a reduction of gaseous ammonia. The deliming products are usually based on various organic and inorganic acids, esters of carboxylic acids, non-swelling aromatic acids, etc. A deliming auxiliary based on esters of carboxylic acids will normally be added at a concentration of 1.5% on pelt weight. These agents increase the COD load [13]. No data have been made available to evaluate the substitution of ammonium in the effluents against a higher COD load and against the effects of the various substitutes mentioned above.

The technique can be applied to both new and existing plants. Negative opinions have not been reported on the quality, on the contrary, positive effects on the quality of the pelts are observed.

A significant disadvantage is that ammonia-free deliming with commercial products may be more than six times as expensive as deliming with ammonium salts; on the other hand, less bating agent is subsequently needed. [12, 13].

## Conclusions

Within the ShoeBAT project, there have been identified nearly seventy BAT for tannery and footwear industries, which gives an opportunity to nearly every company to improve their eco-friendliness; however, many of these BAT are beyond the capabilities of various tanneries. Tanning process requires several stages to process a leather from raw hides up to high quality leathers. It is not possible to make the whole process completely environmental friendly; it simultaneously offers a great opportunity to improve even a single stage. Entrepreneurs, encouraged by legislation (ban on several chemical products) as well as increasing cost of management of several products (for example water), have developed/introduced various methods. Their successful implementation depends on several factors, sometimes independent of the entrepreneur (climate, availability of raw materials). Additionally, tanneries in Europe are under heavy pressure of competition from countries (Pakistan and India foremost), which (in practice) do not take care of the environment and therefore may offer much cheaper products. Therefore, European tanneries, before introduce any BAT, have to take into account many factors, mostly economical. One should admit that some investments may be supported financially by EU, but this support is limited only to initial investments, whereas regular activity (e.g. purchase of chemicals) is entirely on the entrepreneur.

## Acknowledgment

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## Promocja najlepszych dostępnych technik oraz proekologicznych rozwiązań dla przemysłu skórzanego w świetle prac prowadzonych w projektach programu life+

### Słowa kluczowe

Ślad węglowy, najlepsze dostępne techniki, BAT, przemysł skórzany, $CO_2$, protokół z Kioto.

### Streszczenie

Oddziaływanie na środowisko i jego ochrona odgrywają coraz istotniejszą rolę w trakcie prowadzenia działalności przemysłowej. Przemysł skórzany od lat stara się dopasować do wzrastających wymagań. Najlepszym przykładem są zmiany w garbarniach, które znacząco zmniejszyły emisję zanieczyszczeń. Obecne czasy stawiają przed producentami nowe wyzwania. Wzrasta presja, aby zmniejszyć poziom generowanych przez przemysł gazów cieplarnianych. Do promowania najlepszych dostępnych technologii (BAT) i obniżenia „śladu węglowego” produktów włączyła się również Unia Europejska, finansując

szereg projektów. W obszarze przemysłu skórzanego przykładem takich projektów są „ShoeBAT” oraz „$CO_2$Shoe” realizowane w ramach programu LIFE+. Oprócz opracowania narzędzi do obliczania wpływu działalności przedsiębiorstwa na środowisko oraz dostarczania przedsiębiorcom wiedzy na temat niskoemisyjnych technik, w ramach tych projektów są zbierane i opracowywane dane dotyczące postrzegania kwestii ochrony środowiska przez przedsiębiorców z branży skórzanej z takich krajów jak: Polska, Hiszpania, Portugalia, Włochy, Belgia.

Prowadzone dotychczas badania pozwoliły sformułować następujące wnioski:

1. Znajomość BAT oraz problematyki emisji gazów cieplarnianych wśród przedsiębiorców z branży skórzanej jest niska.
2. W znacznej części przedsiębiorstw, zwłaszcza z branży garbarskiej, stosowane są przestarzałe techniki i procesy stwarzające zagrożenia dla środowiska. Niektóre z przedsiębiorstw nie stosują się do regulacji prawnych, wykorzystując niewłaściwe techniki i/lub nie monitorując emisji.

Uzyskany obraz wiedzy przedsiębiorców z przemysłu skórzanego na temat śladu węglowego oraz BAT, a także świadomości ekologicznej, zostanie skonfrontowany z wynikami przewidzianych w projektach badań wśród tych przedsiębiorców, co pozwoli na ocenę skuteczności oddziaływania zbudowanych w ramach projektów LIFE+ narzędzi promowania prośrodowiskowych rozwiązań.

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# INSULATING OIL REGENERATION AND ITS INFLUENCE ON THE TECHNICAL SAFETY OF TRANSFORMERS

## Key words

Paper-oil insulation, insulating oil, diagnostics of transformers, oil regeneration.

## Abstract

Insulating oils are the coolants of the transformer winding. During the operation, they are subjected to numerous and diverse extortion; they accumulate destruction of a variety of products of structural elements of the transformer in themselves and, as a result they change their own properties. The systematic analysis of composition and characteristics of the insulating oil provides information about the condition of the whole transformer. The article presents the results of an investigation of insulating oil condition during operation of a transformer, and it proposes actions to monitor the insulation oil and prolong its service life. Regular tests allow the regeneration of oil (e.g. by vacuum treatment, drying) at the right time, which eliminates the need for costly oil exchange in many cases. Monitoring of the insulating oil also has a large impact on the technical safety, which is related to risk mitigation of major accidents, such as electric shocking or even transformer explosions. The obtained results confirm the validity of the insulating oil regeneration process as

a method for decreasing operating costs, which is simultaneously efficient and environmentally friendly.

## Introduction

The proper functioning of the transformer is determined by the condition of the oil-paper insulation. Transformer oil serves as a coolant, restricts the access of air, protects against corrosion, and serves electrical insulating functions. The main factors that affect the intensity of the transformer oil aging process during operation are high temperature, the impact of oxygen, the presence of water, the catalytic effect of the copper and the depolymerization of cellulose in paper insulation. The cellulose insulation is intended to protect windings made of electrolytic copper [1, 2]. The stability of the transformer insulation determines the transformer operating time and depends on many factors, such as temperature, humidity, impurities, winding displacement at points of expansions and contractions, and vibration [3, 4]. The more wetted cellulose is, the faster the process of depolymerization goes. Under the influence of load and time, the transformer occurs the aging process. The nominal life of a transformer is estimated at approx. 30 years; however, economic considerations have shaped the trend of maximizing the functional life transformers, which entails the need to carry out the regular inspections, modernization, and repairs. These actions are intended to ensure the faultless operation of transformers [5].

Extending the functional life of a transformer requires the fulfilment of the following basic conditions affecting its operation [1]:

- Protection against external factors;
- Maintaining the temperature and the load;
- Controlling the insulating oil parameters;
- The implementation of maintenance and renovation; and,
- Conducting a comprehensive diagnosis of the unit’s technical condition.

One of the primary transformer operation management tools is their comprehensive diagnostics [6]. Proper control of the technical condition of the transformer is based, inter alia, on the determination of moisture and aging of paper insulation, insulating oil moisture measurement, measurement and localization of partial discharge, dielectric loss factor measurement at high voltage and winding resistance, transformer winding deformation detection, and the investigation of gases dissolved in the oil (DGA – *Dissolved Gas Analysis*) [3, 7]. The diagnostic tests selected depend on the type and power of the transformer. It is necessary to appropriately select suitable research techniques, because transformer failures have very serious consequences, both technical and economic. For example, these are power failure costs and the costs of repair and replacement of damaged equipment and facilities, including the contamination of the area. An improperly supervised and maintained transformer can cause environmental problems associated with the possibility of still commonly used mineral transformer oils entering into the environment. Preferably, it would be the best to avoid it leaks into the ground and, consequently, contamination of water reservoir and watercourses [1, 8].

Transformer oil exploitation involves the gradual deterioration of its operating parameters, often as a result of contamination, which may be impurities such as sand, corrosion products, microfiber cellulose, or chemicals such as water, furan derivatives, organic acids, and gaseous products [9].

If irregularities of the technical condition of the transformer or transformer oil, they can be removed depending on their degree of complexity.

One of the major solutions is the regeneration of the oil. This procedure allows improving the operating characteristics, and thus extending the faultless operation of the transformer.

## 1. Insulating oil regeneration methods

For transformer oil regeneration, physical, chemical, and physico-chemical methods are applied. The selection of the appropriate method depends on the degree and the type of oil contamination. Moisture can be removed by draining oil, solid contaminants are removed by appropriate purification, and gaseous products are removed by degassing the transformer oil. For transformer oil purification, the following methods are applied [1]:

- Filtration,
- Centrifugal separation,
- Sorption, and
- Electrostatic separation.

Filtering methods are based on the use of porous materials and allow removal of solid contaminants such as metal particles, carbon black, microfibers, etc. Filtration methods include gravity filtration, in which the oil flows through the filter by gravity forces, pressure filtration, wherein the oil passes through the filter due to the pressure difference before and behind the barrier filter, filtration through extrusion, wherein the solid particles are separated from the oil as a result of extrusion through a filter using a press. The advantage of filtration methods is their high process effectiveness.

The centrifugal methods use the phenomenon of the movement of the impurities contained the oil to separate them. The rates of deposition of the particulate impurities contained in the oil depend on the size and the density difference between them and the oil. In practice, two methods for producing centrifugal force field are used: driving the oil in centrifugal rotation in a stationary apparatus called a hydrocyclone or putting the oil into a centrifuge, which is the more popular technique. The advantage of using these techniques is the ability to quickly remove water and solid contaminants.

Sorption methods are based on the selective retention of the contaminants using absorbents, including aluminosilicates. Selectively removing polar impurities improves the colour of the oil, the thermo-oxidative stability, and dielectric properties. The methods of sorption also reduce acidity and the content of the resins and asphaltenes. A common sorption method is the percolation method, which involves passing oil through an adsorbent layer usually placed in a column. This method may use both stationary and portable devices. The advantages of sorption methods are the low cost of the purchase and maintenance of the apparatus, and the fact that they do not require high pressures and temperatures. The disadvantage is the problem of the waste management of sorbents.

Electrostatic methods rely on the release of polar impurities (endowed with a partial electrical charge) that are deposited on the respective electrodes constituting the cover of the capacitor. Electrostatic methods allow for the removal of moisture as well as solids from transformer oils, which translates into an improvement in the dielectric parameters and physicochemical.

## 2. Research methodology

As the object of investigation, insulating oil working in a 49-year-old transformer with a power 3.6 MVA was chosen. This oil had not been subjected to physical and chemical analysis for over 10 years, which makes it a suitable subject for study. Special analysis for insulating oils collected from such power transformers were performed, including the following: visual evaluation of the sample oil (clarity, separated water content, the content of foreign bodies), acid number, flash point, and the content of dissolved water. Analysis of the insulating qualities of the oil was also performed: breakdown voltage, resistivity, and dielectric loss factor. The used methods have a technical meaning and allow the correct diagnosis of the technical condition of transformers. Appearance evaluation of the transformer oil is based on visual observation of a sample having a thickness of about 10 cm in transmitted light at ambient temperature. This method allows determining the clarity of oil, the presence of visible contamination, and separated water. Water content determination was performed by coulometric titration using a Metrohm apparatus proposed by Karl Fischer. The acid number was determined by acid-base titration with a glass burette and titrated chemicals. Determination of flash point was performed with a Pensky Martens closed cup semi-automatic apparatus by Herzog. To determine the value of breakdown voltage, automatic apparatus by MEGGER was used. For each sample, 6 determinations were performed and the relative standard deviation was found. Measurements of the resistivity and dielectric loss factor were made using an automatic oil tester by BAUR DTL C. The oil resistivity measurements were performed at a constant voltage at a field strength of 0.25 kV/mm after 60 seconds from the time of application of voltage. The oil tgδ measurement was performed under alternating voltage of 50 Hz frequency and an intensity of the electric field of 1 kV/mm.

To examine the degree of cellulose insulation aging, the measurement of the concentration and changes in the content of furan compounds in particular 2-furfural (2 FAL) was performed. The content of furan derivatives in the oil was determined using the authors' methodology developed under the guidelines of the standard PN-EN 61198:2002. Analyses were performed using a high performance liquid chromatograph Perkin Elmer equipped with a UV-VIS detector for separation using a C18 reverse phase column.

## 3. Test results

An exemplary analysis chromatogram of an insulating oil collected from a 49-year-old transformer with a power of 3.6 MVA is shown in Fig. 1.

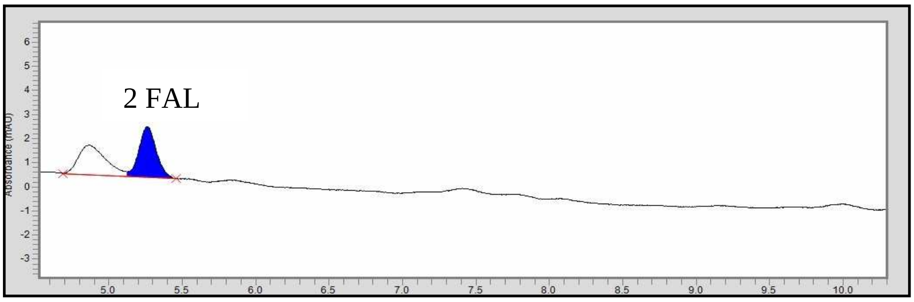

Fig. 1. The chromatogram of the transformer oil

In the chromatogram shown in Fig. 1, the peak of 2-furfural is marked. Based on a calibration curve prepared earlier, the content of 2-furfural in the test oil is 0.09 mg/kg. Such a low content of this compound in the oil provides minimal cellulose insulation aging, which has the non-negative effect on the mechanical strength of the cellulose. [10].

The results of physico-chemical properties of insulating oil are shown in Table 1. The tested oil successfully passed a visual assessment. It was limpid, and there was no separated water content or the presence of particulate matter. Resistivity, the dielectric loss factor, acid number, and flashpoint meet the requirements of the relevant standards. However, it was found that the value of the breakdown voltage is lower than required, which is undoubtedly a result of excessive water content in the oil, which was much higher than the permissible values. As a result, it was found that the test oil does not meet the requirements of the posed insulating oils in transformers group II in terms of breakdown voltage and water content. Allowing such oil to continue to work in the transformer without regeneration is therefore impossible. The oil was regenerated through the filtration under reduced pressure, after its previous heating to a temperature that allows the simultaneous dehydration. This procedure prevents the overheating of the oil during dewatering and its degradation and enables a reduction of the amount of heat energy needed to heat the oil. The properties of the regenerated oil are shown in Table 1.

Table 1. Transformer oil test results

| **Type of the test** | **Unit** | **Assessment criteria** | **The required value** | **The oil sampled from the transformer** | **The oil after regeneration** |
|---|---|---|---|---|---|
| The clarity | – | PN-EN 60296:2012 | Limpid | Limpid | Limpid |
| The separated water content | – | PN-EN 60296:2012 | Does not contain | Does not contain | Does not contain |
| The suspended solids content | – | PN-EN 60296:2012 | Does not contain | Does not contain | Does not contain |
| The breakdown voltage | kV | PN-EN 60156:2008 | ≥ 40 | 28.7*) | 68.8*) |
| The relative standard deviation | % | PN-EN 60156:2008 | ≤ 20 | 19 | 10 |
| The resistivity at 50°C | Ωm | PN-EN 60247:2008 | $\geq 5 \text{ x } 10^9$ | $5.8 \text{ x } 10^{10}$ | $7.4 \times 10^{10}$ |
| The dielectric loss factor Tgδ (50°C) | – | PN-EN 60247:2008 | ≤ 0.07 | 0.003608 | 0.003225 |
| The water content by Karl Fischer method | ppm | PN-EN 60814:2002 | ≤ 25 | 31.1 | 13.1 |
| The acid value [mg KOH/g] | | PN-ISO 6618:2011 | ≤ 0.25 | 0.09 | 0.09 |
| The flash-point | °C | PN-EN-ISO 2719:2007 | ≥ 130 | 154 | 154 |
| 2 FAL content | mg/kg | PN-EN 61198:2002 | - | 0.09 | 0.09 |

*) The arithmetic mean of 6 measurements

As the presented data show in Table 1, after oil filtration under reduced pressure, the water content was reduced by 70%, which resulted in an increase in the value of breakdown voltage to the required level. Other parameters such as resistivity and dielectric loss tgδ were also improved. These data allow concluding that, as a result of insulating oil recovery by filtration under reduced pressure, it is possible to restore the oil properties required for the insulating oils used in transformers Group II.

## Summary

In order to assess the technical condition and suitability for further transformer operation, a series of diagnostic tests were performed. Physical and chemical properties of the dielectric oil were investigated. Visual inspection of the sample, the acid number, water content, breakdown voltage, and dielectric loss factor were determined. Based on the test results, it was found that the tested transformer oil does not meet the requirements for insulating oils in transformers group II in operation. The oil contained too much water and had breakdown voltage below the required limit. The content of furan derivatives indicated a good state of transformer cellulose insulation. Taking into account the results of the analyses, it was decided to regenerate the oil such way that removing the excess water does not degrade the oil. The oil was filtered under reduced pressure. As a result of such a treatment, the water was removed from the oil, which raised value of the breakdown voltage to the required level. An additional benefit resulting from the purification of oil and reduction of its water content is to slow or inhibited degradation of cellulose insulation, which is hydrolytic and quickly occurs in the presence of water. Oil with such properties can be further exploited in a transformer in accordance with its intended purpose and technical parameters. However, due to the age of the transformer (49 years), there must be systematic control of the stat of the transformer oil and its regeneration, when necessary. This will enable the safe and reliable operation well beyond its originally estimated service life.

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## Regeneracja olejów elektroizolacyjnych i jej wpływ na bezpieczeństwo techniczne transformatorów

### Słowa kluczowe

Izolacja papierowo-olejowa, olej elektroizolacyjny, diagnostyka transformatorów, regeneracja olejów.

### Streszczenie

Oleje elektroizolacyjne są czynnikiem chłodzącym uzwojenie transformatora. Podczas pracy urządzenia poddawane są one licznym i różnorodnym wymuszeniom, gromadzą w sobie różnorodne produkty destrukcji elementów konstrukcyjnych transformatora i, w efekcie, zmieniają swoje właściwości. Systematyczne badanie składu i właściwości oleju elektroizolacyjnego dostarcza więc informacji o stanie technicznym całego transformatora. W artykule przedstawiono wyniki badań stanu oleju elektroizolacyjnego w trakcie eksploatacji transformatora oraz zaproponowano działania mające na celu kontrolę stanu izolacji olejowej i wydłużenia czasu jej eksploatacji. Regularne badania pozwalają na regenerację oleju (np. poprzez wirowanie, osuszanie) we właściwym czasie, co w wielu przypadkach eliminuje konieczność kosztownej wymiany oleju. Monitoring właściwości oleju elektroizolacyjnego ma również duży wpływ na bezpieczeństwo techniczne związane z ograniczeniem ryzyka wystąpienia poważnych awarii, takich jak przebicia elektryczne, a nawet wybuch transformatora. Uzyskane rezultaty potwierdzają zasadność procesu regeneracji oleju elektroizolacyjnego jako metody obniżającej koszty eksploatacji, a przy tym efektywnej i przyjaznej środowisku.

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# THE USE OF LOST ENERGY FOR SUPPLYING THE DISPERSED NETWORKS OF SENSORS

**Key words**

Coal mining, energy harvesting, piezoelectric energy harvester, self-powered sensor.

## Abstract

The possible use of self-supplying sensors, which use energy, lost during physical phenomena, for monitoring the selected parameters of mining machines operating in areas threatened by methane and/or coal dust explosion hazard, is presented. Self-supplying sensors are more and more often used in intelligent control systems. They use in their supply systems phenomena such as heat flow, the energy of vibrations, or light. The analysis showed that this technology could be used in automatics and diagnostics systems of mining machines and equipment.

## Introduction

The results of projects associated with development of wireless, self-supplying sensor networks for operation in areas threatened by methane and/or coal dust explosion hazard are given. Analysis of possible sources of energy to be used in building the networks of sensors, as well as the methods for energy conversion and tests on a piezoelectric energy harvester are presented in the article.

The use of the systems for monitoring the operational parameters of the machines in areas threatened by methane and/or coal dust explosion hazard is regulated by the 94/9/EC (ATEX) Directive, which puts limitations on the designer. Directive 94/4/EC (ATEX) is a obligatory legal act for the entire European Union. General requirements concerning the design of electric devices used in areas threatened by explosion hazard are included in the PN EN 60079 0:2009 Standard harmonized with the ATEX Directive. Requirements of the regulations limit the possibilities of the modification of existing control and monitoring systems.

This especially concerns the following cases:

- Extensive technical systems in mine roadways – e.g. belt conveyors of length up to a few kilometres for transportation of run-of-mine;
- Changes in the equipment configuration of the machines and devices in mining areas, resulting from the advance of the mining front;
- The accumulation of heavy machines in a small area and the necessity of removing heat; and,
- The automation of technological processes in mining the minerals to limit the number of people working in threatened areas.

Bearing in mind the needs of the mining market [1, 11], work aiming at the development of wireless networks of self-supplying sensors in the machines operating in areas threatened by methane and/or coal dust explosion hazard was undertaken. There are on the market systems of dispersed pressure sensors, which organize communication with use of wireless networks, supplied from batteries [11], which generates a problem associated with the duration of sensor operation and the frequency of measuring data transfer.

When building the self-organizing network of wireless sensors [4], it is necessary to determine an alternative method to supply its components, based on lost energy during physical phenomena in the surrounding environment, e.g. energy of mechanical vibrations [12, 13, 14], thermal energy [3], energy of rotary movement or energy of electromagnetic radiation [18].

## 1. Methods for conversion of energy

There are the following popular methods for energy conversion, which can be applied undergrounds in mining operations:

**The electromagnetic method**, which uses Faraday’s law saying that electromotive force, is induced in a conductor placed in an alternating magnetic field. The alternating magnetic field is most often generated by moving magnets, and systems of coils play the role of conductor. [9, 17, 18].

**The piezoelectric method** uses the phenomenon consisting in generation of electric charges on the surface of piezoelectric material under mechanical stresses. A piezoelectric component is placed in a device in a way ensuring maximal use of energy of mechanical phenomena, which occur in the device [6, 7, 8, 16, 18].

**The electrostatic method** includes conversion of kinetic energy of vibrations into electric energy with use of variable capacitor, which is polarized by operation of electrets (a dielectric material that has a quasi-permanent electric charge or dipole polarisation). Electret generates an external electric field and is the electrostatic equivalent of a permanent magnet [9, 18].

**The magnetostriction method** is based on the phenomenon of ferromagnetic materials deformations in magnetic fields. The Villari effect is the inverse effect. The change of dimensions under a magnetic field can have a linear or volumetric character [9].

**The thermoelectric method** is based on recuperation of thermal energy [3, 5]. To convert, e.g., thermal energy to electricity, thermogenerators are used. These devices produce electricity as a result of temperature difference and the stream of thermal energy. There are two main types of thermogenerators; those based on the Seebeck effect (Peltier Cells) and those using the phenomenon occurring in Stirling engines. Peltier Cells are based on Seebeck thermoelectric phenomenon (Seebeck effect), which consists in the generation of electromotor force (also called *thermoelectric force*) in a circuit consisting of two different materials, contacts of which have different temperatures [3]. It is the result of the relationship between the contact potential difference between materials and the temperature. Contact potential is generated as a result of diffusion through the contact surface of electrons from one material to another [3, 18].

## 2. Sources of energy available in underground

Considering the specific character of the processes realized in hard coal mines, the sources of energy, which can be used to supply components of self-supplying, wireless network of sensors, were identified. Sources of energy available underground in mining operations are as follows [2, 14]:

**Sources of mechanical energy**:

- The vibrations of machines,
- Rotary movement,
- Braking energy, and,
- Human motion,

**The sources of thermal energy**:

- The heat from machines and equipment (lost energy),
- The heat from the human body, and
- The heat from rock mass.

**The sources of energy coming from electromagnetic radiation**:

- Electric motors, transformers, and
- Power cables.

**The sources of energy coming from the air flow**:

- The flow of air in vetube fans, and
- The flow of air ventilating the mine workings.

## 3. Energy of mechanical vibrations – Piezoelectric Energy Harvester

Machines operating in underground workings generate vibrations from rotating components, toothed gears of electric motors, etc., as a result of mining processes and transportation of run-of-mine.

It is possible to use the energy of vibrations to supply the sensors measuring the following parameters:

- The temperature at any place and the change of sensor's position during the machine exploitation,
- The pressure of medium in a hydraulic system,
- Vibrations (vibrodiagnostics),
- The tension of flight-bar conveyor's chain, and
- The illuminance of mine railways (suspended monorails and floor-mounted railways).

Piezoelectric components (piezoelectric transducers, Piezoelectric Energy Harvester) and electromagnetic generators are most often used components, which convert the energy of mechanical vibrations into electricity. These components have to be tuned to the machine's vibrations, or automatic tuning has to be applied.

Available piezoelectric components most often are adapted to operation within the range 40–250 Hz. The amplitude of vibrations also affects the generated power. After the initial laboratory test [2], the Piezoelectric Energy Harvester MIDE V-21BL-ND (Fig 1) was selected for further tests associated with use of piezoelectric components in the process of supplying the sensors [10].

V21BL-ND transducer has a narrow range of resonance frequency, and it is tuned by adding a weight at its end. Voltage generated by the transducer changes, depending on operational frequency and transducer articulation. The relationship between power and voltage at an operational frequency 40 Hz is presented in Fig. 1. The weights that should be used to load the transducer as well as amplitude of articulation, at which a specified output voltage can be reached, are defined in the catalogue card of the transducer.

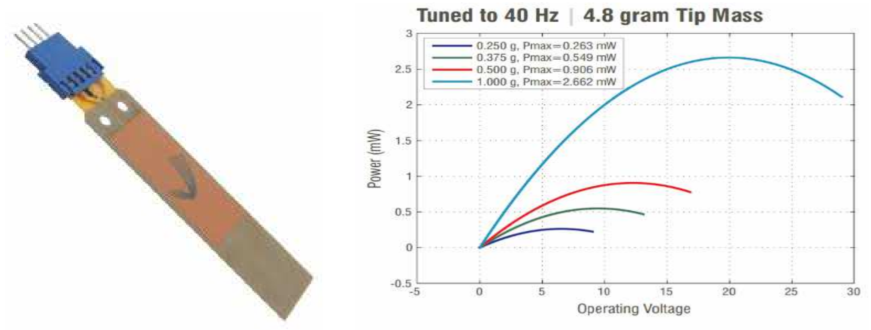

Fig. 1. V21BL-ND piezoelectric transducer and its operational characteristics at 40Hz [10]

Piezoelectric Energy Harvester MIDE V-21BL-ND tests were carried out using a diesel engine (Volvo Penta D5AT, which is the engine used in mining machines). The engine was installed on the test bench in order to set torque. During tests, the voltage generated by the Piezoelectric Energy Harvester MIDE V-21BL-ND, the operating parameters of the inverter (input UIN and output UOUT voltage), and vibration measurements were recorded. Figure 2 shows an electronic system of the test rig. A LTC3588 converter was used as the basic element of the electronic system. The following parameters recorded by the oscilloscope are indicated in the following diagram:

- $U_{IN}$ – input voltage, generated by the Piezoelectric Energy Harvester MIDE V-21BL-ND,
- $U_{OUT}$ – output voltage, to supply the sensor (simulated load),
- $U_{PGOOD}$ – system status, the high value of this parameter indicates that the “unit” (the sensor) is supplied by energy of vibrations. The theoretical considerations assume that, for the proper operation of the sensor, the power-on time must be at least 100 ms, which is the time necessary to take measurement and to send a signal by radio.

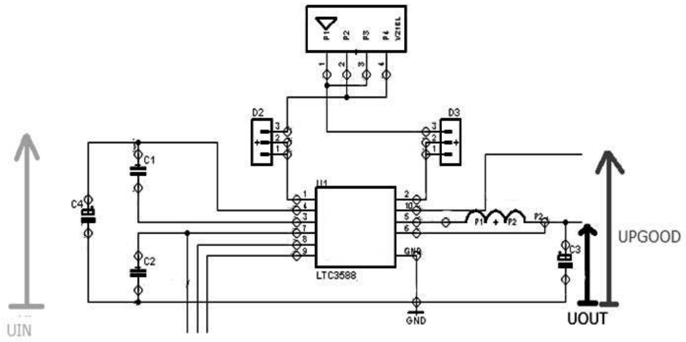

Fig. 2. Diagram of the measurement system [12]

Verification of the results of laboratory tests in real conditions was the work objective. These tests allowed us to determine how the electronic system works under changing operational conditions. It was decided to use the additional mass of the 2 g installed at the end of the Piezoelectric Energy Harvester. According to the data sheet, the oscillation frequency is tuned to 60 Hz. In the study, nine series of measurements were taken at various engine speeds (in the range of 820 to 1796 r.p.m.). In the test, the elements are installed in a horizontal position (Fig. 3) with a magnetic holder.

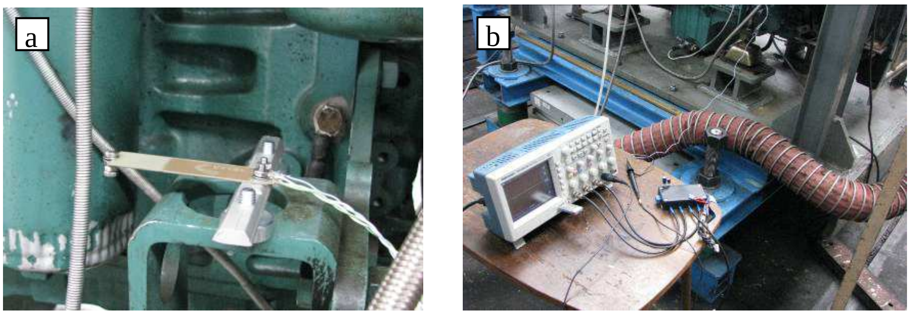

Fig. 3. a) Piezoelectric Energy Harvester MIDE V-21BL-ND installed on Volvo Penta D5AT, b) test rig [12]

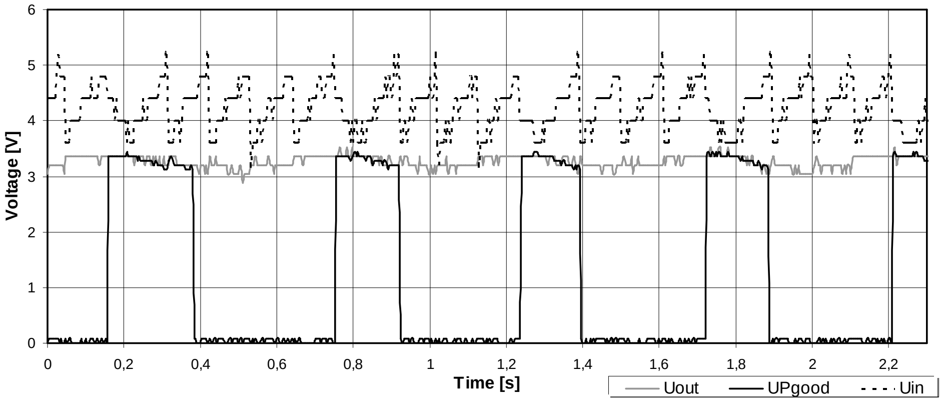

Fig. 4. An example of the time process of voltage signals recorded during the test [12]

Then the analysis of signals recorded during tests was made to verify how the electronic system responsible for the management of generated energy works under the simulated load (Fig. 2).

The demand for energy of the temperature sensor was calculated. It was found that the sensor has to operate minimum for 100 ms (UPGOOD signal) to take the correct measurement and to send the information by radio signals. The sensor was simulated by adding the load resistance R = 10 kΩ to the electronic system. The voltage of simulated receiver is equal to 3.3 V and the current is 0.33 mA.

The sample time process of the signals recorded during the measurements are given in Fig. 4. The UPGOOD signal was at high level for 152 ms in intervals of about 320 ms.

## Summary

More and more solutions appear on the "energy harvesting" devices market, which is a sign that this relatively new branch is under development. This is possible mainly due to the commercialization of low-energy electronic systems. In the case of underground mining in the areas threatened by methane and/or coal dust explosion hazard, it is impossible to use common solutions.

The possibility of using the energy lost in physical phenomena to supply the components of network self-supplying sensors is presented. It was proven that the utilization of the energy of mechanical vibrations and energy of rotary movement is possible.

The laboratory tests of the piezoelectric energy harvester were made with a diesel engine used to drive mining machinery. The results of the study allowed selecting the Piezoelectric Energy Harvester MIDE V-21BL-ND to conduct further research work on self-powered sensor networks. The results showed that it is possible to supply the electronic system with a microcontroller and a radio system by the piezoelectric energy harvester.

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## Wykorzystanie energii odpadowej do zasilania rozproszonych sieci czujników

### Słowa kluczowe

Górnictwo, energy harvesting, przetwornik piezoelektryczny, czujniki samozasilające.

### Streszczenie

W artykule zaprezentowano możliwości wykorzystania czujników samozasilających, które wykorzystują energię traconą w trakcie zjawisk fizycznych, do monitorowania wybranych parametrów maszyn górniczych działających w obszarach zagrożonych wybuchem metanu i/lub pyłu węglowego. Czujniki samozasilające są coraz częściej stosowane w inteligentnych systemach sterowania, wykorzystują do zasilania takie zjawiska jak przepływ ciepła, energię drgań lub światło. Przeprowadzona analiza wykazała, że taka technologia może być stosowana w układach automatyki i diagnostyki maszyn i urządzeń górniczych.

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# A DEVICE AND A METHOD FOR RECYCLING EMULSION CUTTING FLUIDS

**Key words**

Waste cutting fluids, recycling, coagulation, post-emulsion water.

## Abstract

Environmental requirements, increasing costs, and water usage are generating the need for closed water cycles in the production processes and for reclaiming water from sewage. Activities in this regard also include the emulsion fluids used in subtractive machining processes used as mixtures with 90–98 percent water. This article presents a method for recycling waste cutting fluids consisting in separating of the oil/water emulsion and treating the water to the level that will allow its reusing for technical purposes. The waste emulsion fluids that had been used in subtractive steel machining were subjected to testing after coagulation, barrier filtration, adsorption, and aeration. The subsequent processes were carried out using the developed device. The changes between the physicochemical properties of the cutting fluid and the reclaimed water phase were determined to reflect the effectiveness of the processes. The reclaimed water was subjected to a detailed analysis of its physicochemical properties, which would consequently determine its suitability for reuse for the manufacturing of cutting fluid. It was found that, as a result of destabilization processes and wastewater treatment, the reclaimed water properties that allow its reuse for technological purposes were restored. The method and the device can be used in the metal industry.

## Introduction

In Poland, the annual consumption of the concentrates for metal machining is at about 8.7 thousand tonnes. These are concentrates, intended to be used as 2–10% emulsions or water solutions [1, 2]. Therefore, the amount of generated waste fluids can reach as much as 87–435 thousand tonnes. In view of the complex chemical composition and the presence of ecologically harmful components, the European Commission Decision 2000/532/EC of May 3, 2000, and in the Waste Act from April 27, 2001, deemed waste cutting fluids hazardous waste [3, 4]. In contrast to other wastes, they must be treated separately in regards to the disposal and they must be rendered harmless [5, 6]. The most effective technique for the disposal of waste cutting fluids is the separation of oil/water emulsions and the maximum recovery of the resultant ingredients. Due to more than 90% water content, an important step in the recycling of cutting fluid is the separation of emulsion into a water phase and an oil phase. Subsequently, the treatment of the obtained water phase must be rendered to a state allowing its reuse for technical purposes or safe introduction into the wastewater system, and the maximum density of separated sludge must be reached. As a result, this leads to minimizing the amount of produced sewage of hazardous waste and protecting water resources [7–9].

For separating waste water-oil emulsion, chemical, physicochemical, electrochemical, and physical methods are used. Chemical methods are based on the destabilisation effects of selected chemical compounds on the Stern ion layer surrounding individual droplets of oil, then their coalescing and the production of emulsion. Physicochemical methods include the small droplet process of aeration, the evaporation of the water phase, flocculation, and the destruction of the oil phase by special strains of bacteria. Electrochemical methods are based on a process of the destabilization of emulsions in an electrostatic field and electrocoagulation. Modern physical methods include filtration, using membranes working in the micro- and ultrafiltration. Especially effective is the de-emulsifying method using specially introduced components. They are inorganic salts of metals and inorganic acids or polymeric organic compounds. In addition, carbon dioxide and hydrogen peroxide can be used. [10–14].

The article presents a method and a device for destabilising waste cutting fluids by chemical methods and a multi-step wastewater treatment of the water phase.

## 1. Characteristics of the method and the device for recycling of waste cutting fluids

Waste cutting fluid recycling occurs in two basic stages – destabilisation of the fluid and the treatment of the separated water phase. The diagram for this method is presented in Fig. 1.

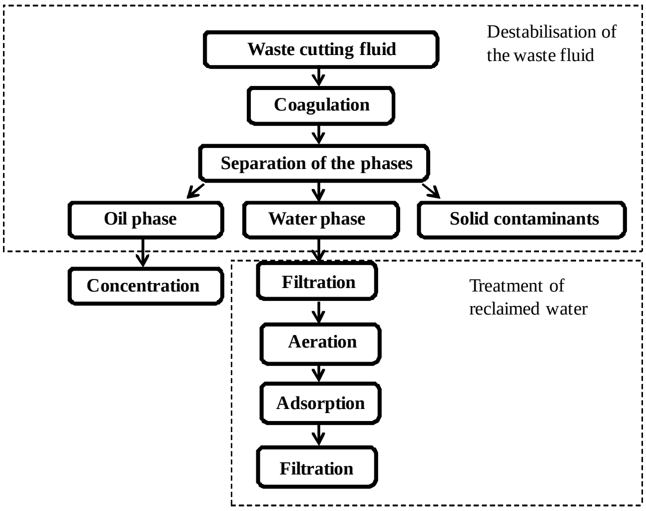

Fig. 1. Diagram of the recycling method for cutting fluid

The destabilisation of the fluid is achieved by the process of coagulation. Prior to the process, the Chemical Oxygen Demand is evaluated. The COD assessment allows a preliminary estimation of the concentration of coagulant required to effectively destabilize the fluid. Since waste cutting fluids are characterized by very diverse chemical composition, a suitable type of coagulant is selected at this stage. The process utilises organic polymer coagulants and sulphates of aluminium and iron. The coagulation process runs in the processing Tank I, at room temperature. In order to carry out destabilizing of the fluid, small portions of the coagulant are introduced during mixing. Contact of components is maintained for 30 min during continuous stirring. This is followed by a process of settling and sedimentation. After a clear separation of the water and oil phase (20–24 h), the oil phase is drained from the tank. It is transferred to the filtration press, where it is subjected to a process of filtration and concentration. Meanwhile, the water phase is subjected to a process of treatment by the barrier filtration method. The process lasts for 30 minutes, and after this time, the water is pumped to processing Tank II, where the water is subjected to adsorption and aeration or just aeration. The quantity of the adsorbent necessary to carry out the process depends on the rate of the COD indicator of the reclaimed water phase. In order to carry out the process of adsorption during mixing, the absorbent is introduced into the water. The mixing lasts 30 minutes. After this time, the water is subjected to a filtration process, while aeration may be conducted before or after the adsorption process. Optionally, instead of aeration, a deep oxidation reaction can be applied. The treatment is carried out until the required parameters are obtained (Tab. 1). The quality of the water described by the parameters is sufficient for reusing it in the manufacturing of cutting fluid [15].

Table 1. Criterial values of recycled post-emulsion water

| Parameter | Criterial value | Research method |
|---|---|---|
| COD, $O_2$ mg/dm$^3$ | < 1000 | PN ISO 6060: 2006 |
| Total organic carbon, mg/dm$^3$ | < 200 | PN-EN 1484:1999 |
| pH | 6.5–9.0 | PN–EN ISO 0523:2012 |
| Dissolved substances content, mg/dm$^3$ | < 500 | PN-C-04541:1978 |
| Organic compounds content, ppm | < 10 | Infra-Cal analyser |

The processes of the destabilization of waste cutting fluids and the treatment of the separated water phase are carried out using the developed and manufactured device shown in Fig. 2.

Fig. 2. A device for the recycling of waste cutting fluid

Technical specifications of the device are as follows:

- Destabilizing output – 200 dm$^3$/24h
- Filtration output – 100 dm$^3$/h
- Aeration output – 120–150 dm$^3$/min,
- Oil fraction separation output – 30 dm$^3$/10 min
- Filtration size – 5–15 µm
- Processing tank volume – 200 dm$^3$
- Electrical supply – 380 V, 50 Hz
- Semi-automatic control.

The basic technological modules are the following:

- The destabilisation module for waste cutting fluid, which is used to separate oil and water phase in the fluid;
- A module for sludge separation and thickening, which aims to isolate the separated oil phase and to concentrate it by separating out the remaining water;
- The barrier filtration module, which is used to remove solid pollutants from the separated water phase; and,
- The post-emulsion water treatment module, which is designed to remove dissolved organic and inorganic components from the water.

The modular construction of the device allows any configuration according to the technological needs.

## 2. An example of the recycling process of waste cutting fluids

Using the constructed device, the recycling of used cutting fluids was performed. There were two types of emulsion fluids. In the first stage, the type and amount of coagulant was selected, which is required to carry out the process of the destabilisation of the fluid. In both cases, it was the hydrated aluminium sulphate. The coagulant concentration was 0.25% for Fluid I, and 0.28% for Fluid II. The water separated after the destabilisation both for Fluid I and II was subjected to barrier filtration by a set of three filters with a filtering size of 5 µm. Next, the purified water from Fluid I was aerated and subjected to adsorption using solid adsorbents. The adsorbent was bleaching earth with a maximum grit size 0.2 mm and specific surface area of 75 m3/g. The aeration supported intensive growth of bacteria and biological treatment of water. The aeration process lasted 10 days at room temperature. Adsorption was performed at 5% concentration of bleaching earth, also at room temperature. Tab. 2 shows the change of physicochemical properties of waste cutting Fluid I subjected to the process of coagulation and of the separated water after aeration process and adsorption.

Table 2. Changes of physicochemical and microbiological properties of waste emulsion cutting Fluid I after subsequent treatment processes

| | Research method | Waste Fluid I | Reclaimed water phase | Water after aeration | Water after adsorption |
|---|---|---|---|---|---|
| COD, $O_2$ mg/dm$^3$ | PN ISO 6060: 2006 | 45 000 | 5 100 | 2 300 | 800 |
| Oil content, ppm | Infra-Cal analyser | 29 000 | 70 | 50 | 15 |
| pH | PN –EN ISO 10523:2012 | 6.8 | 6.6 | 6.3 | 6.0 |
| Bacterial content | dip slide | $10^7$ | $10^7$ | $10^7$ | $10^7$ |
| Fungus content | dip slide | medium | medium | medium | medium |
| Conductivity mS/cm | PN-EN 27888:1999 | – | – | 1.06 | 1.10 |
| The content of dissolved substances, g/l | PN-C-04541:1978 | – | – | 0.5 | 0.4 |
| Total organic carbon, mg/dm$^3$ | PN-EN 1484:1999 | – | – | 650 | 120 |

Waste cutting Fluid I was characterised by a high content of oxidating organic and some inorganic biodegradable components, which is indicated by the high value of the COD. It contained many oil components and was contaminated with bacteria at a high level and with fungus at a medium level. After destabilising, the separated water phase had a 9-fold lower value of COD and 400-fold less oil content. Microbiological contamination did not change, but there was a slight change in pH towards an increase in acidity. After the subsequent processes of aeration and adsorption, a further reduction in the content of organics and oils occurred in the fluid and a slight increase in acidity. After the adsorption, the fluid conductivity, which reflects the presence of ions (cations and anions), increased slightly, which could be a result the introduction of ions from the bleaching earth in the acid used as an activator. The value of total organic carbon decreased more than 5-fold. The microbiological contamination of the fluid remained unchanged. It was necessary to disinfect the water phase with UV radiation, which reduced contamination of bacteria to a level of 103. The fungi content was not found. As a result, the treated water, separated from the waste cutting liquid reached the level of properties that allowed its re-use as a thinner for cutting fluid concentrates.

Because waste cutting Fluid II did not contain bacteria or fungi, in the process of treatment of the separated water phase, aeration was replaced by deep oxidation. The basic reaction reagents were hydrogen peroxide and ferrous sulphate. The process was carried out at a temperature of about 70°C, in the presence of a catalyst. After oxidation, the water was subjected to the adsorption process using bleaching earth at 3%. Tab. 3 shows the changes in the physicochemical and microbiological properties of waste cutting Fluid II subjected to the process of coagulation and treatment of the separated water phase.

Table 3. Changes of physicochemical and microbiological properties of waste emulsion cutting Fluid II after subsequent treatment processes

|  | Research method | Waste Fluid II | Reclaimed water phase | Water after oxidation | Water after adsorption |
|---|---|---|---|---|---|
| COD, $O_2$ mg /dm$^3$ | PN ISO 6060: 2006 | 66 000 | 8 100 | 2 900 | 750 |
| Oil content, ppm | Infra-Cal analyser | 37 000 | 90 | 60 | 8 |
| pH | PN –EN ISO 10523:2012 | 7.3 | 7.0 | 6.9 | 6.6 |
| Bacterial content | dip slide | none | none | none | none |
| Fungus content | dip slide | none | none | none | none |
| Conductivity mS/cm | PN-EN 27888:1999 | - | - | 1.11 | 1.11 |
| The content of dissolved substances, g/l | PN-C-04541:1978 | - | - | 0.8 | 0.8 |
| Total organic carbon, mg/dm$^3$ | PN-EN 1484:1999 | - | - | 700 | 100 |

Compared to Fluid I, waste cutting Fluid II contained a larger amount of organic and inorganic pollutants, susceptible to the action of oxygen (higher COD) and oil ingredients. However, they did not contain bacteria or fungi. After the coagulation, the separated water phase was characterised by the COD value that was 8-fold lower than the fluids and oil content of 400-fold lower. Subjecting the water to subsequent treatment processes resulted in further improving its quality. As a result, the process of adsorption and deep oxidation applied in the separated water phase resulted in obtaining high-quality water. The treated water had a low COD value, practically contained no oil, was not contaminated with bacteria or fungi, and the contents of the soluble substances and substances present in organic compounds was low. The high level of assessed properties allowed its re-use in technology.

## Conclusions

The results of research showed that the described method for recycling waste emulsion cutting fluids, implemented using the constructed device, provides the means to reclaim the water used for the preparation of these fluids and to give it a quality suitable for its reuse in technological processes. The treated water was characterised by low values of indicators reflecting the presence of compounds dissolved and suspended in water, organic and inorganic, oil ingredients, and cations and anions. This indicated an effective destabilisation of waste fluids, a separation of the water phase, and the removal of the remains of the cutting fluid and coagulant components. Using the developed methods and the designed device provides the means to use it on-site of the waste cutting fluid.

Taking into consideration the amount of cutting fluid used quid per year (over 400 thousand tonnes), containing more than 90% water, even a one-time reclamation treatment and returning part of it to service brings a quantifiable economic effect and an incalculable but a very important ecological effect embracing the global trends in the protection of water resources.

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## Metoda i urządzenie do utylizacji emulsyjnych cieczy obróbkowych

### Słowa kluczowe

Zużyte ciecze obróbkowe, utylizacja, koagulacja, wody poemulsyjne.

### Streszczenie

Wymagania środowiskowe oraz rosnące koszty i zużycie wody generują potrzebę zamykania obiegów wodnych w procesach produkcyjnych oraz odzysku wody ze ścieków. Działania w tym zakresie obejmują także emulsyjne ciecze obróbkowe stosowane w procesach ubytkowej obróbki metali jako 90–98-procentowe mieszaniny z wodą. W artykule przedstawiono metodę zagospodarowania zużytych cieczy obróbkowych polegającą na rozdzieleniu emulsji olej/woda oraz uzdatnieniu wydzielonej fazy wodnej do postaci umożliwiającej ponowne wykorzystanie jej w celach technicznych. Badano zużyte ciecze emulsyjne stosowane podczas ubytkowej obróbki elementów stalowych poddane procesom: koagulacji, filtracji przegrodowej, adsorpcji i napowietrzaniu. Kolejne procesy realizowano za pomocą opracowanego urządzenia. Wyznaczono zmianę fizykochemicznych właściwości cieczy obróbkowych oraz odzyskanej fazy wodnej odzwierciedlające skuteczność stosowanych procesów. Odzyskane wody poddano szczegółowym badaniom fizykochemicznym decydującym o możliwości ich ponownego wykorzystania do wytwarzania cieczy obróbkowych. Stwierdzono, że w wyniku zastosowanych procesów destabilizacji i uzdatniania ze zużytych cieczy obróbkowych odzyskuje się wody o właściwościach pozwalających na ponowne ich wykorzystanie w celach technologicznych. Metoda i urządzenie mogą znaleźć zastosowanie w przedsiębiorstwach przemysłu metalowego.

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# A DEVICE AND METHOD FOR THE EVALUATION OF HYDRAULIC OILS PERFORMANCE USING IMPEDANCE PARAMETERS MEASUREMENT

**Key word**

Hydraulic oils, dielectric parameters, oil quality.

## Abstract

The global trend to reduce operating costs of machinery and equipment, while improving their reliability without harming the environment, makes it necessary to monitor the quality potential of industrial oils. This generates the need for inexpensive and fast methods for oil testing in working conditions that would greatly limit or replace the current labour-intensive and time-consuming laboratory assessment. This article presents a method and a device for diagnostic assessment of the performance of industrial oils by measuring the impedance parameters of a serial replacement system or a parallel inductive measuring capacitor with oil as its dielectric. The object of this study was used hydraulic oil subjected to the process of monitoring. The physicochemical properties were studied that reflect the ageing of the oil and its electrical properties. The correlations between the impedance parameters of inductive measuring capacitor and selected parameters describing the physical and chemical characteristics of oils are presented. The study confirmed the usefulness of the method and the diagnostic device for monitoring changes in hydraulic oils during their service lives.

## Introduction

The fundamental direction of a pro-ecological economy is minimizing the amount of produced waste [1–3]. This also applies to industrial oils and lubricants. In respect to such products, this means, e.g. the maximum use of performance potential and lengthening service life [4, 5]. The quality status of oil determines the proper functioning of the machinery and equipment. It reflects not only the level of performance properties of the oil, but also the degree of the wear of machinery and equipment, in which it functions. Continuous and strictly specified in time and scope, control of the properties makes it possible to monitor the predefined oil performance in lubrication systems. It makes it possible to apply appropriate treatment to re-create the qualitative potential of the oil or to replace it at the most optimal moment. It also makes it possible to diagnose the condition of machinery [6–8].

Monitoring the quality of the oils includes a number of individual indicators, usually measured in laboratory conditions [6, 7] and often by time-consuming, expensive methods, requiring a considerable amount of research samples and specialised equipment. Such a situation is not conducive to frequent oil testing. Thus, solutions are sought to find a means for fast, inexpensive, and comprehensive assessment of oil quality, preferably at the place of operation. The indicators of oil quality that can be measured in all conditions are dielectric parameters [9, 10]. This article presents a method and a diagnostic device for the assessment of the performance of industrial oils by measuring the impedance parameters of an inductive measuring capacitor with oil as its dielectric.

## 1. Diagnostic device for the evaluation of working oils

The device is used for the examination of the changes in the quality of industrial oils in service. The measured impedance parameters reflect the content of polar components, which are diagnostic for chemical aging, among others, for chemical ageing products, water, and metallic wear products from friction elements. The device is shown in Fig. 1.

The set consists of a volume measuring microprocessor and a measuring capacitor (volume sensor) submerged in the sample oil, combined with a measurement using a specialized measuring cable (Fig. 1). The meter measures the impedance parameters of the measuring capacitor with the tested oil as is its dielectric. The parameters are the following: capacity, loss of resistance, and loss coefficient D, or a goodness coefficient (Q) for both parallel and serial equivalent circuit capacitor. The assessment of the degree in the performance change of the oil is made by comparing the results of the measurements of impedance parameters for used oil and fresh oil. The meter can be used with a computer and with the dedicated software, and the measurements can be recorded in the text files.

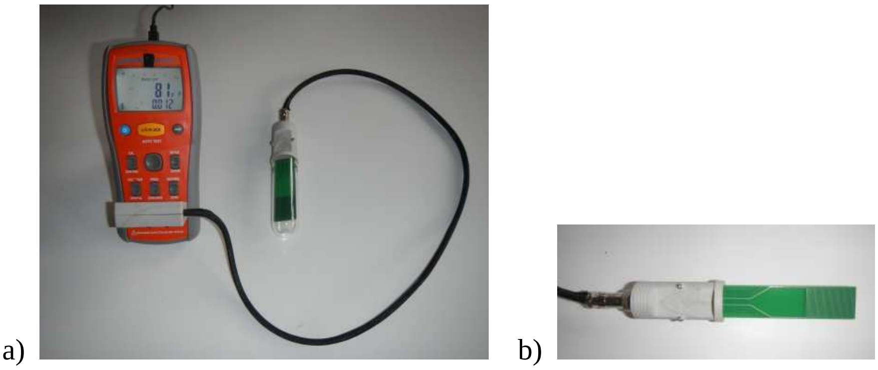
a) b)

Fig. 1. The evaluation device for changes in industrial oils (a), and measuring capacitor (b)

Technical specifications of the device:

*Measuring capacitor*:

- A double-sided printed circuit board with the electrodes in ridge arrangement are in the casing with a socket for plugging it to the volume sensor. The dimensions of the active part of the sensor are 25 × 30 × 1.6 mm.
- Impedance parameters of the capacitor in the air are set for a frequency of fp = 10 kHz.
- For serial the equivalent capacitor system, the specifications are as follows: serial capacity Cs = 100.70 pF, serial resistance Rs = 2.27 kΩ, and goodness coefficient Qs = 70.
- For the parallel equivalent capacitor system the specifications are as follows: parallel capacity Cs = 100.6 pF, parallel resistance Rr = 11 MΩ, and goodness coefficient Qs = 70.

*Volume meter*: Type APPA 703 – technical specifications as per instruction manual of the meter.

## 2. Method of the evaluation of the quality of hydraulic oil using a diagnostic device

The method of quality evaluation of hydraulic oils uses the measurement of the dielectric properties of the oils, which are the following: leakage conductance q, and resistance r in parallel, and serial measuring system. Because the dielectric properties of themselves are not included in the requirements of the norms for hydraulic oils, and they are a reflection of the presence of polar particles in oil (mostly the thermo-oxidising ageing products, water, and functional additives), their changes have been correlated with the changes in the normative parameters, showing the relationship of such products as acid number and water content. According to the guidelines of the manufacturers and companies involved in the oil economy, the value criterion of the acid number change in oil during operation is 20–30%, and the maximum water content can reach the level of 0.2% [2, 7, 11].

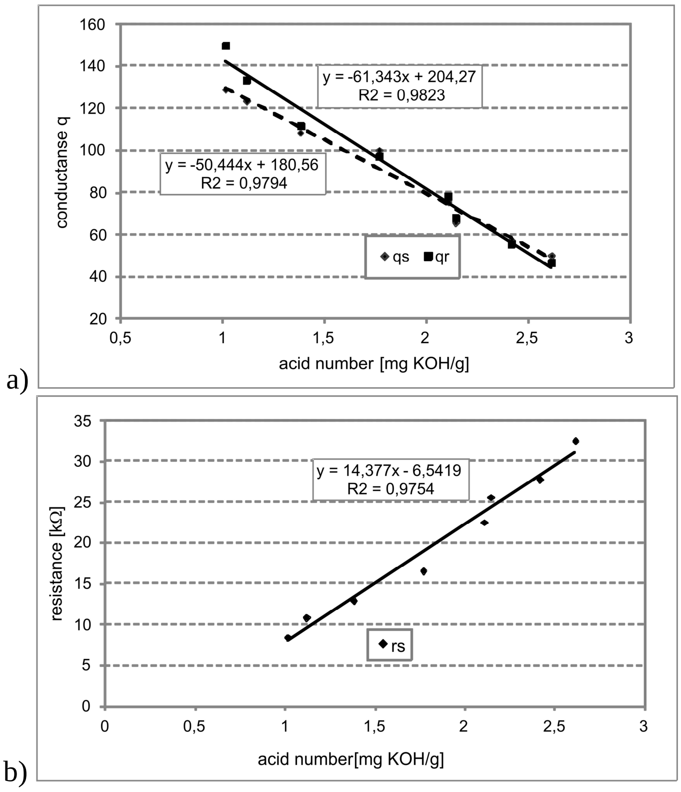

Fig. 2. The correlation of the leakage conductance (a), resistance, (b) and the acid number in aged hydraulic oil LHL 46

Figure 2 presents the relationship between selected dielectric parameters on the selected acid number of the LHL hydraulic oil aged under laboratory conditions, while Figure 3 presents the relationship between the same parameters and water content in hydraulic oil. The acid number was determined according to the PN-ISO No.6618: 2011, while the water content was determined according to PN ISO 3733:2008, and dielectric parameter values were obtained through the diagnostic device.

Changes in the value of leakage conductance determined for parallel (qr) and serial (qs) equivalent system showed a directly proportional dependence, while in the resistance is measured in the rs serial system, and the changes had an inversely proportional dependence in relation to the acid number of the oil (Fig. 2). The correlation between the changes in the dielectric parameters and the acid number was high. The $R^2$ coefficient of the determination of the obtained lines was very high (greater than 0.9). Therefore, the measurement of dielectric properties can indicate chemical ageing of hydraulic oils.

The designated trend lines between the leakage conductance, the resistance, and the water content in hydraulic oil LHL 46 showed the parameters to be highly correlated (Fig. 3).

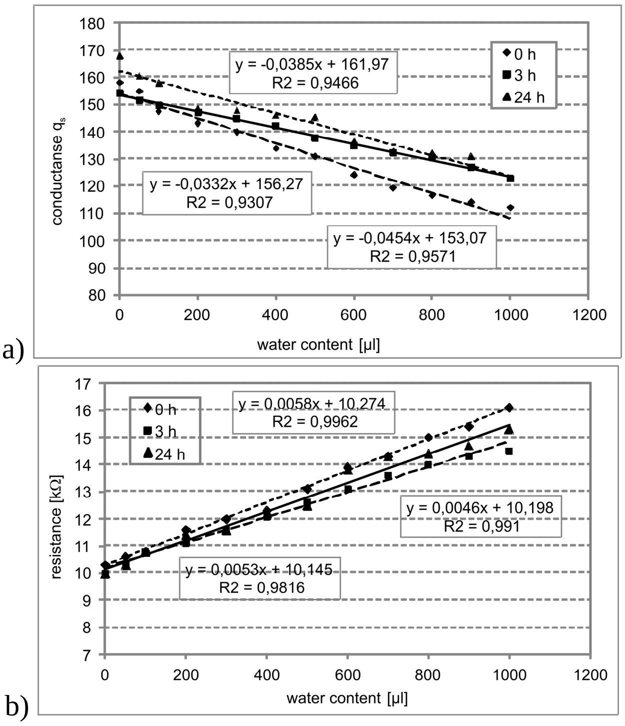

Fig. 3. The relationship between leakage conductance (a), resistance (b), and the water content in hydraulic oil LHL 46

Because water suspended in oil has a tendency to sink, testing for leakage conductance and resistance in water-contaminated oil were carried out at intervals of 3 h and 24 h. For each series of tests, resulting curves were linear in shape. The coefficient of determination was within the 0.93–0.99 range, which indicated a high correlation between variables. With the increase in water content, the value of leakage conductance decreased and oil resistance values increased.

The determined correlations between the selected dielectric parameters and the acid number or water content in hydraulic oils have a linear form, and the values of the coefficients of determination were very high. It was found that the dielectric properties can be an indicator of chemical changes and water content changes occurring in oil. A survey of many different oils differing in their viscosity class, and in varying degrees of chemical ageing and water content, has enabled the determination of the criterial change values in the selected dielectric parameters exceeding the limit of acid number and water content (Tab. 1) [12]. They are key indicators of the test methods of the state of functioning using the described diagnostic device.

Table 1. Boundary values of changes in the dielectric parameters of oils for which the acid number increased by 20%, and the water content exceeded the value of 0.2% (measured at the frequency of 1 kHz)

| | Leakage conductance $q_s$ | Leakage conductance $q_r$ | Resistance $r_s$ |
|---|---|---|---|
| Acid number | | | |
| Boundary value of changes | 7.5 | 6.5 | 1.0 |
| Water content | | | |
| Boundary value of changes | 6.0 | 5.5 | 1.0 |

Figure 4 is a diagram illustrating the method for the evaluation of the fitness for use of hydraulic oils using the diagnostic equipment.

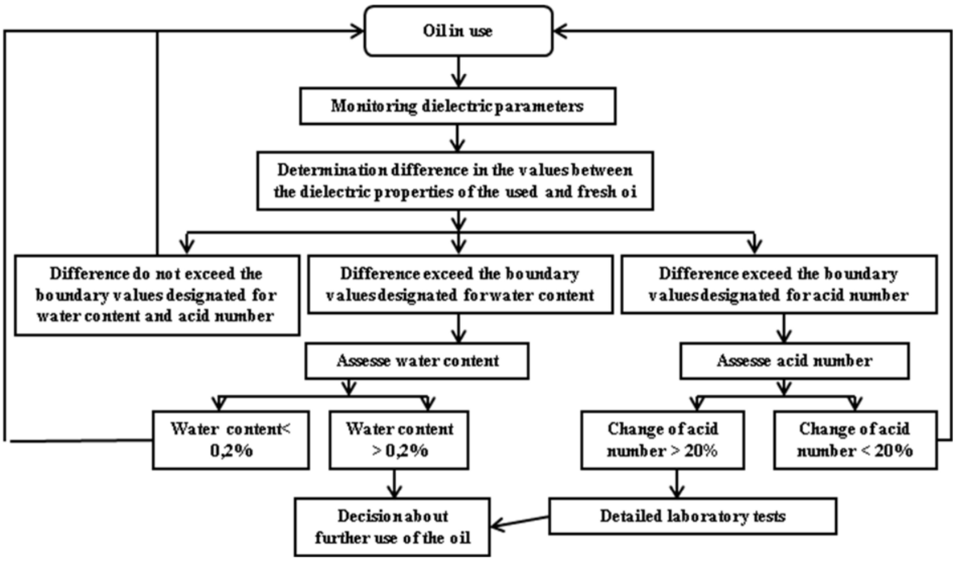

Fig. 4. A diagram of the method for assessing the fitness for use of hydraulic oils using diagnostic device

The method involves monitoring the following changes in the dielectric properties of oil: leakage conductance in serial and parallel systems and circuit resistance in a serial system. The measurements are carried out at an electrical frequency of 1 kHz, at the same temperature for fresh oil and used oil. The measured differences in the values between the properties of the used and fresh oil determine further steps in regards to the used oil. When one of the boundary values designated for water content or the acid number is exceeded, the value of these parameters is assessed. If the water content is less than 0.2% and an increase in the number of acid number is less than 20%, the monitoring of the dielectric properties of oil is continued. However, if the water content or the increase in the acid number exceeds the boundary values, the oil is subjected to detailed laboratory tests. Depending on the values of the evaluated parameters, a decision is made concerning further use of the oil.

## 3. An example of a practical application of the method

A study was conducted on dielectric and physicochemical properties (correlated with the indicator) of the hydraulic oil used in various pieces of equipment in the same enterprise. The time of active operation was different for in different pieces of equipment. Direct values of the parameters were measured and the differences in reference to fresh oil were calculated. Table 2 presents the results.

Table 2. Dielectric and physicochemical properties of the tested hydraulic oils

| | Fresh oil | Oil 1 | Oil 2 | Oil 3 | Oil 4 | Oil 5 |
|---|---|---|---|---|---|---|
| qs | 78.60 | 73.50 | 71.10 | 71.10 | 69.80 | 69.50 |
| Change qs | – | 4.90 | 7.50 | 7.50 | 8.80 | 9.10 |
| qr | 77.60 | 73.30 | 70.30 | 70.6 | 71.10 | 70.30 |
| Change qr | – | 4.30 | 7.30 | 7.00 | 6.50 | 7.30 |
| rs [kΩ] | 23.60 | 24.10 | 24.80 | 24.7 | 24.70 | 24.90 |
| Change rs [kΩ] | – | 0.50 | 1.20 | 1.10 | 1.10 | 1.30 |
| Acid number [mg KOH/g] | 0.46 | 0.55 | 0.86 | 0.88 | 0.90 | 0.94 |
| Acid number change [%] | – | 19.60 | 86.90 | 91.30 | 95.60 | 104.30 |
| Water content [%] | 0.003 | 0.007 | 0.011 | 0.009 | 0.009 | 0.009 |

The water content in the tested oils did not exceed the limit value of 0.2%; however, oils 2–5 were characterised by an acid number of more than 20% in relation to the fresh oil. Moreover, the values of the selected dielectric parameters were greater than the criterial values. For Oil 1, the dielectric properties did not exceed these values.

## Summary

The products of chemical ageing and water content that have a very negative impact on the functional properties of hydraulic oil have a polar character. Having a dipole moment of these particles makes it possible to determine their concentration by examining the dielectric properties. This study has shown a highly linear correlation of the measured dielectric properties with the acid number, indicating the degree of chemical ageing of oils and the water content. The high indicator of determination among the obtained results indicates the possibility to test the status of oil in use by evaluating the dielectric properties using the diagnostic device. The method described is intended for hydraulic oils; however, it may also be used to assess the quality of any other type of industrial oils. However, due to the different performance requirements and very different chemical composition, it is required that separate criterial values are set for the changes in the dielectric properties of these oils.

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## Zestaw i metoda do oceny stanu eksploatacyjnego olejów hydraulicznych z wykorzystaniem pomiarów parametrów impedancyjnych

### Słowa kluczowe

Oleje hydrauliczne, parametry dielektryczne, jakość olejów.

### Streszczenie

Ogólnoświatowa tendencja do ograniczania kosztów eksploatacji maszyn i urządzeń, przy jednoczesnej poprawie ich niezawodności oraz bez szkody dla środowiska naturalnego, stwarza konieczność monitorowania potencjału jakościowego olejów przemysłowych. Generuje to potrzebę stosowania tanich i szybkich metod badania olejów możliwych do stosowania w warunkach eksploatacji, które znacznie ograniczają lub zastępują stosowaną obecnie praco- i czasochłonną ocenę laboratoryjną. W artykule przedstawiono metodę oraz urządzenie diagnostyczne do oceny stanu eksploatacyjnego olejów przemysłowych poprzez pomiar parametrów impedancyjnych zastępczego układu szeregowego lub równoległego kondensatora pomiarowego, którego dielektrykiem jest olej. Przedmiotem badań były oleje hydrauliczne pochodzące z eksploatacji poddane procesowi monitorowania. Badano właściwości fizykochemiczne odzwierciedlające stopień chemicznego zestarzenia olejów oraz właściwości elektryczne. Przedstawiono korelację parametrów impedancyjnych kondensatora pomiarowego ze zmianami wybranych parametrów opisujących właściwości fizykochemiczne olejów. Stwierdzono przydatność zastosowanej metody i urządzenia do diagnostyki zmian stanu olejów hydraulicznych w trakcie ich eksploatacji.

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# A MANUFACTURING METHOD FOR ORGANIC LUBRICANTS FROM REFINING BY-PRODUCTS OF VEGETABLE OIL

## Key words

Lubricant, refining of oils, refinement by-products, vegetable oils, tribo-active substances.

## Abstract

The requirement for the use of "environmentally safe" lubricants in many areas of technology makes it necessary to search for new raw materials for their manufacture, and its potential source may be the by-products obtained during the refining of natural oils. The article describes a methodology for the isolation of tribo-active substances from refinement by-products of rapeseed oil, which resulted in producing ecologically safe additives. The lubricating compositions obtained in this process were then tested in regards to their physicochemical and lubricant properties. The results obtained have shown that they have a higher effectiveness of anti-wear properties and more advantageous rheological properties in comparison with commercial oils recommended to be used in conditions of moderate loads and node friction velocity. A high degree of the biodegradability of lubricant allows its application in settings where there is a risk of direct contact with natural environment.

## Introduction

Lubricating products based on petroleum raw materials have a number of beneficial properties related to their purpose; however, they simultaneously constitute a very high ecological risk, due to their low biodegradability. Biodegradability is defined as the ability of the particles to decompose as a result of the complex interactions of living organisms and their enzymes [1–5]. These processes lead to the transformation of organic compounds into low molecular non-organic forms, such as water or carbon dioxide.

The basic ingredients of the lubricants are lubricant base oils (70–99%), which largely determines the ecological character of the lubricant and additives. The most common additives include oxidation inhibitors, detergents and dispersants, corrosion and rust inhibitors, thickeners, and additives to improve the lubricating properties of the oil (anti-wear, anti-friction, extreme pressure, friction modifiers). Some of them – particularly lubricating additives – contain sulphur, chlorine, phosphorus, and heavy metals in its molecules, which are all elements harmful to human health. Most of them exhibit low biodegradability, which is equivalent to their concentration in the natural environment [3, 6, 7].

A main alternative to the mineral base oils, which are not able not meet the ecological requirement (biodegradability 10–40%), are vegetable oils and a few synthetic oils (ester, polyalkylene, poly-$\alpha$-olefines) [8–11]. Often, however, their desirable characteristics are negated by their toxic, non-biodegradable lubricating additives. Therefore, the content of these additives in lubricants should be minimised or replaced by a new generation of non-toxic, biodegradable, and ashless additives. These types of additives are required to improve the basic properties of base oil without increasing the emission of pollutants into the environment. The compounds that meet these criteria contain, in their composition, active functional groups, for example, ester, hydroxyl, and carboxyl. Often these are esters of higher carboxylic acids, aliphatic alcohols, or hydroxy-carboxyllic acids.

A potential raw material for organic additives may be the by-products formed during the refining of natural oils. The following components are removed during the refining process that can be used in the manufacture of organic additives: free fatty acids, phospholipids, monoglycerides and diglycerides, provitamins, alcohols, waxes, tocopherols, and sterols.

The aim of the study was to develop a method for the manufacture of additives using refining by-products of rapeseed oil and to create a biodegradable lubricant using these additives.

## 1. Research objects and methods

The natural waste materials for the manufacture of biodegradable additives for lubricants were technical fatty acids, which is a by-product of the deacidification process (neutralising). These waste products underwent esterification using enzymatic processes.

The manufacturing technology of ecological additives out of natural waste materials consisted of several unit processes, which are the following:

- The production of enzyme preparation;
- The production of esters out of the fatty acids in the presence of the enzyme preparation;
- The separation of biomass; and,
- Final biological product.

A technological diagram of microbiological synthesis is shown in Fig. 1.

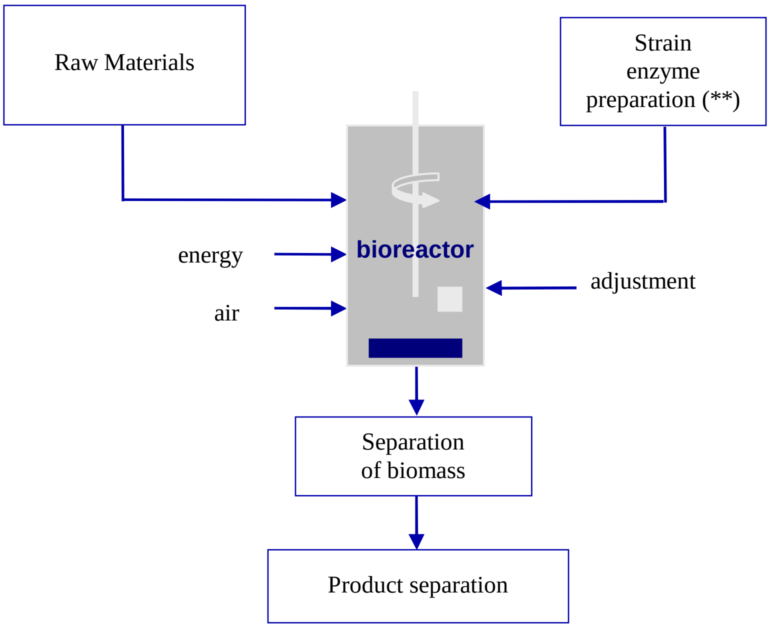

Fig. 1. A diagram for the microbiological synthesis of biological products

### *Biological material*

The cultures used the strains of non-pathogenic *Mucor circinelloides* TB mold, extracted from the shells of shrimp, from the resources of the Institute of Technical Biochemistry of the Technical University of Łodz. The strains were stored at 4°C, on slanting agar containing brewer wort at a concentration of 8.5° Blg and pH 5.8.

**The method for obtaining the enzyme (*Mucor circinelloides* lipase TB80301A) included the following**:

1. *Creating mould culture*;
2. *Growing mycelium of mould Mucor circinelloides TB80300A selectant containing a preparation of the lipase*;
3. *Producing a biomass of Mucor circinelloides TB80300A; and,*
4. *The separation, purification, stabilisation of the enzyme preparation*.

### *The production of TKT_EMC1 in the presence of Mucor circinelloides lipase as an enzyme catalyst*

Enzymatic reactions were carried out in a Radleys chemical reactor.

### *Separation of the biomass, producing the bio-product*

The reaction mixture, after being drained in order to separate the biocatalyst, was separated using flash chromatography.

After the separation and ester fraction are collected, they were combined and concentrated in a vacuum evaporator.

The tested additives were synthesised at the Institute of Industrial Biochemistry, Technical University of Lódź by a team headed by Prof. T Antczak. The method of production of these additives is the subject of patent application.

### *Creating TKT_EMC6b*

Ozonizing was conducted in a measuring set made up Ozone Generator 803N and an Ozone analyser BMT 964 meter.

### *Manufacture of lubricants*

Lubricants were prepared in the laboratory conditions by introducing a suitable aliquot of the additive into the oil base (PAO4). The concentration of additives obtained from the post-refinement raw materials of rapeseed oil was 1% of weight for TKT_EMC1 and 2% of weight for TKT_EMC6b. These are the optimal concentrations from the point of view of the anti-wear effectiveness [12]. After thorough mixing of additives with the base oil by using an electromagnetic mixer at a temperature of approximately 50□C, in order to check the stability of the composition. Then, it was stored for 48 hours at room temperature.

To analyse and verify the results of the performance research of bio-additives, they were compared with the lubricating compositions based on selected oils and Acorox 880, a commercial product (by Jaschem, Rafineria Jasło), containing ca. 80% (m/m) ZDTP (Zinc Dialkyl Dithiophosphate) in mineral oil. It is a widely used commercial additive with good AW (anti-wear) properties and poorer EP (extreme pressure) properties and showing antioxidant and anti-corrosive actions.

Lubricating compositions with the participation of bio-additives were compared with commercial oil EKO-PIL (by EKOMAX, Gliwice). According to the manufacturer recommendation, it is a biodegradable mineral oil, and it probably contains a viscosity modifier, a depressor, and zinc dithiophosphate. It is designed for the lubrication of chains and mechanical saw guides.

### *Testing lubricating and physicochemical properties of lubricants*

*Lubricating properties* (anti-wear) of the produced composition were evaluated in the conditions of mixed friction, according to PN-76/C-04147 and WTWT-04/MPS-025, in relation to the base oil, and it is based on the wear value of load index $G_{oz}$. Tribological tests were carried out using the four-ball apparatus (T-02) in the following conditions: running time = 3,600 sec., rotational velocity = 500 rpm, and load = 392 N.

*Dynamic viscosity* (*authors' method*) was determined using a rotational viscosity meter *Physica MCR 101* (by Anton Paar). The apparatus is equipped with a Peltier system with a temperature control range of –40–200°C and external thermostatic system (VISCOTHERM V2), operating in the temperature range of –20–200°C. Rheometer control and the analysis of the measuring data is done using Rheoplus software. The measurements were performed using the cone-plate measurement system in the cutting velocity range of 100 $s^{-1}$ and in the temperature range of 19–200°C.

*Flow temperature* indicates the lowest temperature at which the fluidity of the oil is still observed during oil cooling in standardized conditions (PN ISO 3016). Flow temperature allows evaluating the behaviour of the oil in changing ambient conditions, and particularly, in temperatures below zero. Flow temperature was determined using the *ISL CPP 5Gs analyser*.

*A study of corrosive action on copper*, according to PN-EN ISO 2160: 2004 norm, was carried out at a temperature of 100°C for 3 h. After this time, the appearance of the copper plate was compared with corrosion patterns according to ASTM D 130.

*Resistance to oxidation* (*authors' method*) was measured using the automatic device *Quantum™ Oxidation-Tester* by Tannas in the following conditions:

- Temperature: 140°C,
- Initial pressure: 90 Psi,
- Oxidizing factor: oxygen,
- Sample volume: 50 $cm^3$.

The measured quantity was the amount of time after which there was a decrease in the maximum pressure of 25 psi. The longer the time of oxidation, the greater is the resistance to the oxidation of the lubricant.

Measurement of *sulphur content* was made with a *SINDIE-7039* device, which uses monochromatic x-rays from a low-powered x-ray lamp, air-cooled with a built-in compressor. The radiation excites the electrons of the K-layer of sulphur atoms, which emit characteristic K$\alpha$ radiation for the sulphur at a wavelength of 0.5373 nm. The radiation is collected by the monochromator and its quanta are counted by the detector. The measurement was taken at room temperature within 30 to 300 sec.

Testing *biodegradability using CEC L-33-A-94* consisted in measuring the decrease of hydrocarbon concentration in the test samples.

The concentration of hydrocarbons was measured spectrophotometrically in infrared at 2930 ± 10 cm-1, after ultrasound sonification and extraction in 1,1,2-trichloro-1,2,2-trifluoroethane. In parallel, a sample of biocide was set with $HgCl_2$ as a control of the changes in the concentration of hydrocarbons without the participation of microorganisms („poisoned" sample). The absorption in the IR is measured at 0.7 after 21 days of experiment. The concentration of microorganisms was > $10^7$/ml. As the biodegradable pattern, di-isotridecyl adipate (DITA) was used.

## 2. Test results

The results of the study indicated that all the produced compositions in the tested range of concentrations have better anti-wear properties than the base oil [Fig. 2]. The introduction of 1% by weight of the TKT_EMC1 (analogically as in 2% Acorox) additive to PAO-4 resulted in an over 50% increase of the wear load index. The 2% content of TKT_EMC6b results in a slightly smaller increase of the wear load index in comparison to the 2% content of the commercial Acorox additive in the oil base. All lubricating compositions exhibit better anti-wear properties than the commercial oil EKO-PIL.

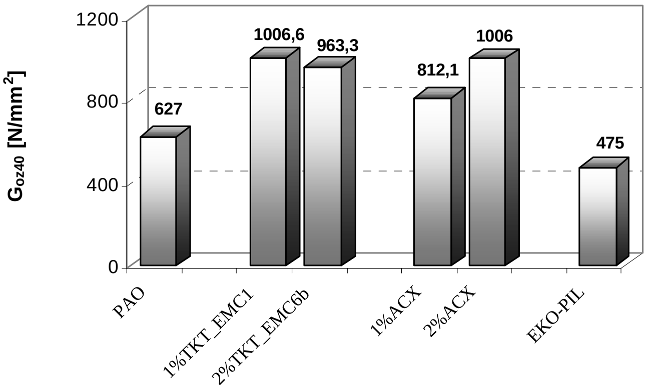

Fig. 2. The effect of additives on the anti-wear properties of oil PAO4

The effects of additives on the viscosity-temperature properties of the synthetic oil PAO4 were examined [Fig. 3].

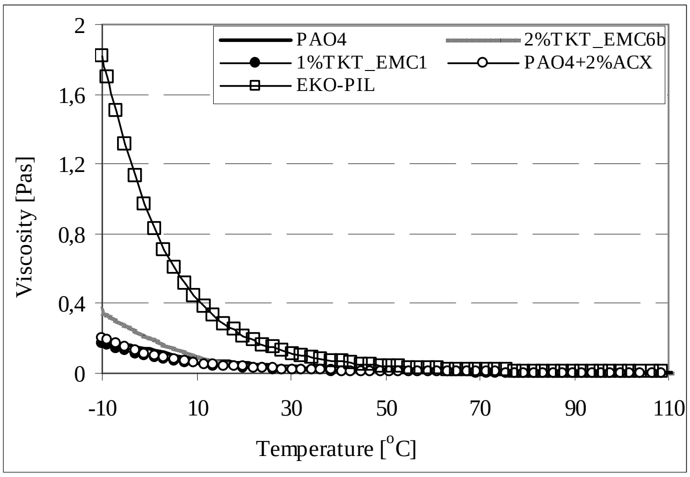

Fig. 3. A comparison of viscosity-temperature properties of compositions based on PAO4 oil and additives and EKO-PIL oil

It was found that the smallest variation in viscosity in the total temperature range was in lubricating compositions containing bio-additive TKT_EMC1 and Acorox. Somewhat more variation in temperature was evidenced by a base oil containing TKT_EMC6b additive. The worst viscosity-thermal properties were evidenced by the commercial oil EKO-PIL. An additional rheological description of lubricating oil is provided by flow temperature [Tab. 1]. It was found that the introduction of bio-additives and the commercial Acorox additive does not affect the low-temperature properties of base oil. For each composition in which bio-additives played the anti-wear role, the degree of corrosion was 1a or 1b (no corrosive effects on copper). The tendency to cause corrosion in copper plates was shown only in compositions containing Acorox, a multi-purpose additive, including anti-corrosive properties.

Table 1. Physicochemical and ecological properties of lubricants

| Physicochemical and ecological properties | Lubricant | | | |
|---|---|---|---|---|
| | 1%TKT-EMC1 | 2%TKT-EMC6b | PAO_2%ACX | EKO-PIL |
| Flow temperature [°C] | –72 | –73 | –75 | –25 |
| Corrosion level | 1a | 1b | 3b | 1b |
| Oxidation time [min] | 603 | 607 | 1.187 | 2.387 |
| Sulphur content [ppm] | 2.7 | 2.6 | 2.943 | 7.108 |
| Biodegradation | 96 | 97 | – | – |

The table indicates that the compositions with bio-additives practically contain no sulphur (less than 3 ppm). It should be emphasized that the high antiwear efficiency, comparable to Acorox, was obtained for the additives that do not contain sulphur. Lubricants with bioadditives are highly biodegradable, and thus easily decompose in the environment [13].

## Conclusions

The obtained results indicate that it possible to replace environmentally harmful additives (e.g. Acorox) in the conventional oil bases with additives that are based on carbon, oxygen, and hydrogen compounds alone, resulting in the improved wear properties of the lubricant composition. The use of ecological lubricants makes their operational and disposal costs lower than mineral lubricants. These lubricants may be used to lubricate friction nodes working under moderate conditions (temperature, load), and working in areas under special protection, such as forests, water intakes, national parks, recreation areas, farm areas, as well as road construction.

*Scientific work executed within the Strategic Programme "Innovative Systems of Technical Support for Sustainable Development of Economy" within Innovative Economy Operational Programme.*

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## Metoda wytwarzania ekologicznego środka smarnego z produktów porafinacyjnych oleju roślinnego

### Słowa kluczowe

Środek smarowy, rafinacja olejów, produkty porafinacyjne, oleje roślinne, substancje triboaktywne.

### Streszczenie

Wymóg stosowania „ekologicznie bezpiecznych" środków smarowych w wielu obszarach techniki sprawia, że zasadne stają się poszukiwania nowych surowców do ich wytwarzania. Potencjalnym źródłem mogą produkty uboczne powstające podczas rafinacji olejów naturalnych. W artykule przedstawiono metodykę wyizolowania substancji triboaktywnych z produktów porafinacyjnych oleju rzepakowego, która w efekcie doprowadziła do otrzymania ekologicznie bezpiecznych dodatków uszlachetniających. Otrzymane z ich udziałem kompozycje smarowe poddano badaniom właściwości fizykochemicznych i smarnych. Uzyskane wyniki wykazały, że charakteryzują się one wyższą skutecznością przeciwzużyciową i korzystniejszymi właściwościami reologicznymi w porównaniu z komercyjnym olejem zalecanym do stosowanych w warunkach umiarkowanych obciążeń i prędkości węzła tarcia. Wysoki stopień biodegradacji otrzymanego środka smarnego pozwala na zastosowanie go w skojarzeniach, w których istnieje niebezpieczeństwo bezpośredniego kontaktu ze środowiskiem.

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# METHODOLOGY FOR TESTING CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS USING THE TD-GC-MS TECHNIQUE

**Key words**

Volatile organic compounds, thermal desorption, GC/MS.

## Abstract

An adult spends approximately 80% of the time indoors. Building materials and the furnishings that are in the room emit volatile organic compounds (VOC – *Volatile Organic Compounds*). Many of the emitted VOC might adversely affect the human body, especially when their concentration in the air exceeds certain critical thresholds. For this reason, it is desirable and often necessary to monitor their concentrations in the air. For many VOC, the highest permitted air concentrations are set at extremely low levels. Therefore, their detection and quantitative determination requires the use of sophisticated analytical tools. Qualitative and quantitative methodology was developed for measuring VOC concentrations in the air at very low levels, which is necessary for the quality control of the equipment used in VOC testing from any source. For this purpose, gas chromatography (GC) in conjunction with mass spectrometer (MS) was used, supported by thermal desorption (TD). Using this methodology, the volume of emissions was studied for several different VOC derived from common materials in enclosed work areas. The key aspects of the applied methodology are discussed, from the preparation stage of the apparatus through the collection and preparation of the sample for analysis, ending with the appropriate analysis with the TD-GC-MS technique and the interpretation of the result analysis. This methodology is used for testing for the presence of VOC in the membrane station and for verifying the purity of the test chambers for VOC emission form various materials.

## Introduction

Volatile organic compounds (VOC) are a group of substances, which include a wide range of carbon compounds such as aldehydes, ketones, and micromolecular hydrocarbons. The number of substances classified in this group exceeds 500 [1], and they have been divided into 3 basic sub-groups: very volatile VOC (VVOC) with the boiling point (BP) in the range of 0–100°C, VOC with BP in the range of 100–240°C, and SVOC with BP in the range of 240 to 400°C [2–3]. The majority of the total VOC emissions into the environment (86%) are natural sources, called biogenic [4], the remaining emissions come from anthropogenic sources and are emitted mainly by a broadly defined industry, which is to the greatest extent associated with the production and use of plastics [5–6]. In the development of civilization, these proportions have been in a continuous flux; and although contamination is not a new phenomenon, over the recent years, their qualitative and quantitative compositions have been changing. Taking into account the fact that more than 70% of Europeans live in urban areas, the protection of air quality and continuous monitoring of pollutants (including VOC) becomes a necessity [2, 3]. There is substantial evidence that large amounts of VOC are harmful to human health [7]. For example, substances such as 1,3-butadiene and benzene have been proven to have teratogenic and carcinogenic effects [8, 9]. In addition to direct influence, the volatile organic compounds may have damaging indirect effects, contributing to the formation of secondary pollutants, including tropospheric ozone. Reducing the emissions of air pollutants, including the amount and type of VOC, is a complex, global issue. From an environmental point of view, any steps taken in this direction must be related to both the elimination of specific sources of pollution (management of specific chemicals) and the general restriction of the consumption of raw materials and energy in the industrial, residential, and transport sectors [10, 11].

Due to the harmfulness of volatile organic compounds, it has become mandatory to analyse the levels of their concentration and to establish maximum levels for contaminants in buildings, workplaces, etc. These issues are regulated by a number of national (VDI, US EPA, PN) and international (ISO) standards, for the classification of compounds, the ranges of their maximum permitted concentrations in ambient atmosphere, as well as procedures for obtaining and analysing samples.

At present, the aim is to be able to simultaneously analyse as many VOC as possible at the lowest levels of concentrations. In the vast majority of studies, the final analysis uses the gas chromatography (GC) technique with FID detection or in combination with mass spectrometry (MS) [12]. This may be done in combination with other methods of obtaining and preparing the samples for analysis. Among them, combinations of thermal desorption with GC and MS analysis seems to offer a comprehensive approach with the most advantages despite the considerable complexity of the required apparatus.

The aim of this study was to develop a methodology for determining the presence of volatile organic compounds by the TD-GC/MS method in air samples collected by the aspiration method. For these experiments, samples of air were obtained from the laboratory premises during remodelling and construction, which included a newly purchased piece of furnishing (under-desk cabinet). The changes were analysed of the concentration of volatile organic compounds emitted from building materials in the conditions of temperature and air exchange increase. The changes of the VOC concentration were analysed in the laboratory room equipped with membrane systems.

## 1. Research method

In developing the methodology for the determination of VOC, a Perkin-Elmer TurboMatrix 650 ATD thermal desorber was used. The commercial, steel sorption tubes by Perkin-Elmer filled with 200 mg of Tenax TA were used, which were conditioned prior to use for 6 hours at a temperature of 300°C in the flow of carrier gas (helium clean N6, 0) of 100 ml/min. Air samples were collected on the sorption tubes using the layout shown in Figure 1, consisting of a membrane pump – Schwarzer Precision SP670EC – with a stabilised power supply unit, combined with a rotametre flow range 3–30 dm$^3$/h and flow regulator.

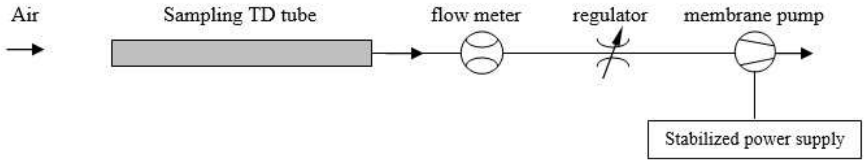

Fig. 1. Schematic diagram of the sampling system

The values of the volume and force of the airflow selected based on previous experiments (3 dm3 at a velocity of 100 ml/min.) meet the normative requirements, including ISO 16000-6: 2011, and they are safe for the stability of sorption deposits and allow for the analysis of a wide range of concentrations. The assumed volume was positively verified (by examining the second, serially attached tube) because of the lack of a "break" of the adsorptive deposit. The tube were subjected to thermal desorption at a temperature of 280°C for 10 minutes in a carrier gas flow of 30 ml/min. The original stream of desorption was routed to the cryogenic trap chamber (–20°C) from which, by means of the heated transfer line (225°C), it entered the gas chromatograph.

The tests used the GC/MS Perkin-Elmer Clarus 680/Clarus 600MS chromatographic system. The RTX-VMS Restek capillary column was used, which was 30 m in length and 0.25 mm in diameter with a stationary phase 1.4 µm thick. The temperature programme started at 40°C for 3 min, then increasing at the rate of 5°C/min. until 200°C was reached, followed by a further momentary increase to 250°C at 25°C/min. without sustaining it. Separated analytes were then routed through a heated transfer line (220°C) for the mass detector (ionization in a stream of electrons, mass range 20-400 m/z, a single scan time, and the internal between each scan of 0.2 and 0.1 s.). The carrier gas that was used had a purity of 6.0 N. The system was calibrated using commercial multicomponent standards for volatile organic compounds (VOC-Mix 18 OEKANAL®, Fluka) by a direct jet onto the sorption tube 1 µL in a dilution series and by plotting calibration lines for all identified compounds in at least four levels of concentrations. For the quantification of substances for which the apparatus was not calibrated, the results were given as the equivalent toluene quantity. For the analysis of chromatograms, TotalChrom and TurboMass software was used, which was produced by Perkin-Elmer, and the obtained mass spectra were identified using the NIST libraries.

## 2. Results and discussion

New elements of an interior (construction materials, furniture, and commercial equipment) are characterized by increased emissions of VOC, which is related to the properties of materials themselves, as well as to activities related to their processing. In order to verify the assumptions of the methodology, the qualitative and quantitative composition of VOC air was examined, which was collected from the newly bought, closed under-desk cabinet with an interior volume of approximately 105 litres, and the surface area of the inside walls was approximately 2.4 $m^2$. The cabinet was made of laminated particleboard; and after being manufactured, it was tightly wrapped with stretch film. Before obtaining the sample, airflow (chromatographic lab) of 525l was run through the cabinet (5 x V of the cabinet). The chromatographic testing identified 16 volatile organic compounds with clear the dominant signals. Then, in order to examine the changes in emissions, again the same portion of air was exchanged and the second sample was obtained. The results are presented in Table 1, and the observed changes are shown in the diagram (Fig. 3).

Table 1. Amounts of identified VOC before and after venting of the tested piece of furniture

| **Compound** | **RT** | **Initial conc. [µg/m$^3$]** | **Conc. after venting [µg/m$^3$]** |
|---|---|---|---|
| Hexane | 3.63 | 641.70 | 668.80 |
| Acetonitrile | 3.89 | 4.50 | 448.20 |
| Methylcyclopentane | 4.14 | 518.80 | 68.70 |
| Trichloroethene | 5.65 | 140.80 | 150.30 |
| Pentanal | 6.47 | 91.70 | 88.50 |
| Toluene | 7.06 | 160.50 | 132.80 |
| Tetrachloroethene | 7.46 | 71.80 | 0.00 |
| Hexanal | 8.42 | 210.10 | 185.40 |
| Xylene | 8.95 | 20.60 | 12.50 |
| a-Pinene | 9.66 | 230.10 | 216.00 |
| Heptanal | 10.28 | 32.60 | 14.80 |
| N/A 1 | 10.58 | 74.70 | 79.60 |
| 3-Carene | 10.99 | 48.60 | 79.80 |
| D-Limonene | 11.37 | 30.00 | 29.70 |
| N/A 2 | 11.62 | 42.90 | 36.10 |
| Octanal | 12.07 | 31,8 | 33,5 |

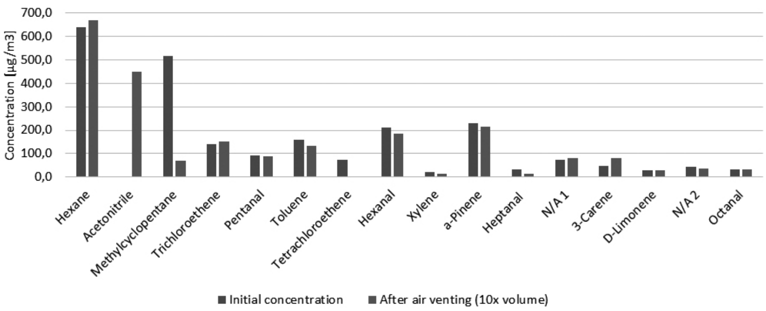

Fig. 2. Changes in concentration of the identified compounds before and after venting the container

After a 5-fold air exchange inside the test object, a decline in concentrations of most compounds was observed, including α-pinene (terpene, resin present in coniferous trees), D-Limonene (plant component of essential oils), and organic compounds related to the production processes of plastics (toluene, xylene, methylcyclopentane, pentanal, hexanal, tetrachloroethylene).

There was also a registered decrease in concentrations of two substances that had not been identified using the compound library. Furthermore, increases in concentrations of hexane and acetonitrile were noted because of the “airing” of the tested object with air from the chromatographic lab, where, among others, hexane was used as a solvent for samples in gas chromatography, and acetonitrile, as an eluent in HPLC. To confirm this, a sample of air from chromatographic laboratory was analysed, where elevated levels of these solvents were found, explaining their detection in the analysis of the air from inside the cabinet.

During construction and remodelling works, both construction and finishing materials are used, as well as secondary materials such as adhesives, silicones, varnishes, etc. In order to verify the effectiveness of the developed methodology for VOC analysis, air samples were taken from the room in which an interior door was replaced with new one made of wood-based materials. In the process of installation, the door was fitted (cut to size). In order to register potential changes of concentrations through time, another sample was obtained after 72 hours. A number of low-boiling-point organic compounds were identified, and they were analysed quantitatively (Tab. 2, Fig. 3).

Table 2. The quantities of identified VOC at the moment of new door installation and after 72 hrs

| **Compound** | **RT** | **Initial conc. [μg/m$^3$]** | **Conc. after 3 days [μg/m$^3$]** |
|---|---|---|---|
| Acetone | 3.55 | 242.60 | 19.06 |
| Acetonitrile | 3.90 | 70.50 | 58.30 |
| Pentanoic acid (methyl ester) | 4.78 | 190.70 | 4.70 |
| Methyl-cyclohexane | 5.69 | 56.40 | 4.70 |
| Toluene | 7.11 | 234.30 | 5.90 |
| Acetic acid (butyl ester) | 8.31 | 16.50 | 0.00 |
| p-Xylene | 9.00 | 41.70 | 2.90 |
| a-Pinene | 9.66 | 710.20 | 1.60 |

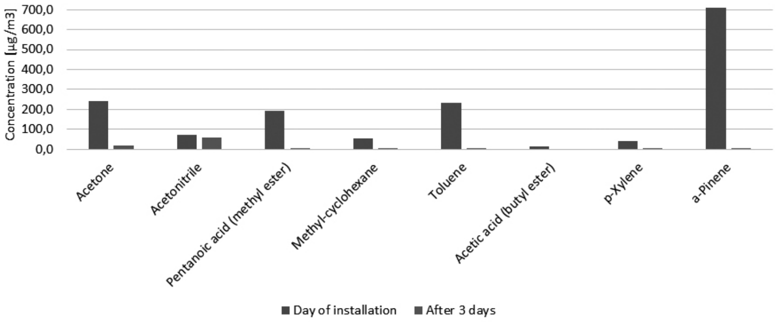

Fig. 3. Changes in concentration of the identified compounds at the moment of new door installation and after 72 hrs

On the day of the door installation, elevated concentrations of acetone, methylcyclohexane, toluene, xylene, and α-pinene were observed. It is likely that significant quantities of the last element were released into the environment while the door was being cut, while the rest is most likely the ingredients of materials used in the course of installation, i.e. adhesives, polyurethane foam, varnish, and sanitary silicon. With the exception of acetonitrile, after 72 hours, the concentrations of all compounds listed decreased below the point of detection within this method.

Volatile organic compound emission by many construction materials, for obvious reasons, increases as their temperature rises. In order to examine the changes in the emissions of VOC as a function of temperature (and indirectly - time function), samples of air were taken from the premises where the tests were carried out on the microfiltration membrane system. There were many plastic components used for its construction, mainly PVC tubes and rubber. The first measurement was made before turning on of the system (temp. approximately 19°C). Another measurement was taken after an hour of operation, when the temperature increased about 10°C. As a result of analysis, 12 substances were identified whose concentration increased during the experiment of both samples. The results are presented in Table 3 and Figure 4.

For all identified substances, approximately a 90% increase of emission was observed – the greatest being for 1-chlorooctadecane by 119.3%, and the smallest for tetradecane by 79.7%. Most of these compounds are organic substances used in the plastics industry, including solvents, i.e. toluene, xylene, and 1, 3, 5-trimethylbenzene. However, in this time period, the maximum allowed concentrations (WEL – workplace exposure limit) of the listed substances were not exceeded.

Table 3. Quantities of the VOCs identified at the start and after 1 hr of operation

| **Compound** | **RT** | **Initial conc. [μg/m$^3$]** | **Conc. after 1 hour [μg/m$^3$]** |
|---|---|---|---|
| Heptane | 5.13 | 51.80 | 104.40 |
| 1-Dodecanol | 5.69 | 35.20 | 58.60 |
| Toluene | 7.08 | 10.40 | 20.20 |
| Xylene | 9.01 | 28.40 | 49.10 |
| 1-Chlorooctadecane | 10.49 | 25.20 | 60.20 |
| 1, 3, 5-trimethylbenzene | 11.31 | 28.20 | 48.80 |
| Undecane | 12.18 | 36.30 | 61.20 |
| Dodecane | 13.76 | 24.60 | 48.30 |
| Tridecane | 15.24 | 14.70 | 30.50 |
| Tetradecane | 16.64 | 11.20 | 17.80 |
| Pentadecane | 18.03 | 6.60 | 13.10 |

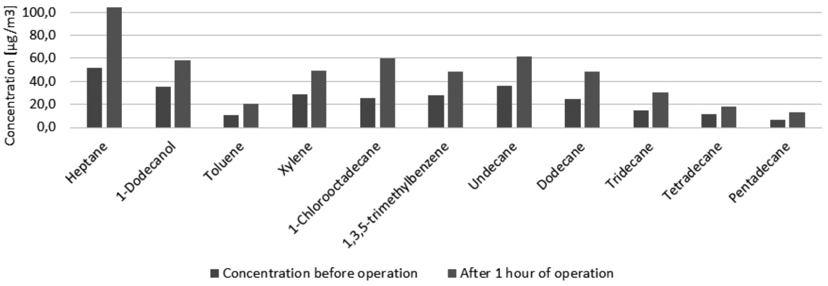

Fig. 4. Changes in concentration of the identified compounds before starting and after 1h of operation of the membrane system

## Conclusions

The examples presented in this paper confirm that the TD-GC-MS technique, and the methodology designed for it, is useful in the analysis of the concentrations of VOC in the air. Despite the high degree of the complexity of the apparatus, labour consuming calibration, and somewhat high costs of materials, this method, nonetheless, has the most advantages in comparison to other methods of analysis. It allows for the simultaneous identification of the qualitative (chemical composition) and reliable quantitative assessment of VOC in the tested object. It also allows an approximate estimation of the concentrations of the substances for which no calibration has been carried out. Moreover, the compact size of both the sorption tubes and aspiration systems for sampling make the TD-GC-MS method broad in application – from miniature personal devices, and portable systems for fieldwork, to extensive stationary analysers for continuous monitoring of contamination.

*Scientific work executed within the Strategic Programme "Innovative Systems of Technical Support for Sustainable Development of Economy" within Innovative Economy Operational Programme.*

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## Metodyka badania stężenia lotnych związków organicznych z zastosowaniem techniki TD-GC-MS

### Słowa kluczowe

Lotne związki organiczne (LZO), termiczna desorpcja, GC/MS.

### Streszczenie

Dorosły człowiek spędza ok. 80% czasu w pomieszczeniach zamkniętych. Zarówno materiały budowlane, jak i sprzęty znajdujące się w pomieszczeniu emitują lotne związki organiczne (VOC – *Volatile Organic Compounds*). Wiele z emitowanych VOC może negatywnie oddziaływać na organizm ludzki,

szczególnie gdy ich stężenie w powietrzu przekroczy pewne krytyczne progi. Z tego powodu zasadne, a często nawet konieczne, jest monitorowanie ich stężenia w powietrzu. Dla wielu VOC najniższe dopuszczalne stężenia w powietrzu są ustalone na skrajnie niskim poziomie. Dlatego też wykrywanie ich i ilościowe oznaczanie wymaga zastosowania wyrafinowanych technik analitycznych. Opracowano metodykę jakościowego i ilościowego oznaczania VOC w powietrzu na bardzo niskich poziomach stężeń, niezbędnych do kontroli jakości pracy urządzeń do badania emisji VOC z dowolnego źródła. Do tego celu zastosowano chromatografię gazową (GC) w sprzężeniu ze spektrometrem mas (MS), wspomaganą termiczną desorpcją (TD). Przy zastosowaniu opracowanej metodyki zbadano wielkość emisji do otoczenia kilkudziesięciu różnych VOC, pochodzących z materiałów powszechnie występujących w zamkniętych pomieszczeniach pracy. Omówiono kluczowe aspekty realizowanej metodyki, od etapu przygotowania aparatury, poprzez pobieranie i przygotowanie próbki do analizy, właściwą analizę techniką TD-GC-MS, do interpretacji wyników analizy. Opracowana metodyka stosowana jest do badania obecności VOC na stanowisku membranowym oraz do weryfikacji czystości komór służących do badania emisji VOC z różnych materiałów użytkowych.

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# SYSTEM FOR THE DISINFECTION OF CUTTING FLUIDS USING A PULSED ELECTRIC FIELD

**Key words**

Contamination of cutting fluid, microorganism cell, pulsed electric field (PEF), electroporation.

## Abstract

During applying cutting fluids (coolants), which are used in the surface treatment of metals, different microorganisms develop. The effects of microbial growth in the cooling system are the following: the shortened life of coolants, increased operating costs, downtime connected with the replacement of coolant, and the exposure of workers to the harmful impact of infected oil mist on skin, eyes, and upper respiratory tract.

The paper presents the possibility of an innovative application of a pulsed electric field method to disinfect cutting fluids. The contaminated coolant is subjected to a pulsed electric field with the result that there is a rapid destruction of living microorganisms therein, and their spores.

Furthermore, the article demonstrates a laboratory system equipped with a high voltage generator and a control system enabling, inter alia, to change the parameters of the pulsed electric field as well as the laboratory model of the

disinfection cell with variable spacing of the electrodes. A research stand made according to the predefined assumptions is also shown.

The research stand is intended for testing the effectiveness of reducing the degree of biological contamination of the coolant as a function of the parameters of pulsed electric field. The obtained results are related to the results of a research task of a strategic programme entitled: „Support systems of ecological exploitation of industrial oils and technological liquids". Obtaining promising test results will be a stage leading to the development of a system for the disinfection of cutting fluids on a technical scale.

## Introduction

Cutting fluids (cutting oils, coolants) are applied in machining processes. Their use increases the efficiency of machines by increasing the cutting speed, improving the quality of machined surfaces, prolonging the life of the cutting tool, reducing friction and energy consumption, as well as by the dissipation of the heat produced during this type of treatment. The most commonly used cooling and lubricating fluids are oil-water emulsions, prepared from concentrates, which are mixed with water in any ratio in order to obtain a stable emulsion [1]. The presence of water and organic matter makes coolants susceptible to contamination by microorganisms [2, 3, 4]. These are mainly bacteria (including pathogens), but also moulds and yeasts, and immunologically reactive compounds of microbial origin. In practice, the microorganisms get into the liquid in a continuous manner during its use. The intensity of their growth depends on the composition of the cutting fluid. The main source of contamination is the water used for the preparation of oil-water emulsions and the pollution getting into the cooling systems from metal workpieces and the environment. In addition to water, a prerequisite for the development of microorganisms is the presence of hydrocarbons or other organic substances such as fats and esters. The presence of bacteria and fungi results in a marked deterioration in the quality of coolants (cooling parameters decrease), and they may accelerate the corrosion processes of both metal workpieces and the elements of machine tools.

During metalworking, oil mist rises around the working stand. On the particles of the mist, there are biological agents – mainly bacteria and endotoxin. The droplets of the mist are of such size that they can easily penetrate the human respiratory tract, and with them, bacteria, fungi, and the fragments resulting from their degradation. The contact of the respiratory epithelium with microorganisms, their cell fragments, and other chemical compounds present in the oil mist (e.g. Sulphur compounds) influences the proper functioning of the respiratory system and may lead to the occurrence of various diseases among workers employed in metal processing [5, 6, 7]. The most common symptoms of diseases associated with the exposure to oil mist are respiratory diseases such as asthma, inflammation of the upper respiratory tract, chronic bronchitis, and allergic alveolitis. As a result of contact with cutting fluids, dermatological disorders such as allergies, acne oil, and bacterial and fungal infections can also occur. In order to reduce the exposure of workers and ensure the high quality of the produced metal objects, it is necessary to prevent microbial contamination of coolants and to take appropriate corrective actions when the number of bacteria or fungi exceeds the norm.

In practice, there are two methods to prevent the microbial contamination. One of them is the replacement of the fluid with a new one, combined with careful washing of the installation for applying the fluid. Research shows that the method gives a short-term effect, because just after several hours, microorganisms start developing again, and after a week, the bacteria levels could rise by 3–4 orders of magnitude. Another method used to reduce the microbial contamination of cutting fluids is adding biocides to the fluid [8]. Formaldehyde, isothiazolins, and boric acid salts are most commonly used as biocides. The formaldehyde was the earliest introduced biocide. However, because of its rapid degradation and evaporation from the liquid, it was used in high concentrations, which resulted in its penetration into the air at the workplace.

In connection with the planned entry into force of the "EU biocide directive" (from 2014) imposing significant restrictions on the use of biocides, new liquid coolants and lubricants, which do not contain such measures, will appear on the market. The main advantage of these liquids is that they possess the capacity to prevent the growth of bacteria and lack toxic additives with bactericidal action. An alternative to the above methods of coolant disinfection are new technologies in which no chemicals are used for decontamination. An environmentally friendly method for decontamination of cutting fluids mixed with water, containing mineral oils, is provided by Kaysser, which is a HP manufactured device, which uses ultraviolet light (UV-C) for disinfection [9]. The germicidal UV-C impact is performed by passing a thin film of coolant (approx. 1.5 mm) on a rotating cylinder surrounded on one side by shielded fluorescent tubes. This arrangement provides an additional circuit of coolant that flows back into the machine after disinfection. The method is effective even in the case of microorganisms that have developed a resistance to bactericidal and fungicidal chemical measures. Works on the use of UV for the disinfection of coolants are performed in ITeE – PIB in Radom within the research task of strategic programme entitled: "Support systems of ecological exploitation of industrial oils and technological liquids". The method of pulsed electric field (PEF) used for disinfection of cutting fluids seems to be innovative and at the same time ecological [10, 11]. This method has been tested for several years in a pilot or semi-technical devices for food preservation. It uses the impact of high voltage pulses on the food placed between two electrodes [12, 13]. The main preserving factor is the electric field acting destructively on microflora existing in food. The essence of the influence is the use of high voltage for a very short period of time, expressed in microseconds, for a single pulse.

## 1. The mechanism and the influence of the electric field on the cell

The microbial cells are surrounded by a cell membrane, which acts as a barrier and allows the cell to maintain different substances within itself such as a cytoplasm and organelles [14, 15]. Each cell membrane is polarized. It means that there is a difference of charges (the positive charges carried by the cations and the negative charges carried by the anions) between its outer and inner surface. This implies that, across the membrane, there is a potential difference, or voltage, called a resting potential (membrane potential), which usually ranges from -20 to -200 mV depending on the type of organism and the type of cell. This potential is expressed as a negative value because there are slightly more negative charges inside the cell than the positive ones.

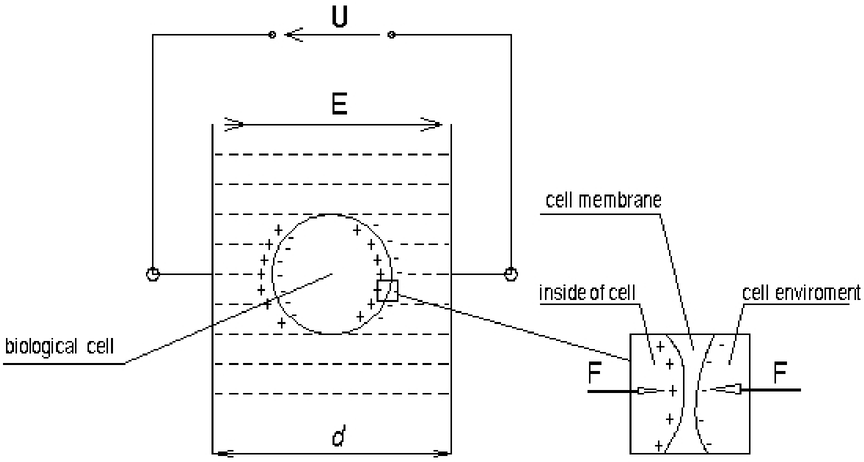

Fig. 1. Schematic representation of the impact of the electric field on the cell

The mechanism of the inactivation of the cells under the influence of electric field is not fully understood. There are various theories that attempt to explain this phenomenon. Currently, the most popular and most widely accepted explanation for this phenomenon is the electroporation of the cell membrane (Figure 1). A biological cell behaves in a manner similar to a capacitor with a low dielectric constant. Therefore, when it is placed in the electric field,

$$\mathbf{E} = \mathbf{U}/d,$$

where $\mathbf{U}$ – the voltage applied to the area of influence of the electric field,
$d$ – distance between the electrodes defining the area of influence of the electric field,

the ions inside and outside the cell will move in the direction of the applied electric field. This in turn leads to the accumulation of free, opposite electric charges on both sides of the cell membrane. These charges are influenced by force **F** proportionally to the intensity of the electric field **E** and the size of the charge q,

$$\mathbf{F} = \mathbf{E}\, q,$$

causing localised pressure increases on the cell membrane, which leads to changes in its thickness and to the formation or growth of existing membrane pores. A defective cell membrane is more permeable to small molecules, which facilitates the equalization of the osmotic pressure between the external environment and the contents of the cell. This may cause the cell to further swell. If the natural cell membrane potential rises above the natural, which is the critical value of about 1V due to the applied electric field, the disruption of the cell membrane occurs causing the cell death – irreversible electroporation occurs. The critical voltage depends on the size of the cell. The smaller it is, the higher the critical voltage must be applied.

## 2. Disinfection system of cutting fluids

Figure 2 shows a diagram of the system using the pulsed electric field method in food processing [16]. It consists of three basic components: a high-voltage pulse generator, disinfection cell, and a control system with process control.

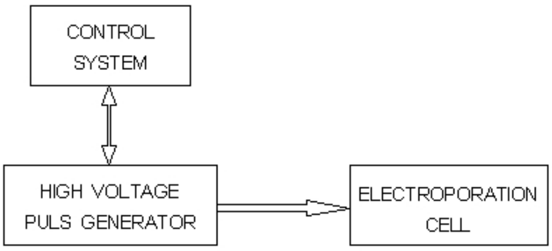

Fig. 2. Diagram of the system of pulsed electric field in food processing

The Institute for Sustainable Technologies – National Research Institute in Radom developed and built a research stand for disinfecting cutting fluids in laboratory conditions, which is shown in Fig. 3.

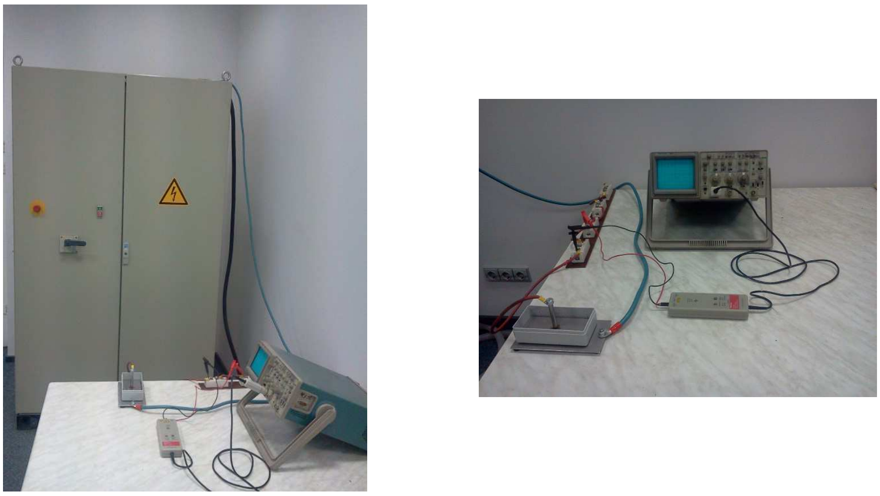

Fig. 3. Laboratory research stand for the disinfection of cutting fluids

The stand consists of a high voltage pulse generator with an integrated microprocessor control system and a stationary disinfection cell, which comprise a PEF system as well as a digital oscilloscope. The oscilloscope allows the registration of the voltage pulse waveforms for analysis with a view to select optimal parameters of the pulsed electric field for the disinfection of the coolant.

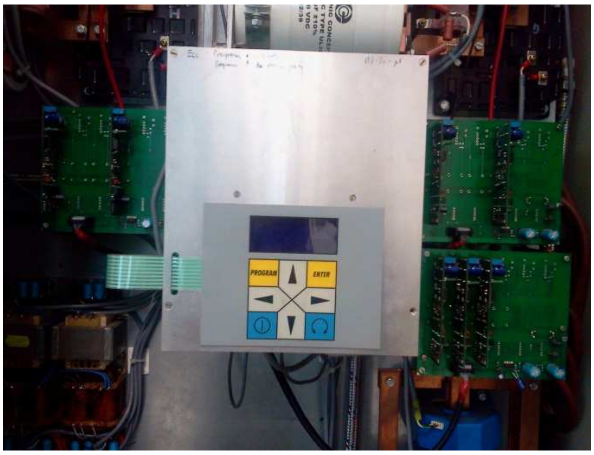

Fig. 4. The control system integrated with the high voltage pulse generator

The high voltage pulse generator produces rectangular pulses with a pulse power up to 3 MW, with energy expended up to 90 kWs per second in continuous operation. The control system integrated with the generator (Fig. 4) is equipped with a keyboard that allows for setting the following output voltage pulse parameters:

- The voltage up to 20 kV,
- Pulse repetition frequency in the range of 1 Hz to 3 kHz, every 1 Hz,
- Pulse width in the range of 1 μs to 200 μs, every 1 μs, and
- The generation of pulse „packages" with the set number of pulses in the range of 1–99 and the set frequency and pulse width in the "package".

The stationary cell for coolant disinfection is shown in Fig. 5.

Fig. 5. Stationary cell for disinfection of cutting fluids

It was made based on the cuboid, polycarbonate container, wherein two rectangular stainless steel electrodes of dimensions 70 × 145 mm were placed. One of the electrodes connected to the negative grounded pole of the generator is permanently attached to the cell and forms its bottom. Second, the movable electrode is connected to the positive pole of the generator. The distance between the electrodes is determined by means of insulating spacers with a height of d = 3, 6, and 9 mm. This creates the possibility of abrupt changes in electric field intensity at a fixed output voltage. For maximum output voltage U = 20 kV and the electrodes distance d = 3 mm, the electric field E in the disinfection cell achieves the value of approximately 66 kV/cm.

## Conclusions

The developed research stand allows for testing the effectiveness of reducing the degree of biological contamination of the coolant with the use of the pulsed electric field method. Additionally, the results obtained in such a way can be compared with the outcomes of the research task developed in the strategic programme entitled: „Support systems of ecological exploitation of industrial oils and technological liquids".

The design of the high voltage pulse generator and laboratory cell for disinfecting enable one to conduct research within a wide range of parameter changes in pulsed electric field. Consequently, it is possible to predict the optimum values of these parameters in terms of technological and economic processes of coolants decontamination. Obtaining promising results will form the basis for designing a system for disinfecting cutting fluids on a technical scale.

*Scientific work executed within the Strategic Programme "Innovative Systems of Technical Support for Sustainable Development of Economy" within Innovative Economy Operational Programme*.

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## System do dezynfekcji cieczy obróbkowych z wykorzystaniem pulsacyjnego pola elektrycznego

### Słowa kluczowe

Skażenie cieczy obróbkowej, komórka mikroorganizmu, pulsacyjne pole elektryczne (PEF), elektroporacja.

### Streszczenie

W obróbce powierzchniowej metali stosuje się ciecze obróbkowe (chłodziwa), w których w trakcie ich użytkowania rozwijają się drobnoustroje. Efektami rozwoju mikroorganizmów w układzie chłodzenia są: skrócenie żywotności chłodziw, zwiększenie kosztów eksploatacji, przestoje produkcyjne związane z wymianą chłodziwa oraz narażenie pracowników na szkodliwe dla zdrowia oddziaływanie zarażonej mgły olejowej na skórę, wzrok czy górne drogi oddechowe.

W artykule przedstawiono możliwość innowacyjnego zastosowania metody pulsacyjnego pola elektrycznego do dezynfekcji cieczy obróbkowych. Skażone chłodziwo poddawane jest działaniu pulsacyjnego pola elektrycznego, w efekcie

czego następuje szybkie zniszczenie żyjących w nim mikroorganizmów, a także ich zarodników.

Przedstawiono laboratoryjny system wyposażony w generator wysokiego napięcia i układ sterowania umożliwiający między innymi zmianę parametrów impulsowego pola elektrycznego oraz laboratoryjny model celi dezynfekcji o zmiennej odległości elektrod. Przedstawiono stanowisko badawcze wykonane według przyjętych założeń.

Wykonane stanowisko badawcze umożliwi przeprowadzenie badań skuteczności zmniejszania stopnia skażenia biologicznego chłodziwa w funkcji parametrów pulsacyjnego pola elektrycznego oraz odniesienie otrzymanych rezultatów do wyników prac uzyskanych w zadaniu badawczym Programu Strategicznego pt.: „Systemy wspomagania proekologicznej eksploatacji olejów przemysłowych i cieczy technologicznych”. Uzyskanie obiecujących wyników badań pozwoli na opracowanie urządzenia do dezynfekcji cieczy obróbkowych w skali technicznej.

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# THE METHOD OF PREPARATION AND USE OF CUTTING FLUIDS BASED ON ORGANIC COMPONENTS

**Key words**

Cutting fluids, cardanol ethoxylates, glycerol fraction.

## Abstract

The specificity of the machining operation, during which the machining fluids have direct contact with the environment and the human body, creates the need to seek solutions that would increase the application of ecologically safe products. An alternative to petroleum and synthetic bases may be vegetable products having good ecological properties. This paper presents a method for producing cutting fluids based on glycerol fraction from the production of biodiesel and a mixture of cardanol ethoxylates and synthetic ester. The produced fluids were studied in terms of their functional properties, which determine their operational suitability as well as their physicochemical and microbiological properties. The wear of a tool bit after working in an environment of such fluids was also determined. It has been found that the cutting fluids, prepared according to the method developed, have preferred functional properties. They meet the performance requirements for these products and can be used in metalworking erosive processes.

## Introduction

Because of the detrimental effects of lubricant oils on the environment, there is an increasing interest in products with less ecologically harmful impact [1, 2]. This also applies to technological fluids, primarily those that interact with the environment during machining operations. A very large group of these products are cutting fluids [3–5]. Their annual consumption in Poland is at 8.7 thousand tons of concentrate used as a 5–10% mixture with water. While using cutting fluids, they have direct contact with the human body and the environment. The fluids penetrate the environment through evaporation, during the removal of chips and cut objects and by leaks in installations. The size of losses can reach 30% of the annual consumption of the liquid. Health risks arise due to oil mists formed during the operation and the direct contact with skin [7–9]. Machining fluids, due to the physicochemical composition, are ecologically and dermatologically harmful [10]. Legitimate enterprises, which fit into the worldwide trends of human health and environmental protection, are those that aim to minimize the environmental and health dangers of cutting fluids. There is an increasing interest in replacing the mineral base components with plant and synthetic products [4, 5, 11].

The glycerol fraction, a by-product formed in the process of esterification of the fatty acids of plant oils, in particular rapeseed oil, may be used as a base for cutting fluid [12]. Chemical separation of glycerol fraction is often applied to isolate the crude glycerol, which is characterized by more stable physicochemical properties. Another vegetal product, for which new applications are being searched, is cardanol, cashew shell oil [13, 14]. Due to its strong antiseptic properties, it is advisable to use the product in the production of cutting fluids, due to its basic functional property of a high resistance to microorganisms. Preliminary studies have shown that cardanol has weak lubricating properties. The parameter improved significantly after subjecting the product to oxyethylation [15]. This article presents the physicochemical and microbiological properties of cutting fluids based on chemically purified fraction of glycerol and cardanol ethoxylates.

## 1. Research object and methods

Two packages of cutting fluids were tested: one having the G1-G3 symbol produced based on chemically purified fraction of glycerol and the other having the C1-C3 symbol based on a mixture of cardanol ethoxylate and synthetic ester. The direct use of ethoxylates as bases of cutting fluids has not been possible due to insufficient stability of ethoxylates and water mixtures. However, the stability was ensured by the use of ethoxylates as a component of binary base containing synthetic ester. The packages G1-G3 and C1-C3 differed in terms of additives.

The cutting fluids were subject to research identifying their physicochemical, microbiological, and technological properties as well as determining the level of their biodegradability. Anti-corrosive properties (PN-M-55789: 1992) and anti-foaming properties (bottle test ASTM D 3519 and blender test ASTM D 3601:1982) for liquids were assessed. Moreover, the value of the pH indicator (PN-EN ISO 10523: 2012), the degree of contamination with bacteria and fungi („dip slide" method through microbiological samplers) as well as stability (visually) were determined. Resistance to microorganisms was tested on a research stand, which was equipped with a main thermostated tank containing a temperature sensor, electrical stirrer, and a thermometer. The main tank was connected with a contactor tank situated next to the main one, containing steel chips and glass beads. The construction of the stand enabled the circulation of the tested liquid between the tanks. The main tank was able to heat and stir its contents. During the study, 5 percent mixtures of liquid and water were subject to aging processes, and contaminated with the used cutting fluid from the operation, which was characterized by a high content of bacteria ($>10^7$). The processes were carried out at a temperature of 36±4°C in 7-hour cycles, repeated every 24 h for 12 weeks. Samples were taken weekly. The changes in the value of pH, anti-corrosive properties, anti-foaming properties and the content of bacteria and fungi were monitored.

The studies on the lubricating properties were conducted in accordance with the requirements of PN-C-04147: 1976. The test elements were spheres with a diameter of ½ inch made of 100Cr6 bearing steel. The size of the defect diameter on the spheres, with a constant load of 392.1 N, speed of 1450 rpm, and time of 1 h was determined.

The biodegradation of the liquid was investigated by the Zahn-Wellens test, in accordance with the guidelines of the OECD 302 B norm.

Technological properties were assessed by the examination of the wear of a tool bit after working in an environment of the fluids under studies. The research was carried out according to the PN-ISO 3685 standard, using tool bits made of P10, P20 and P30 cemented carbide. Shafts having a diameter of $\varphi = 50$ mm and length $l = 500$ mm, made of structural carbon steel of ordinary quality (St 3) alloy steel 40H and stainless steel 0H18N9 were rolled. The study was conducted at a spindle speed of $\omega = 450$ rpm, with a progress of 0.1 mm/rev. and a rolling depth of 1 mm. For each shaft, two passes of the tool bit were used.

## 2. The method for producing cutting fluids

The process of producing cutting fluids includes the following steps:

- The preparation of input materials for the process of modifying the glycerol fraction and cardanol oxyethylation,

- The separation of glycerol fraction or cardanol oxyethylation,
- Monitoring tests of the produced ethoxylate or the isolated glycerine,
- The preparation of the base and refining additives,
- Base and additive blending,
- The control of physical and chemical properties of the liquid, and
- producing the liquids.

A crucial step in the manufacturing process of cutting fluids is cardanol oxyethylation and the separation of glycerol fraction. The research on the synthesis of ethoxylates allowed identifying the optimal process conditions and catalyst type, which ensures that the product achieved has the most favourable properties. For the preparation of cutting fluids, a product having an average degree of oxyethylation n=6 was selected [15]. The synthesis of ethoxylates was carried out in the presence of NaOH catalyst in an amount of 0.1% calculated on the product, at a temperature of 160°C, at a pressure of 0.25–0.35 MPa. The glycerol fraction was separated by means of formic acid. The acid was used at the concentration of 3% at room temperature. The control parameter of both manufactured products was the refractive index. In order to produce the liquid, output components were prepared using a base and appropriate sets of additives (corrosion inhibitor, biocide, anti-foam lubricant). Next, the blending process was carried out at a temperature 25–30°C in a container equipped with a low speed mixer. Upon completion, the basic physicochemical properties of the liquid were examined.

## 3. Overview of the results

Since the cutting fluids are produced as concentrates for dilution with water, the study of physicochemical, microbiological, and lubrication properties was carried out for 5 percent solutions of the tested liquid diluted in water. They were the predicted concentrations of the solutions of operating liquid. For comparison, the commercial water-diluted cutting fluids, which are used in a wide range of processes for deficient metalworking, were examined. They were marked with symbols K1 and K2.

Table 1 presents the research results of physicochemical and microbiological properties of the developed and commercial cutting fluids.

The cutting fluids G1-G3, produced, based on glycerine and C1-C3 based on the mixture of cardanol ethoxylate and synthetic ester, had the physicochemical and microbiological properties similar to the level determined for the commercial products (Tab. 1). They did not show a corrosive effect on steel and cast iron. The pH of the developed and commercial liquids was slightly alkaline (liquids G) and alkaline (liquids C), which was not conducive to the growth of microorganisms. The values of the diameter of the defects on the test spheres, which were determined after the research on the developed

G1-G3 liquids and the commercial K1 and K2, were similar, indicating the same ability to protect against wear caused by friction. In contrast, the anti-wear properties of C1-C3 liquids, which had slightly higher values of the defect diameters, were less effective, but they met the requirements for cutting fluids. All liquids were stable. After 24 hours, there was no delamination of any of them. The developed liquids showed significantly more favourable anti-foam properties than the commercial products, examined by both the bottle and blender tests. None of the cutting fluids contained bacteria and fungi.

Table 1. Physicochemical and microbiological properties of 5 percent solutions of the cutting fluids diluted in water

| Parameter | Cutting fluids | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | G1 | G2 | G3 | C1 | C2 | C3 | K1 | K2 |
| Anticorrosive properties | H0 | H0 | H0 | H0 | H0 | H0 | H0 | H0 |
| pH | 7.7 | 7.7 | 7.9 | 9.5 | 9.0 | 8.7 | 9.2 | 9.0 |
| Anti-wear properties, defect diameter, mm | 0.77 | 0.77 | 0.60 | 0.90 | 1.00 | 0.90 | 0.66 | 0.86 |
| Stability (visually) | s* | s* | s* | s* | s* | s* | s* | s* |
| Anti-foam properties (bottle test), s | 2 | 1 | 1 | 1 | 3 | 4 | 20 | 10 |
| Anti-foam properties (blender test), s | 2 | 1 | 2 | 2 | 3 | 2 | 30 | 40 |
| number of microorganisms (dip slide):<br>bacteria<br>fungi | <br>none<br>none | <br>none<br>none | <br>none<br>none | <br>none<br>none | <br>none<br>none | <br>none<br>none | <br>none<br>none | <br>none<br>none |

The developed cutting fluids demonstrated high resistance to microorganisms (Table. 2).

Table 2. Change of physicochemical and microbiological properties of the 5 percent mixtures of the developed cutting fluids diluted in water as a result of their laboratory aging

| Parameter | | Liquid symbol | | |
|---|---|---|---|---|
| | | C1 | C2 | C3 |
| Total number of bacteria | Before aging | nw* | nw* | nw* |
| | After aging | nw* | nw* | $10^3$ |
| Total number of fungi | Before aging | nw* | nw* | nw* |
| | After aging | nw* | nw* | nw* |
| Anticorrosive properties | Before aging | H0 | H0 | H0 |
| | After aging | H0 | H0 | H0 |
| pH | Before aging | 9.5 | 8.7 | 8.9 |
| | After aging | 9.5 | 8.7 | 8.9 |
| Anti-foam properties<br>Bottle test/blender test, s | Before aging | 4/40 | 5/35 | 5/35 |
| | After aging | 5/55 | 15/60 | 20/60 |

| | | G1 | G2 | G3 |
|---|---|---|---|---|
| duration, weeks | | 12 | 12 | 12 |
| Total number of bacteria | Before aging | n/i* | n/i* | n/i* |
| | After aging | n/i* | n/i* | $10^2$ |
| Total number of fungi | Before aging | n/i* | n/i* | n/i* |
| | After aging | n/i* | n/i* | n/i* |
| Anticorrosive properties | Before aging | H0 | H0 | H0 |
| | After aging | H0 | H0 | H0 |
| pH | Before aging | 7.7 | 7.7 | 9.5 |
| | After aging | 7.9 | 7.7 | 9.5 |
| Anti-foam properties Bottle test/blender test, s | Before aging | 3/5 | 2/5 | 10/15 |
| | After aging | 5/5 | 10/30 | 10/20 |

* not identified

As a result of aging, there was no change in the significant physicochemical and microbiological properties of the liquids produced based on glycerine and cardanol ethoxylates (Tab. 2). Bacteria and fungi appeared in none of the cutting fluids. The anticorrosion properties of the liquid did not change. None of them had a corrosive effect on steel and cast iron. In contrast, antifoaming properties slightly deteriorated. The fluids, however, which underwent the aging process, were comparable in this respect to the fresh commercial cutting fluids (Tab. 1). This indicated that the developed liquids met the performance requirements in terms of resistance to microorganisms.

All prepared fluids, both the ones based on the mixture of cardanol ethoxylates and diisooctyl adipate (C) and the ones based on purified glycerol fraction (G) had a high susceptibility to biochemical decomposition (Table 3).

Table 3. The degree of the biodegradation of produced cutting fluids

| | Fluid symbol | | | | | |
|---|---|---|---|---|---|---|
| | C1 | C2 | C3 | G1 | G2 | G3 |
| biodegradation degree [%] | 94.9 | 92.9 | 90.0 | 98.5 | 99.0 | 98.8 |

Each fluid developed met the criteria of biodegradation process of cutting fluids, according to which the level of biodegradability above 80 percent classifies the fluid to easily biologically degradable products.

The study of technological properties was conducted during the real process of rolling. The test results were expressed using standard geometrical parameters of the tool bit blade wear: KT – the depth of gouge the on the surface, VBB – the average bandwidth of abrasive wear on the contact surface and VBBmax – the highest bandwidth of abrasive wear on the contact surface. They showed similar properties of the developed and commercial cutting fluids (Tab. 4).

Table 4. The wear of the tool bit blade while turning various materials in the presence of 5% test solutions of cutting fluids

| Tool bit type/steel type | Cutting fluids | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | G1 | G2 | G3 | C1 | C2 | C3 | K1 | K2 |
| | KT [mm] | | | | | | | |
| P10/ST3 | 0.64 | 0.42 | N* | N* | N* | 0.63 | N* | N* |
| P10/4OH | 0.33 | 0.43 | N* | N* | 0.39 | 0.46 | 0.35 | 0.19 |
| P10/OH18N9 | 0.03 | 0.11 | 0.03 | N* | N* | N* | N* | 0.01 |
| P20/ST3 | 0.49 | 0.13 | N* | 0.65 | N* | 0.59 | 0.43 | 0.37 |
| P20/4OH | 0.19 | 0.30 | 0.04 | N* | N* | 0.51 | 0.33 | 0.26 |
| P30/OH18N9 | N* | 0.16 | 0.04 | 0.09 | N* | 0.07 | N* | 0.04 |
| | $Vb_b$ [mm] | | | | | | | |
| P10/ST3 | 0.97 | 0.78 | 0.70 | 0.72 | 0.12 | 0.80 | 0.11 | 0.36 |
| P10/4OH | 0.48 | 0.67 | 0.44 | 0.40 | 0.54 | 0.65 | 0.44 | 0.30 |
| P10/OH18N9 | 0.01 | 0.11 | 0.07 | 0.05 | 0.74 | 0.23 | 0.03 | 0.00 |
| P20/ST3 | 0.91 | 0.12 | 0.00 | 0.88 | 0.07 | 0.56 | 0.82 | 0.89 |
| P20/4OH | 0.30 | 0.45 | 0.09 | 0.51 | 0.49 | 0.89 | 0.56 | 0.41 |
| P30/OH18N9 | 0.04 | 0.14 | 0.06 | 0.11 | 0.03 | 0.03 | 0.08 | 0.08 |
| | $Vb_{max}$ [mm] | | | | | | | |
| P10/ST3 | 1.14 | 0.88 | 0.97 | 1.00 | 0.20 | 1.05 | 0.19 | 0.36 |
| P10/4OH | 0.55 | 0.80 | 0.99 | 0.51 | 0.60 | 0.83 | 0.57 | 0.30 |
| P10/OH18N9 | 0.01 | 0.15 | 0.09 | 0.09 | 0.80 | 0.42 | 0.05 | 0.00 |
| P20/ST3 | 0.98 | 0.19 | 0.00 | 1.17 | 0.09 | 1.00 | 0.97 | 0.89 |
| P20/4OH | 0.39 | 0.56 | 0.14 | 0.57 | 0.60 | 1.02 | 0.66 | 0.41 |
| P30/OH18N9 | 0.07 | 0.16 | 0.08 | 0.20 | 0.04 | 0.05 | 0.08 | 0.08 |

N* built-up.

The developed cutting fluids, especially the ones based on glycerol, protected the tool bits against wear during machining of OH18N9 stainless steel and 4OH alloy most effectively. The depth of gouge the on the surface and the wear of the contact area of all the tool bits were the smallest. In this respect, the effectiveness of the G1-G3 liquids was similar to the commercial K2 liquid. Tool bit wear during the machining of the same kind of steel with the use of commercial liquid K1 was greater. However, the use of the liquids developed to process standard quality steel resulted in higher values of the tool bit wear indicators in relation to K2 liquid and similar values to those obtained for K1 liquid.

## Conclusions

The results showed that cardanol ethoxylates and glycerine might constitute the basic components of cutting fluids. The liquids based on them could be characterized by high physicochemical, microbiological, and technological properties. They were similar and sometimes surpassed commercial products in this respect. Both the purified glycerol-based liquids and the mixtures of cardanol ethoxylate and synthetic ester showed a high stability of chemical composition and resistance to bacteria and fungi. They were characterized by high anticorrosive and anti-foam properties. The liquids sufficiently protected cutting tools against wear, especially in processing high quality steel. The use of plant products as a base and additives having low ecotoxicity and relatively high biodegradability provided a high degree of biodegradation of the liquids produced. This is very important for the environment due to the nature of the operation of cutting fluids. Therefore, it can be concluded that these waste products (glycerol fraction and cardanol) can provide the raw materials for the core components of cutting fluids. The cutting fluids based on these components can be applied in the metalworking erosive processes.

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## Metoda wytwarzania i zastosowanie cieczy obróbkowych na bazie składników ekologicznych

### Słowa kluczowe

Ciecze obróbkowe, oksyetylaty kardanolu, frakcja glicerynowa.

### Streszczenie

Specyfika eksploatacji, podczas której ciecze obróbkowe mają bezpośredni kontakt z otoczeniem i organizmem człowieka, generuje potrzebę poszukiwania rozwiązań zwiększających aplikację produktów bezpiecznych ekologicznie. Alternatywą dla baz naftowych i syntetycznych mogą być produkty roślinne charakteryzujące się dobrymi właściwościami ekologicznymi. W artykule przedstawiono metodę wytwarzania cieczy obróbkowych na bazie frakcji glicerynowej z produkcji biodiesla oraz mieszaniny oksyetylatu cardanolu z syntetycznym estrem. Zbadano właściwości funkcjonalne wytworzonych cieczy, decydujące o ich przydatności eksploatacyjnej, a także ich właściwości fizykochemiczne i mikrobiologiczne. Określono także zużycie noża tokarskiego po obróbce w środowisku tych cieczy. Stwierdzono, że ciecze obróbkowe, wytworzone według opracowanej metody, charakteryzują się korzystnymi właściwościami funkcjonalnymi. Spełniają wymagania eksploatacyjne dotyczące tego rodzaju produktów i mogą być stosowane w procesach ubytkowej obróbki metali.

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# METHOD FOR ECOLOGICAL COMBUSTION OF ORGANIC WASTE IN COMMERCIAL LOW POWER BOILER

**Key words**

Biomass, biomass combustion, energetic efficiency, ecological efficiency.

## Abstract

The structure of primary energy in Poland still is formed by a high position of coal from domestic resources. The widespread use of this fuel encourages and facilitates "co-combustion of biomass with coal" in power boilers. Differences in the structure and behaviour during the preparation and combustion of coal and vegetable fuel are the cause of the difficulties with co-combustion of raw biomass in power boilers. Based on research, the effect of biomass characteristics on the basic parameters of the process of combustion and co-combustion of coal in a low-power boiler device was determined. Changes in excess air-ratios and exhaust gas temperatures, and changes in the concentrations of toxic components of exhaust gases during the combustion process were determined. The amount of heat generated in the boiler during the combustion of biomass and fuel blends of biomass and coal was determined. Controlled changes in process parameters of combustion conditions (co-combustion) of coal and selected types of biomass allow for environmentally friendly combustion in commercial low-power boilers.

## Introduction

The use of renewable energy sources has become an essential part of the energy industry. This condition is imposed by the European Union. Poland has committed to use 7.5% of primary energy from renewable sources in 2010, and this number is to be increased to 15% by 2020. Research centres, where numerous studies have been conducted, and investors of small and medium-sized enterprises in the country and the world have been interested in renewable energy sources, especially biomass for many years [2, 6, 9, 12, 17, 19]. The main direction of the use of biomass in Poland is heat production based on the direct combustion of the fuel in boilers.

Co-combustion is considered to be the easiest way to increase the production of energy from renewable sources. This is due to the relatively low funding for the modernization (the possibility of using existing boilers) and ecological benefits (reducing emissions of $SO_2$, $NO_x$ and $CO_2$) [5, 7, 9, 17, 19, 21]. Disadvantages of the use of such combustion are currently problems associated with ensuring availability of biomass, sufficient storage of biomass, and the uncertainty associated with the constant increase of biomass. Biomass can cause environmental hazards and operational problems in the installation [3, 4, 9, 15, 19].

In Poland, the co-combustion of biomass and solid fuel is practically carried out on an industrial scale in most power plants [4, 16]. This process includes a variety of fuel configurations (different species of primary fuels and biomass) and technological configurations (grate boilers, dust boilers and fluid boilers). The research [1, 10, 11, 14, 17, 21] shows that the most common fuel is carbon co-combusted with wooden biomass (sawdust, wood chips, dust), biogas and waste from animal and vegetable production (rapeseed bagasse, chicory coffee bagasse, and bone meal, etc...) According to the authors, biomass, depending on the type, is characterized primarily by a relatively high humidity (35–50%) and low calorific value (6–20 MJ/kg) as compared to conventional fuels parameters.

“Small energetics” (individual heating, small industrial and municipal boilers) having a significant share of the total emissions of the environment, remains in the "grey zone" because of the lack of regulation of the interference in the use of technology to ensure compliance with emission standards for combustion processes. The share of small energetics in the process of energy production is estimated at 20–30% in the country [20], and, because of the poor condition of the operated installation, the sector's share of total emissions is much higher. Despite the dynamic development of the construction of small solid fuel boilers, devices are still operated with low efficiency and high emission rates.

## 1. Aim of the work

The aim of the work was to recognise the effect of biomass properties on the basic parameters of the processes of combustion and co-combustion with coal in low power boilers.

## 2. Realisation

The presented experiments involved the power processing of fuel mixtures prepared of waste materials derived from the food industry (cherry processing waste and sunflower oil pulp) and of coal.

The selected materials were subjected to laboratory tests to evaluate their properties such as fuel ash content, calorific value, the fuel elemental (C, H, N, S).

The essential parts of the work were conducted on a test stand that included a low-power boiler unit adapted to burning coal.

In the course of experiments conducted with the optimal parameters of boiler operation, the temperatures inside the furnace and thermal performance of the device were controlled. Observed factors were the temperature and composition of the gases emitted into the atmosphere.

## 3. Test stand

The basic element of the test stand was a low power energy device designed to burn solid fuels, mainly coal.

The stand used a universal boiler type KJ-WD, with a thermal output of 15 kW, from PPHU “PIECBUD”.

The stand is equipped with a system for measuring and recording the temperature in the combustion chamber and in the exhaust system. The combustion chamber has a system of three sliding temperature sensors (special sleeves in the water jacket) with heat-resistant guards with K-type thermocouples and temperature recorder type KD7 manufactured by Kobold.

A combustion chamber of the boiler is equipped with a system for measuring the amount of air supplied to the combustion. To measure the amount of air used, the Hoffer turbine (probe RPR-51S HO) used flow laminators and mass flow rate computers (Masstrol ST2L10P from KEP). For the analysis of the exhaust gas, a microprocessor analyser (GA-21 plus) is used from Madura. To measure the concentrations of hydrocarbon an MC-218 analyser from Hermann was used. The stand is equipped with a system for measuring and recording the energy output of the boiler during combustion. Measurements of the energy of the boiler were performed with an electronic energy meter (PolluTerm) from SENSUS, which registers the energy of heating medium (GJ) and the momentary power (kW).

## 4. Test results

Before the tests, the fuel properties were assessed, starting with determining the basic chemical composition of the materials used in the study. The results of elemental composition tests of prepared fuel compositions are shown in Table 1.

Table 1. The composition of elements in tested fuels

| Type of fuel | Element concentration [%] | | | | |
|---|---|---|---|---|---|
| | Coal | Hydrogen | Oxygen | Nitrogen | Sulphur |
| Coal ("Eco-grain") | 75.74 | 5.35 | 6.7 | 1.49 | 0.69 |
| Cherry processing waste | 43.5 | 6.4 | 43.7 | 0.70 | 0.14 |
| Sunflower pulp | 45.2 | 5.1 | 38.1 | 0.15 | 0.11 |

From the materials listed above, the fuel mixtures were prepared, which were used for further tests. Table 2 shows the basic parameters of the tested fuels.

Table 2. The basic parameters of the tested fuels

| Type of fuel | Parameter | | | |
|---|---|---|---|---|
| | Humidity | Ash | Fly particles | Calorific value [MJ/kg] |
| | [%] | | | |
| Coal ("Eco-grain") | 6.37 | 7.25 | 32.3 | 28.5 |
| Cherry processing waste | 7.3 | 1.33 | 80.8 | 17.1 |
| Sunflower pulp | 8.1 | 4.32 | 72.7 | 16.1 |

Figs. 1 to 8 presents the results of the combustion of fuels derived from food processing waste (cherry processing waste, sunflower oil pulp). Figure 1 shows the change in the excess air ratio λ during the combustion of selected fuels. The presented data indicates that this parameter fluctuated around the value 2. In all cases, the combustion of fuels of the process a small change of the excess air ratio was observed in the period of 20 to 100 minutes. Coal in the same time period required changes of λ ~2.2, cherry processing waste λ ~2.0, sunflower oil pulp λ ~1.8. This time period can be for all test cases considered to be the primary process of laminar combustion, which is the stabilisation of changes of excess air ratio and the temperature of the process. The biggest change of the excess air ratio was found in all cases of combustion at the beginning and end of the process. The beginning is a rapid combustion of vaporized fly particles of fuel with the simultaneous propagation of flame in a large mass of fuel on the grate. The smallest change of λ was found for cherry processing waste (from 3.9 to 1.9). The end of the combustion process is the inhibition of oxidation by combustion products of the primary process. Combustion in this period requires the smallest changes of λ for sunflower oil pulp and cherry processing waste (from 2.0 to 4.5 and 4.7), and the largest changes were required for coal (from 2.2 to 5.9).

There was a momentary slight change of the λ in a few cases (involving a mixture of 50, 25 and 15% of the cherry processing waste and sunflower oil pulp), resulting from changes in the composition of the instantaneous fuel blends, due to differences in their density. Despite the very good mixing of the components before the tests, their partial separation occurred during fuel delivery, which results in an erratic operation of the furnace. No indication was observed that the composition of fuel mixtures on the grate furnace burned directly affect the value of the excess air ratio (λ).

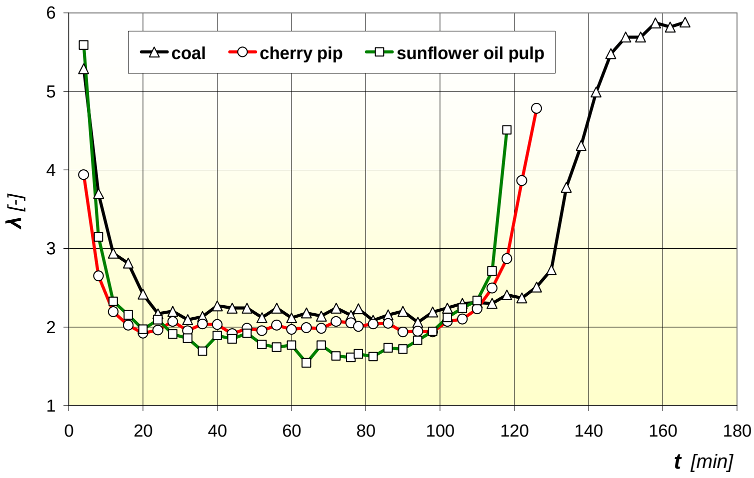

Fig. 1. Variation of excess air ratio during combustion of coal, cherry processing waste and sunflower oil pulp

In whole combustion process, the average excess air ratio was greatest for coal, $\lambda_{av\,c} = 3.03$, and smallest for cherry processing waste, $\lambda_{av\,p} = 2.28$ (see Fig. 8).

Figure 2 presents the changes of the exhaust gas temperature measured in the exhaust pipe. During the tests, the temperature varied in the range 150–350°C, taking the most common values in the range of 200–330°C.

Comparing the obtained data with the values of the excess air ratio (λ), it can be concluded that increasing the exhaust temperature decreases the coefficient λ, and, conversely, the exhaust gas temperature decrease is observed as an increase of excess air ratio. It follows that with constant amount of fuel dispensed into the combustion the factor that effects the coefficient λ and exhaust gas temperature may be the amount (portion) of fuel combusted at any given time on the grate of the furnace.

In all performed fuel combustion processes, it was observed (following the sharp increases of exhaust gas temperatures in the beginning – the combustion of evaporated fly particles) that the speed of the exhaust gas temperature rise was slowed (locally reduction of the temperature of the process) in relation to the takeover of power by the fuel bed on the grate of furnace.

The lowest average exhaust gas temperature in the whole combustion process (see Fig. 9) was observed for sunflower oil pulp, Tav sp = 187°C, the largest for coal "eco-grain", Tav c = 256°C.

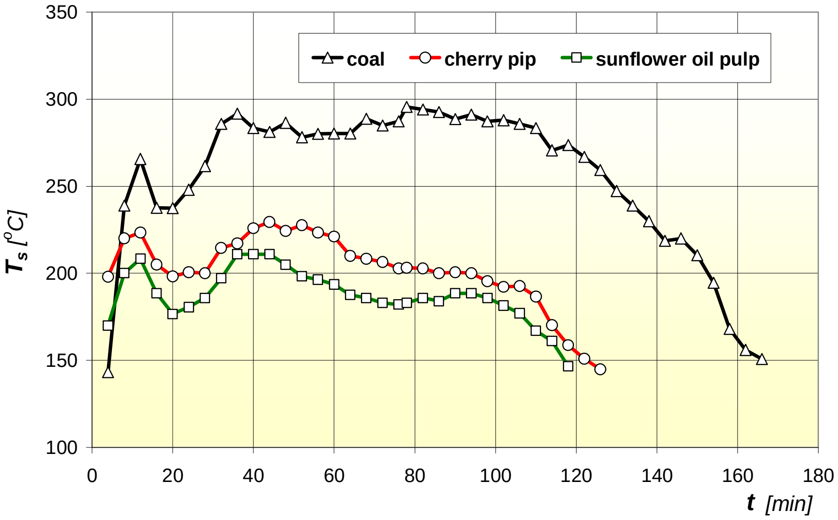

Fig. 2. Variation of temperature of exhaust gases during combustion of coal, cherry processing waste and sunflower oil pulp

Figure 3 presents a comparison of the energy values received by the heat installation during combustion tests of coal or selected types of biomass, and Figs. 4 and 5 present the energy obtained during combustion of fuel mixtures of coal and biomass.

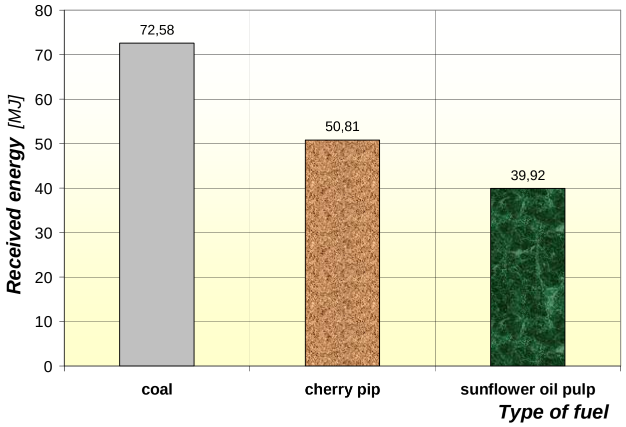

Fig. 3. The amount of heat energy generated in the system of boiler during combustion of coal, cherry processing waste and sunflower oil pulp

The presented data shows that, during the combustion of the same mass of fuel in similar conditions of the thermal process, the energy produced increases with the decrease in the share of biomass in combusted fuel blend from 41.09 MJ for fuel with 100% sunflower oil pulp (50.81 MJ for cherry processing waste) to 72.58 MJ for fuel composed of 100% carbon.

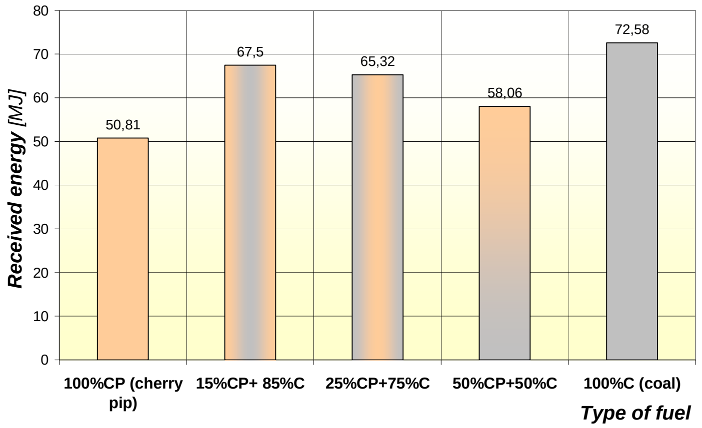

Fig. 4. The amount of generated energy in the boiler during combustion of mixtures of cherry processing waste and coal

It has been found that the energy obtained from the combustion of cherry processing waste, compared to the energy obtained from the combustion of coal is 10% greater than the result from the comparison of calorific values of these two fuels. The uniform, regular, spherical particle size of bulk cherry processing waste (greater surface in contact with air) makes the process of combustion increase the thermal efficiency of the boiler. The combustion of fuel mixtures of coal and cherry processing waste (50, 25, and 15%) results in energy comparatively close to the ratio of calorific values of these mixtures.

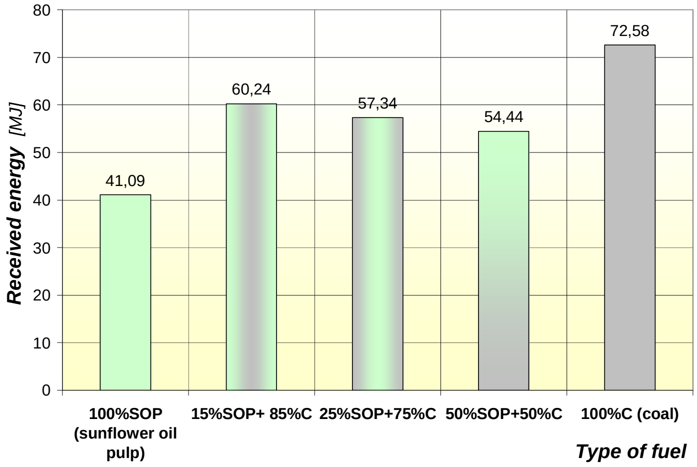

Fig. 5. The amount of generated energy in the boiler during combustion of mixtures of sunflower oil pulp and coal

Tables 3 and 4 show the comparison of the calorific value and the energy generated during the combustion of the different varieties of mixtures of biomass with coal. Only for the case of the combustion of pure sunflower oil pulp was the obtained energy close to the ratio of calorific values sunflower oil pulp and coal. For other cases of the combustion of mixtures, the thermal efficiency of boiler was decreased.

Table 3. Calorific value and obtained energy for combustion of mixtures of cherry processing waste and coal

| Mixture composition [%] | | Calorific value [MJ/kg] | Received energy [MJ] | $W_{pip}/W_{coal}$ [%] | $E_{pip}/E_{coal}$ [%] |
|---|---|---|---|---|---|
| Cherry processing waste | Coal | | | | |
| 100 | 0 | 17.1 | 50.81 | 60 | 70 |
| 50 | 50 | 23.1 | 58.06 | 81 | 80 |
| 25 | 75 | 25.8 | 65.32 | 91 | 90 |
| 15 | 85 | 26.8 | 67.5 | 94 | 93 |
| 0 | 100 | 28.5 | 72.58 | | |

Table 4. Calorific value and obtained energy for combustion of mixtures of cherry processing waste and coal

| Mixture composition [%] | | Calorific value [MJ/kg] | Received energy [MJ] | $W_{pulp}/W_{coal}$ [%] | $E_{pulp}/E_{coal}$ [%] |
|---|---|---|---|---|---|
| Sunflower oil pulp | Coal | | | | |
| 100 | 0 | 16.1 | 41.09 | 56 | 55 |
| 50 | 50 | 22.6 | 54.44 | 79 | 75 |
| 25 | 75 | 25.6 | 57.34 | 89 | 79 |
| 15 | 85 | 26.7 | 60.24 | 93 | 83 |
| 0 | 100 | 28.5 | 72.58 | | |

Figures 6–8 present the concentration of toxic gaseous combustion products for the analysed types of biomass and coal.

Figure 6 shows the changes in the concentration of carbon monoxide in the exhaust gas. The presented data shows that, in the initial stage of combustion, the temperature rise in the furnace caused a decrease in the concentration of CO from about 1600 ppm for coal to about 800 ppm in the main, laminar combustion stage. For cherry processing waste and sunflower oil pulp, the concentrations were 1300–1600 ppm in the beginning and 500–600 ppm during laminar stage.

Probably the primary factor affecting the value of the carbon monoxide concentration was a momentary temperature of the furnace. The low temperature of about 200–400°C in the initial period caused that the oxidation process of steam-gas produced in the furnace proceeded with relatively low yield. The temperature increase to a level 700–900°C during the laminar stage meant that a substantial part of gases produced was combusted. The reason for the observed temperature rises in the later period was the energy derived from the combustion of previously emitted carbon monoxide and hydrocarbons.

Analysis of the results of the effect of the excess air supplied to the combustion of coal and biomass on the concentration of carbon monoxide confirm the fact resulting from the analysis of the combustion process that increasing the value of the excess air ratio usually corresponds with the decrease of the carbon monoxide concentration in the exhaust gas.

In addition, analysis of the results of the effect of temperature in the combustion zone on the concentration of carbon monoxide, resulting in co-combusted of the blends, confirms the fact resulting from the analysis of the combustion process of fuel components that an increase in combustion temperature causes a decrease in the concentration of CO in the exhaust gas. The reduction in CO emissions was observed for all the tested mixtures at a constant load and constant excess air ratio supplied to the combustion chamber.

During combustion, the lowest mean CO concentrations were found for cherry processing waste – 661 ppm, and the largest was found for coal – 1013 ppm (see Fig. 8).

The increase in the percentage of biomass in a mixture with coal resulted in a proportional decrease (cherry processing waste, sunflower oil pulp) of the concentration of carbon monoxide in the exhaust gas.

Fig. 6. Variation of carbon monoxide concentration in exhaust gases during combustion of coal, cherry processing waste and sunflower oil pulp

Analysis of the results of the effect of temperature in the combustion zone on the concentration of nitrogen oxides formed during the combustion of biomass and coal indicates that the increase in combustion temperature causes an increase in the total concentration of nitrogen oxides NOx in the exhaust gas.

In the combustion of coal, NOx held the largest share of the high values of oxide concentrations in fuels, both because of the amount of elemental nitrogen in fuel (1.49%) and because of the relatively high excess air ratio (λ ~2.2) in the main laminar combustion stage. The thermal oxides during combustion only occurred at high temperatures (above 700°C).

The result of combustion of cherry processing wastes was the formation of the lowest values of average concentrations of NOx ($NO_{x\ av\ p}$ = 103 ppm – see Fig. 8) in the whole process, mainly thermal oxides, even though the fuel contained 4 times the amount of elemental nitrogen than the sunflower oil pulp. In this case, the lowest average excess air ratio $\lambda_{av\ p}$ = 2.28 and low average temperature of combustion (exhaust gas temperature $T_{s\ av\ p}$ = 202°C) had the dominant role.

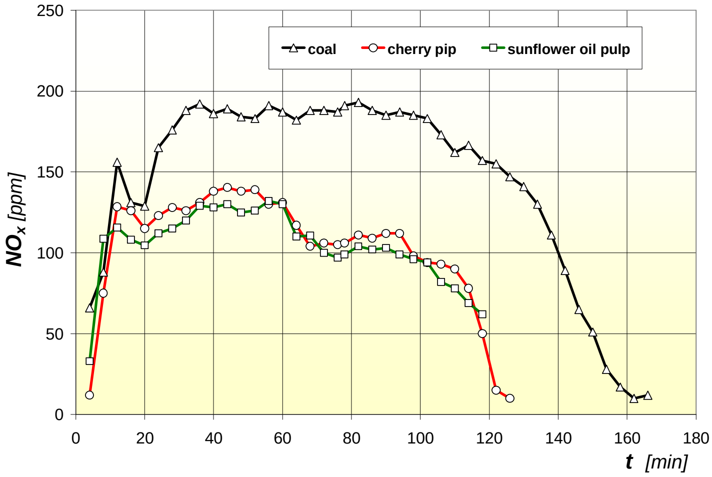

Fig. 7. Variation of nitrogen oxides concentration in exhaust gases during combustion of coal, cherry processing waste and sunflower oil pulp

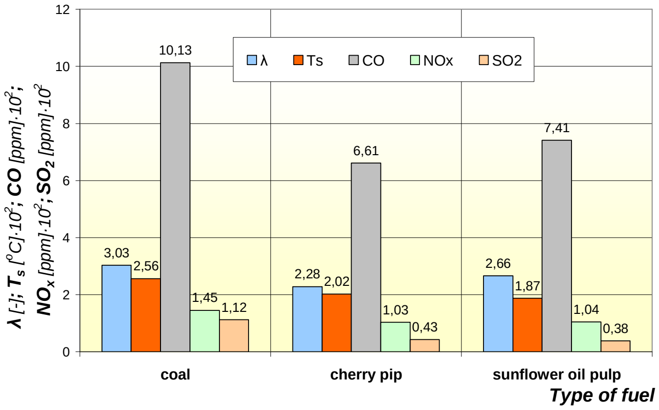

Fig. 8. Average values of changes of excess air ratio, exhaust gas temperature, carbon monoxide concentration, nitrogen oxides concentration and sulphur dioxides in exhaust gases during combustion of coal, cherry processing waste and sunflower oil pulp

The results of nitrogen oxide emissions during the combustion of coal and biomass blends, as expected, show an increase in the concentrations of $NO_x$ due to the increase in the percentage of carbon in the blend during co-combustion of cherry processing waste and sunflower oil pulp.

Analysis of the results of the effect of the type of fuel on the concentration of $SO_2$ formed in the combustion process leads to the conclusion that the emission of sulphur dioxide in the exhaust gas is mainly dependent on the elemental content of elemental sulphur in fuels tested.

During the study of combustion of coal, cherry processing waste and sunflower oil pulp the $SO_2$ concentration was found to be proportional to the sulphur content in the fuel.

Generally, it can be said that the increase in the percentage of biomass with coal mixtures reduces $SO_2$ emissions during combustion.

## Conclusions

- Changes in process parameters, for both the combustion conditions, as well as the co-combustion of coal and certain types of biomass and its impact on emissions of pollutions (CO, $NO_x$, $SO_2$), support the conclusion that the increase in the value of these parameters improves the quality of thermal conversion process of the materials by reducing the concentrations of certain pollutants; however, at the same time, the quality of the combustion process is reduced due to other pollutants.
- An increase in combustion temperature – as an independent variable parameter – improves combustion, reducing the concentration of carbon monoxide, but at the same time increases the emission of sulphur dioxide and nitrogen oxides $NO_x$. The increase in the oxygen supplied with the air to the combustion chamber caused a significant reduction in the concentration of carbon monoxide and sulphur dioxide, while increase in concentrations of $NO_x$. These relationships were observed for all tested fuels.
- Analysis of the energy properties of mixtures of carbon and selected types of biomass showed that the high calorific value of biomass allows the participation of dry biomass in the mixture up to 50%.
- An ecological method of combustion and co-combustion (the assumed maximum thermal efficiency) of selected types of biomass is to control the oxidation process by changing the excess air ratio $\lambda$, especially in the initial period of rapid increases in temperature (combustion of evaporated fly particles). The intensity of oxidation during this period determines the nature of the combustion in the main part of the laminar combustion.
- A change in the excess air ratio during this period should not be larger than $\lambda_{pulp}$ <0.4/min $\lambda_{pip}$ <0.2/min, which reduces the increase rate of $NO_x$ at $eNO_{X\ pulp}$<14.5 ppm/min and $eNO_{X\ pip}$ <10.4 ppm/min. The intensity of the oxidation of CO shows a satisfactory level of $eCO_{pulp}$> 48 ppm/min and $eCO_{pip}$> 55 ppm/min.
- In laminar combustion, the excess air ratio should be maintained at the level of $\lambda$ ~2.0 for cherry waste and $\lambda$ ~1.8 for sunflower pulp.

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## Metoda ekologicznego spalania odpadów organicznych w komercyjnym kotle małej mocy

### Słowa kluczowe

Biomasa, spalanie biomasy, sprawność energetyczna i ekologiczna.

### Streszczenie

Strukturę energii pierwotnej w Polsce wciąż kształtuje wysoka pozycja węgla z zasobów krajowych. Powszechne stosowanie tego paliwa sprzyja i ułatwia tzw. współspalanie biomasy z węglem w kotłach energetycznych. Różnice w budowie i zachowaniu podczas przygotowania oraz spalania węgla i paliwa roślinnego są przyczyną pojawiających się trudności eksploatacyjnych przy współspalaniu surowej biomasy w kotłach energetycznych. Na podstawie przeprowadzonych badań określono wpływ właściwości biomasy na przebieg podstawowych parametrów procesu jej spalania i współspalania z węglem kamiennym w urządzeniu kotłowym małej mocy. Określono zmiany współczynnika nadmiaru powietrza, zmiany temperatur gazów spalinowych, zmiany stężeń toksycznych składników spalin w trakcie procesów spalania. Ustalono ilości energii cieplnej wytworzonej w instalacji kotłowej w trakcie spalania biomasy i mieszanin paliwowych biomasy z węglem kamiennym. Kontrolowane zmiany parametrów procesowych warunków spalania (współspalania) węgla i wybranych rodzajów biomasy pozwalają na ekologiczne prowadzenie procesów spalania w komercyjnych kotłach małej mocy.