Досліджено процеси анодного окиснення карбонових кислот та катодного відновлення альдегідів та кетонів в модельних розчинах та водно-спиртових екстрактах спрацьованих олив. Встановлено, що процеси електрохімічного перетворення оксигеновмісних сполук однаково перебігають, як в модельних розчинах, так і в екстрактах спрацьованих олив. Визначено, що продуктами електрохімічного перетворення оксигеновмісних сполук є вуглеводні

Ключові слова: електроокиснення карбонових кислот, електровідновлення альдегідів і кетонів, регенерація, спрацьована олива

Исследованы процессы анодного окисления карбоновых кислот и катодного восстановления альдегидов и кетонов в модельных растворах и водно-спиртовых экстрактах отработанных масел. Установлено, что процессы электрохимического преобразования кислородсодержащих соединений одинаково протекают, как в модельных растворах, так и в экстрактах отработанных масел. Определено, что продуктами электрохимического преобразования кислородсодержащих соединений являются углеводороды

Ключевые слова: электроокисление карбоновых кислот, электровосстановление альдегидов и кетонов, регенерация, отработанное масло

UDC 621.899(047.31)
DOI: 10.15587/1729-4061.2018.123649

ELECTROCHEMICAL REGENERATION OF OXYGEN-CONTAINING COMPOUNDS IN THE EXTRACTS OF USED OILS

O. Davydenko
Postgraduate student*
E-mail: dom237@ukr.net
V. Ledovskykh
Doctor of Chemical Sciences, Professor*
E-mail: uchneftexim@bigmir.net
*Department of Chemistry and Chemical Technology
National Aviation University
Kosmonavta Komarova ave., 1, Kyiv, Ukraine, 03058

1. Introduction

Regeneration of used oils is an important problem related to large-scale contamination of the environment by them. Oil reserves in the world are being depleted while there is a constant growing demand for oil products, including motor oils. There was produced 38.6 million t of commodity oils in 2014 alone [1]: they become unsuitable for re-use after having being used and create toxic waste that must be disposed of [2].

Most of the oils are used under tough conditions, the main of which are elevated temperature, the presence of oxygen, water, the catalytic action of metals and products of wear, etc. Oil undergoes transformations as a result of the ongoing processes of oxidation, the accumulation of products of oxidation of the oil itself and structural materials, products of wear and contamination. The most dangerous products of oil oxidation include oxygen-containing derivatives – carboxylic and carbonyl compounds. The presence of oxygen-containing substances causes corrosion of structural materials, neutralization of alkaline additives, deterioration of washing-dispergating properties and resistance against oxidation, thereby reducing the operational resource. As a result, the oil fails to meet operational characteristics – there is an increase in the formation of soot, varnishes, and sludge, which adversely affects engine operation. The main direction in the disposal of used oils is regeneration. Most of the known methods of regeneration are based on treating used oils with chemical reagents or adsorbents of various types, causing the formation of the new toxic waste that is difficult to dispose of [3]. Therefore, it is a promising and relevant task to develop new methods for the regeneration of used oils.

2. Literature review and problem statement

Industrial oils are produced based on petroleum hydrocarbons of various molecular structure (alkanes, cycloalkanes, arenes and cycloalkanes-aromatic compounds). When they are used, they undergo physical-chemical transformations and oxidation, and need replacing. The formation of harmful oxygen-containing derivatives of hydrocarbons occurs through the initial stages of creation of hydro- and di-hydroperoxides [4]. They are subsequently transform to organic acids, low- and high-temperature sedimentation, coke substances. Consequently, there is strong darkening of oils and deterioration of their physical-chemical and operational properties [5]. Specifically, there is an increase in viscosity, corrosion aggressiveness, acid number; there is a decrease in thermal oxidation stability and stability for the induction period of sedimentation; tribological characteristics become worse [4, 6]. The most undesirable transformations occur to those motor and gear oils, which are used at elevated temperatures and in the presence of water and metals that are capable of generating a catalytic effect in the processes of oxidation. The most dangerous products of oil degradation are aldehydes, ketones and, especially, carboxylic acids [4].

At the same time, used oils are a valuable raw material for the production of commodity products by applying the processes of regeneration and subsequent addition of the required additive package. Due to this, a large part of the global need for oils of various purposes is satisfied, while production of 10 dm^3 of commercial oil requires 220 dm^3 of petroleum [7].

Common are such methods of regeneration od used oils that imply using adsorbents (bleaching clays, zeolites, etc.) and coagulants in order to remove harmful substances. However, along with contaminants, part of the regenerated oil is also removed, while the used adsorbent acquires toxicity, which complicates its disposal and leads to the accumulation of harmful waste [8].

The processes were also proposed that are based on treating used oils with concentrated sulfate acid. Acid, however, greatly enhances corrosion aggressiveness of the medium, leads to the formation of hard-to-dispose acidic goudron, which can contain a significant portion of the unreacted sulfuric acid. The output of regenerated oils obtained using the treatment with sulfate acid does not typically exceed 45–65 % [9]. In addition, there is an accumulation of various sulfo-compounds due to the reaction between sulfate acid and useful hydrocarbons. This leads to the need for further alkali purification in order to neutralize, remove acidic products and the residue of sulfate acid. The essence of thermos-oxidative methods of regeneration is to additionally oxidize the products of degradation of used oils to resin-asphaltene substances with subsequent energy-intensive vacuum distillation of the entire mass of hydrocarbons [10].

There is a technique of regeneration of used mineral oils by ozone treatment with further purification by the solutions of hydrazychloride and polyvinyl alcohol. This leads to the complication of the technology and processes of waste disposal [11].

There were attempts to use the fluxes of electrons in the processes of treatment and regeneration of used oils [12]. The method is based on inducing a reaction of destruction of aging products, polymerization of hydrocarbon compounds. The result is the insoluble condensed residue that causes the adsorption of products of aging and mechanical impurities. It was also stated [13] that the purification of used oils from resins can be conducted by a flux of accelerated electrons, without reagents. These methods, however, require specialized equipment, their implementation is complex, they are energy-intensive and non-selective.

To reduce the acid number of used oils, an electrical method was proposed. Because oils are characterized by very significant specific resistance, it was necessary to impose a large difference of potentials of the order of 1,000 V. This technique cannot be considered satisfactory because the products of treatment remained undefined. In addition, the possibility of oxidation reactions of oil to carcinogenic aromatic compounds, especially multicore polyaromatic hydrocarbons, was not accounted for.

Known technical methods for the regeneration of used oils mainly imply the irreversible removal of oxidation products or insufficiently qualified application of oils. At the same time, such products of hydrocarbon oxidation as carboxylic and carbonyl derivatives can serve as valuable raw materials in the process of regeneration. Especially appropriate are to be considered those technologies of regeneration that imply the transformation of oxygen-containing compounds to the less harmful substances or back to useful hydrocarbons. It is promising to study the processes of electrochemical conversion of oxygen-containing compounds as the products of hydrocarbon degradation in the extracts of used oils, applying the results of research into individual oxygen-containing substances [14–17]. This would make it possible to utilize electrochemical processes in the technologies for regenerating used oils without new waste formation.

3. The aim and objectives of the study

The aim of present study is to develop effective methods for the regeneration of used oils that imply electrochemical transformation of oxygen-containing substances isolated from used oils by the extraction with an aqueous-alcohol solution.

To accomplish the aim, the following tasks have been set:

– to develop an affordable and environmentally safe method for the extraction from the medium of used oils oxygen-containing products of their oxidation and to estimate the depth of substance removal and reduction of corrosion aggressiveness of oils;

– by using potentiostatic polarization measurements, to investigate the progress of anode and cathode electrode reactions involving carboxylic and carbonyl compounds in comparison with the results of research into model solutions, and to establish working potentials for the implementation of these processes;

– to perform and explore electrolysis processes of regeneration of oxygen-containing oil degradation products in extracts to hydrocarbons, and to estimate the rate and depth of the course of reactions on electrodes.

4. Materials and methods to study extraction-electrochemical regeneration of oxygen-containing products of used oils

4. 1. The examined materials; methods applied, and equipment used in experiments

In the course of present study, we investigated used mineral oil with a density of 885.3 kg/m^3 (GOST 3900), acid number 1.76 mg KOH/g of oil (GOST 11362). Indicator of corrosion aggressiveness was determined on plates made of copper, lead, and steel 08kp in line with GOST 2917. Values of corrosion aggressiveness: on the copper plates, it corresponds to group II, point 2s, on the lead plates, group III, point 3v; on the steel 08kp plates, group I, point 1a. The results obtained indicate significant corrosion activity of the used oils.

Alkaline extraction of carboxylic acids was performed by using an aqueous solution of 3–5 % KOH at ambient temperature. To avoid intensive emulsifying, we used a ratio KOH of 2:1. After separating the alkaline aqueous extract, for complete removal of oxygen-containing compounds, the oil layer was extracted with a mixture of isopropyl alcohol and water in the ratio of 1:1. Both extracts were mixed, filtered, and neutralized. Following the extraction, we removed a small amount of the residue of emulsified water and alcohol from oil, and determined its acid number and corrosion aggressiveness.

4. 2. Research methods for electrochemical and electrolysis processes

Electrochemical polarizing measurements were performed using the potentiostat P-5827 M (made in Belarus)

under potentiostatic mode applying a standard procedure. To investigate the anode process of anode decarboxylation of organic acids, we used working electrodes made from natural graphite (carbon content is 92 %) and shungite (carbon content is 35 %). To study the cathodic process of electroreduction of aldehydes and ketones – electrodes made of aluminum. Chlorine silver electrode served as a reference electrode; the measured potentials were converted to the standard hydrogen scale. Based on the results of polarization study, we defined patterns of the mechanisms for the course of electrode processes and working potentials for performing the anode and cathode reactions.

The processes of extract electrolysis were performed at controlled potential and agitation. The rate and depth of the progress of electrode reactions were estimated by the descending current density of electrode processes.

A decrease in the magnitude of pH in the process of electrolysis also reflects the progress of electrode reactions, the cause of which is the release of carbon dioxide during transformation of carboxylic acids into hydrocarbon.

5. Results of research into extraction of oxygen-containing compounds of used oils and processes of electrochemical regeneration

5. 1. Study of extraction processes

As a result of extraction of the used oil, sequentially with aqueous alkaline and aqueous-alcohol solution of propanol-2, we managed to reduce the acid number from 1.76 mgKOH/g to 0 mgKOH/g. In other words, all carboxylic acids were removed. Accordingly, corrosion aggressiveness of oil after extraction significantly reduces. This is caused by the transition from a significant degree of corrosion (group II, point 2s for copper, group III, point 3v for lead) to group I, point 1a, for all metals tested.

5. 2. Study of electrochemical processes on electrodes during electrolysis of extracts

In the anode process of electrolysis, carboxylic acids are capable of oxidation with decarboxylation to hydrocarbons with a double molecular weight in line with the Kolbe's reaction [14, 18, 19]:

$$R-COO^- \xrightarrow{-e^-} R\cdot + CO_2,$$

$$R\cdot + R\cdot \longrightarrow R-R,$$

where R is the hydrocarbon radical.

A typical anode metal, which was used in most studies, is smooth platinum. However, the use of platinum in the industrial processes is economically impractical. More affordable for practical purposes is graphite and its natural analog – shungite, on which rapid anode decarboxylation of carboxylic acids occurs [14, 18, 19].

Fig. 1 shows anode polarization curve of shungite electrode in the extract of used oil. The curve demonstrates a clear section of the boundary diffusion current of oxidation of carboxylic acids of used oils at potentials 2.0–2.5 V. The character of the curve is similar to the curves obtained in the studies into model solutions of individual organic acids (Fig. 2). Such a correspondence indicates the analogy between electrode processes and the formed products. Anode reaction of decarboxylation of organic acids, separated from used oils, similarly for the case of solutions of individual carboxylic acids, occurs quickly. PH indices of solutions during electrolysis remains within pH=8.5–9.5.

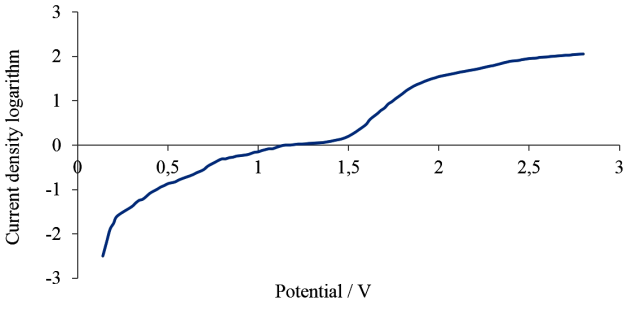

Fig. 1. Anode potentiostatic polarization curve of shungite in an aqueous-alcohol extract of used oil

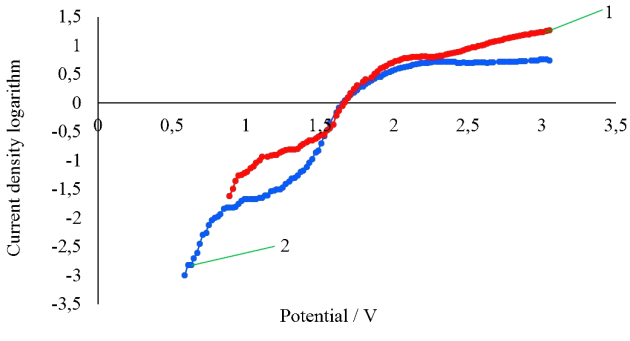

Fig. 2. Anode potentiostatic polarization curves in the model aqueous solution of 0.5 mol/l hexane acid: 1 — shungite; 2 — graphite

To regenerate aldehydes and ketones, we applied electrolysis processes for the cathodic reduction of carbonyl compounds extracted from used oils. The reactions of carbonyl substances reduction are typically performed on metals with a high hydrogen overpotential (Hg, Cd, Pb, Zn). Mixtures of alcohols, hydrocarbons and hydrodimers – compounds of the pinaconic type – form on such metals [15, 18]. Research into electroreduction of carbonyl compounds in model solutions revealed that the specified toxic metals can be replaced with affordable and safe aluminum, which is also characterized by a relatively high hydrogen overpotential. It is important that on Al the reaction of reduction of carbonyl substances occurs precisely in the direction of formation of useful hydrocarbons (Fig. 3) [16, 17].

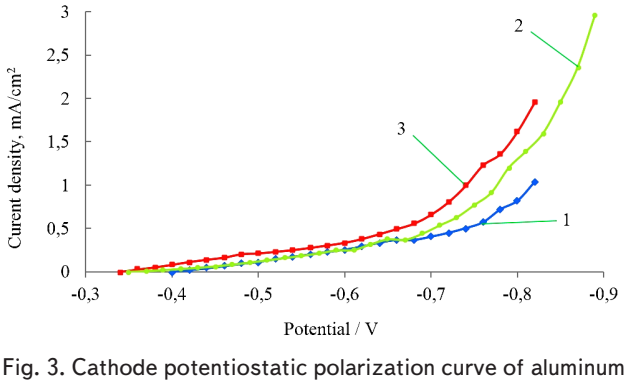

Fig. 3. Cathode potentiostatic polarization curve of aluminum in the model alcohol-aqueous solution: 1 — background; 2 — pentanon-2 (0.5 mol/dm^3); 3 — isovaleric aldehyde (0.5 mol/dm^3)

Fig. 4, *a* shows a cathode polarization curve of aluminum electrode in the extract of used oil. It has waves of boundary current, inherent to the processes of reduction of carbonyl compounds.

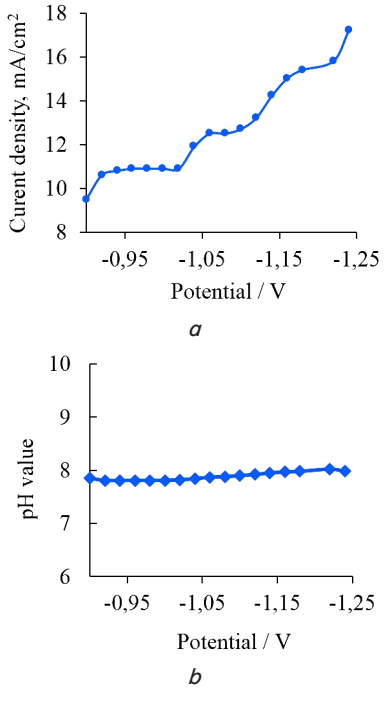

Fig. 4. Study of aqueous-alcohol extract of used oil: *a* – cathode potentiostatic polarization Al curve; *b* – dependence of the magnitude of pH on potential when acquiring the polarization curve

By using the polarization measurements, we demonstrated similarity in the course of cathodic reduction of oxygen-containing substances in model solutions and aqueous-alcohol extracts of used oils. Stable pH value during polarization measurements indicates the absence of side reactions, the consequence of which could be the alkalization of the medium (Fig. 4, *b*).

5. 3. Procedure for conducting electrolysis processes of regeneration of oxygen-containing products of extracts of used oils

Preparative electrolysis processes in the extracts of used oils were performed in the electrolyzer with no separation between the anode and cathodic spaces. We used as electrodes: the anode is graphite or shungite, the cathode is aluminum. Working anodic potentials of the decarboxylation of organic acids were fed from the stabilized voltage source – a potentiostat, and they were measured relative to the chlorine silver electrode. The magnitudes of working potentials were identified based on the results of potentiostatic polarization measurements (Fig. 1, 4). The anode potential was 2.4 V. During electrolysis process, at a stable potential of 2.4 V, we observed natural descending current due to the progress of electrode processes (Fig. 5, *a*). This agrees well with the results of research into model solutions of the oxygen-containing organic compounds (Fig. 2, 3) [13–15].

Electrolysis is accompanied by the oxidation of the medium, which can be explained by active release of CO_2. Upon completion of the process and cessation of carbon dioxide release, reaction of the medium stabilized (Fig. 5, *b*).

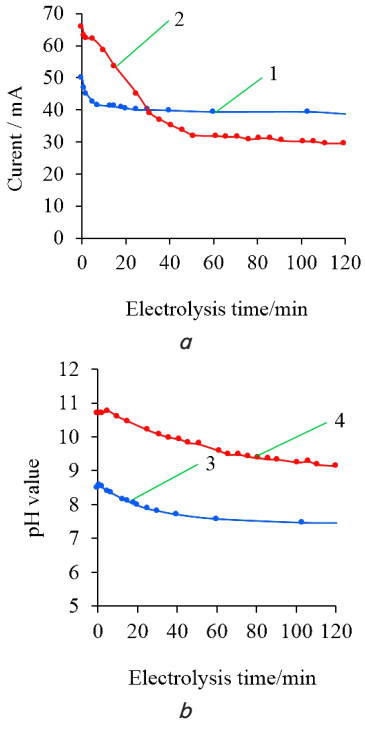

Fig. 5. Electrolysis of the extracts of used oils at agitation and anode potential 2.4 V: *a* – dependence of current in the course of electrotransformation of oxygen-containing substances on shungite (1) and graphite (2) anode and Al-cathode; *b* – dependence of pH of the solution on time of conducting electrolysis of oxygen-containing substances on shungite (3) and graphite (4) anode and Al-cathode

6. Discussion of results of research into processes of electrochemical regeneration of oxygen-containing products of the used oil degradation

Studies have shown that it is more appropriate to preliminary extract used oils by solvents that provide deep removal of oxygen-containing hydrocarbons and allow normal application of electrolysis processes. This is achieved when employing successive processes of extraction by an alkaline aqueous solution and a mixture of water with isopropyl alcohol in the ratio of 1:1 with their subsequent mixing and neutralization.

The curves of descending current in the course of electrochemical processes (Fig. 5) demonstrate that the duration of electrolysis is 30–60 min. The dependence of current during electrode reaction to a flat electrode on the concentration of depolarizer is described by equation:

$$i = n \cdot F \cdot C \sqrt{\frac{D}{\pi \cdot \tau}},$$

where n is the number of electrons participating in the potential of the defining stage of reaction; F is the Faraday's number; C is the molar concentration of depolarizer (oxygen-containing compounds), mol/dm^3; D is the diffusion coefficient of the substance; τ is the duration of electrolysis. The equation shows that current is directly proportional to the concentration, and an increase in the duration of electrolysis leads to a decrease in the concentration of salts of carboxylic acids, leading to a decrease in the density of current.

The extraction of used oils was carried out in the temperature range from 20 to 50 °C. At lower temperatures the viscosity of the used oil increases dramatically, which prevents the full extraction of oxygen-containing substances. When the temperature of the process exceeds 50 °C, a strong emulsification of the medium is observed, which leads to deterioration in the effectiveness of the process of removal of oxygen-containing substances and increases energy costs.

For the extraction of oxygen-containing compounds from used oils, the most selective extractant is an alkaline aqueous-alcohol solution in the ratio of 1:1. The presence of alkali in the composition of extractant enables the neutralization of carboxylic acids whose salts are water soluble in contrast to the acids themselves, which increases the selectivity of the process. Isopropyl alcohol provides sufficient solubility of carbonyl compounds, which contributes to the transfer of the used oil into an aqueous-alcohol extract. Increasing the content of alcohol in an extractant leads to partial dissolution of hydrocarbons of the used oil, which is undesirable for electrochemical processes in the technology of regeneration of used oils.

Chromatographic analysis of the products of electro-oxidation of model aqueous solutions of individual acids after electrolysis on graphite and shungite anodes at a potential of 2.4 V revealed that the products are hydrocarbons (Fig. 6) [17].

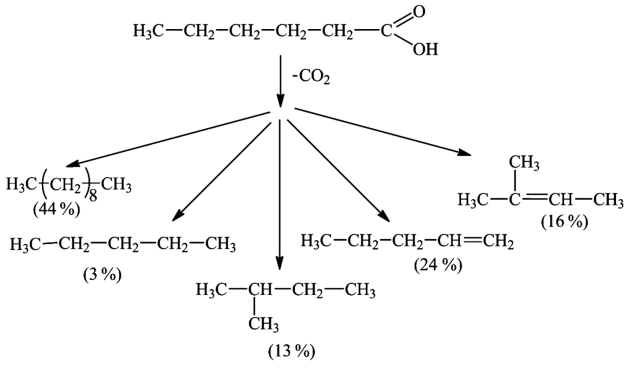

Fig. 6. The course of anode oxidation of carboxylic acid in a model aqueous solution (the percentage of each of the products in the mixture is shown in brackets)

Based on the results of research into model aqueous systems, we can argue that the extracts of used oils on the anode undergo the processes of regeneration of carboxylic acids to the corresponding carbohydrate acids. The processes of cathodic reduction of carbonyl compounds, performed in model systems (Fig. 3), also indicate that the resulting products of transformation of aldehydes and ketones are the respective hydrocarbons (Fig. 7) [18, 19].

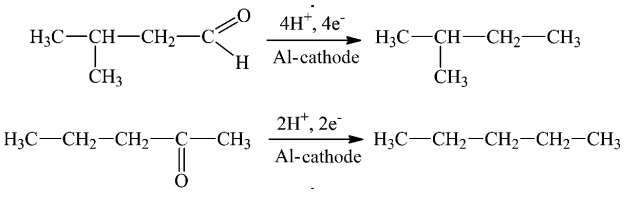

Fig. 7. The course of cathodic reduction of carbonyl compounds on the aluminum electrode

Thus, when conducting the electrolysis of extracts of used oils on electrodes, there is a simultaneous oxidation regeneration of organic acids on the anode, and reduction – of aldehydes and ketones on the cathode, to the respective carbohydrate acids.

7. Conclusions

1. We have developed processes of the extraction removal, by an alkaline aqueous-alcohol solution, of the oxygen-containing products of oil degradation, which ensure almost complete extraction of oxygen-containing substances – almost 100 %. This is confirmed by the reduced acid number, from 1.76 to 0 mg KOH/g of oil, and by a significant decrease in corrosion aggressiveness of the used oil.

2. Polarization study into electrochemical processes revealed that working potentials of the electro-transformation oxygen-containing compounds in model solutions and extracts are close to each other and correspond to the anode polarization of 2.4 V.

3. The benefits of the proposed method for electrochemical regeneration of oil degradation products include the transformation of undesired products in the electrode process to the carbohydrate products that are included in the composition of base oils. The processes can be carried out on the affordable and non-toxic electrode materials (Al-cathode and graphite or shungite anode). The study showed a high rate (up to 0.5–1 hour) and depth of the progress of processes of electro-transformation of oxygen-containing derivatives, both in solutions of individual substances and in the extracted mixtures from used oils. The proposed method for the extraction and electrochemical transformation of oxygen-containing substances in used oils does not lead to the formation of new waste that is difficult to dispose of; it increases the output of the regenerated oil and prolongs the use of oils.

References

1. Chemical Sector Research Lubricating Preparations lubricants // KPMG. 2015. URL: http://investingeorgia.org/en/ajax/downloadFile/640/
2. Yu M., Ma H., Wang Q. Research and Recycling Advancement of used Oil in China and All Over the World // Procedia Environmental Sciences. 2012. Vol. 16. P. 239–243. doi: 10.1016/j.proenv.2012.10.033
3. Effect of Treatment Methods on Used Lubricating Oil for Recycling Purposes / Abdulkareem A. S., Afolabi A. S., Ahanonu S. O., Mokrani T. // Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2014. Vol. 36, Issue 9. P. 966–973. doi: 10.1080/15567036.2010.549920
4. Performance Deterioration Analysis of the Used Gear Oil / Zeng Q., Dong G., Yang Y., Wu T. // Advances in Chemical Engineering and Science. 2016. Vol. 06, Issue 02. P. 67–75. doi: 10.4236/aces.2016.62008

5. Studies on the Aging Characteristics of Base Oil with Amine Based Antioxidant in Steel-on-Steel Lubricated Sliding / Singh A., Gandra R. T., Schneider E. W., Biswas S. K. // The Journal of Physical Chemistry C. 2013. Vol. 117, Issue 4. P. 1735–1747. doi: 10.1021/jp309824r
6. Muhammad Q., Tariq M. A., Mazhar H. Physico-chemical characteristics of Pakistani used engine oils // Journal of Petroleum Technology and Alternative Fuels. 2016. Vol. 7, Issue 2. P. 13–17. doi: 10.5897/jptaf2015.0121
7. Ogbeide S. O. An investigation to the recycling of spent oil // Journal of Engineering Science and Technology Review. 2010. Vol. 3, Issue 1. P. 32–35.
8. Regeneration of Used Engine Oil / Isah A. G., Abdulkadir M., Onifade K. R., Musa U., Garba M. U., Bawa A. A., Sani Y. // Proceedings of the World Congress on Engineering. London, UK, 2013. Vol. 1. P. 54–76.
9. Sterpu A. E., Dumitru A. I., Popa M.-F. Regeneration of used engine lubricating oil by solvent extraction // Ovidius University Annals of Chemistry. 2012. Vol. 23, Issue 2. P. 149–154. doi: 10.2478/v10310-012-0025-2
10. Chervinskyi T. I. Hrynyshyn O. B., Korchak B. O. Reheneratsiya vidpratsovanykh naftovykh olyv termookysnym metodom // Naftohazova haluz Ukrainy. 2016. Issue 2. P. 32–34.
11. Ibraeva O. T., Ibraev I. K., Suyundikov M. M. Regeneraciya maslosoderzhashchih othodov shestiklet'evogo stana holodnoy prokatki 1400 // Nauka i tekhnika Kazahstana. 2010. Issue 3. P. 39–43.
12. Pererabotka smesey otrabotannyh masel puchkami uskorennyh elektronov / Zaykin Yu. A., Zaykina R. F., Nadirov N. K., Sarsembinov Sh. Sh. // Mezhdunarodnaya nauchno-prakticheskaya konferenciya i vystavka «Novye tekhnologii v pererabotke i utilizacii otrabotannyh masel i smazochnyh materialov». Moscow, 2003. P. 113–114.
13. Zaykina R. F. Fahrutdinov I. M., Yagudin Sh. G. Poluchenie smazochnyh materialov putem obrabotki mazutov i smesey otrabotannyh nefteproduktov uskorennymi elektronami // Mezhdunarodnaya nauchno-prakticheskaya konferenciya i vystavka «Novye tekhnologii v pererabotke i utilizacii otrabotannyh masel i smazochnyh materialov». Moscow, 2003. P. 115–116.
14. Davydenko O. M., Ledovskykh V. M. Carboxylic acids electrooxidation on shungite electrode // Proceedings of the National Aviation University. 2017. Vol. 70, Issue 1. P. 120–130. doi: 10.18372/2306-1472.70.11432
15. Ledovskykh V., Davydenko O., Rogova E. Cathode reduction of aliphatic aldehydes on cadmium electrode for regeneration of used motor oils // Proceedings of the National Aviation University. 2014. Vol. 60, Issue 3. P. 93–97. doi: 10.18372/2306-1472.60.7574
16. Ledovskykh V. M., Davydenko O. M. Electroreduction of aliphatic aldehydes on aluminum cathode // Proceedings of the National Aviation University. 2015. Vol. 63, Issue 2. P. 106–111. doi: 10.18372/2306-1472.63.8875
17. Ledovskykh V. M., Davydenko O. M. Elektrokhimichna reheneratsiya karbonilnykh spoluk vidpratsovanykh naftovykh olyv na aliuminievomu katodi // Naftohazova haluz Ukrainy. 2015. Issue 1. P. 21–24.
18. Organic Electrochemistry / H. Lund, O. Hammerich (Eds.). 4th ed. New York: Marcel Dekker, 2001. 1406 p.
19. Beyzer M. M., Lund H. Organicheskaya elektrohimiya. Kn. 1 / V. A. Petrosyan, L. G. Feoktistov (Eds.). Moscow: Himiya, 1988. 469 p.