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CATHODE REDUCTION OF ALIPHATIC ALDEHYDES ON CADMIUM ELECTRODE FOR REGENERATION OF USED MOTOR OILS

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Abstract. *The results of studies of aliphatic aldehydes electroreduction as products of oxidation of motor oils on cadmium cathode in sulfuric acid-water-alcohol media are provided. With potentiostatic polarization measurements was determined the diffusion mechanism of the cathodic process and conditions of its proceeding. Chromatographic analysis has revealed the major products of aldehyde electroreduction – the corresponding alcohols and hydrocarbons.*

Keywords: aldehydes; carbonyl compounds; chromatography; electroreduction; hydrocarbons; oil; oxidation; regeneration; sulfuric acid-water-alcohol solution.

1. Introduction

World volume of lubricants, which are produced on the basis of major mineral oils and, partially, synthetic ones reach 0,8 % from the total of crude petroleum application [3].

When used, oils undergo physical and chemical transformations which are induced by: oxidation of hydrocarbons, the additives decompositions, engine parts wear products accumulation, mechanical impurities and water pesence.

These changes impair the performance properties of oils and lead to the impossibility of their application.

The main reason for the negative transformation of oils is an effect of oxygen action on the hydrocarbon components at increase temperatures.

Consequently, there are formed carbonyl compounds, end products of oxidation of which are carboxylic acids.

The last belong to the most dangerous impurities in oils, as they increase the acid number, corrosivity of construction materials, viscosity of the medium, change the thermal conductivity [2, 3, 4].

2. Analysis of researches

However, waste oils are a valuable raw material for recycling. Yield of oil from recycled raw materials is 80 %, while from petroleum is only 10-15 % [2, 3, 5, 8, 9, 10].

Therefore, the development and improvement of the waste oils regeneration process is an important scientific and engineering task.

Purpose of work – a study the electrochemical reduction of aliphatic aldehydes in sulfuric acid-water-alcohol solution on cadmium electrode and analysis of the formed products by gas-liquid chromatography.

3. The processes of oxidation of oils

Hydrocarbons that compose the bulk of major oils greatly differ in molecular structure (paraffin, naphthenic, aromatic and naphthenic-aromatic compounds), of which 60-70% are naphthenic-paraffin hydrocarbons [6].

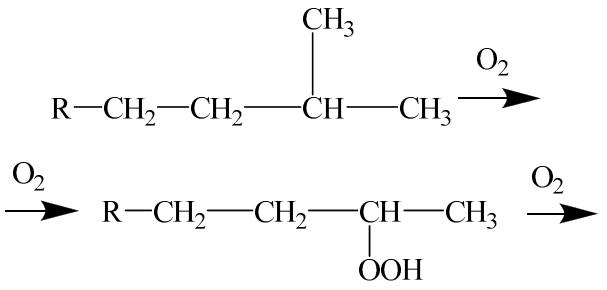
Oxidation of oils in the process of their use takes place through a chain reaction.

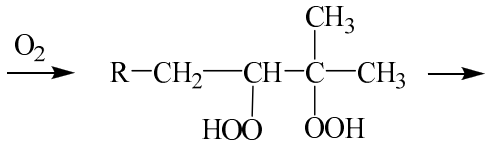
The primary products are organic hydroperoxides (C – O – OH), which are formed at addition of oxygen to the C-H bond of hydrocarbon.

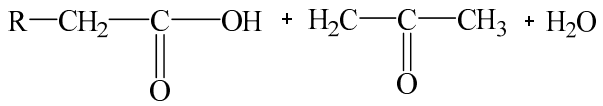
Later they undergo decomposition into groups of compounds.

The first group comprises aldehydes, ketones, acids, hydroxy acids, asphaltenic acid, and the second one does neutral products, i.e. – phenols, resins, pyrobitumens, carbenes [6, 12].

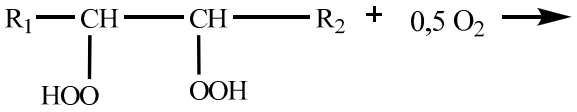
Hydroperoxide may also undergo oxidation by oxygen at C-H bond to form diatomic hydroperoxide groups at two adjacent carbon atoms which promotes decomposition of substances at the C-C bonds into ketones and acids [1]:

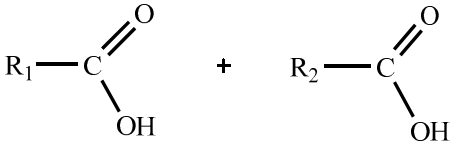




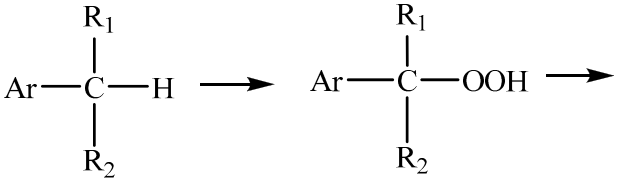


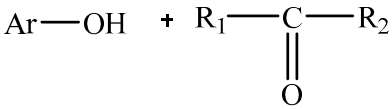
The oxidative decomposition of diatomic hydroperoxides to two carboxylic acids is acceptable, which explains the formation of various acids from formic to high molecular ones [1, 6]:



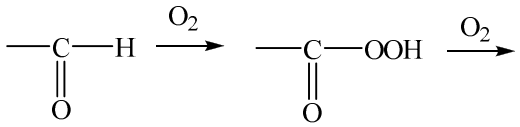


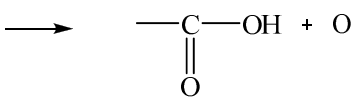
Oxidation of alkylaromatic hydrocarbons with short chains also proceeds via the stage of hydro peroxides and gives phenols and ketones:





Aldehydes, in their turn, may undergo oxidation to carboxylic acids with the same number of carbon atoms and these processes also occur through the stage of formation and decomposition of peroxide compounds [11]:





During storage at low or normal temperature petroleum oils "age" relatively slow.

But at 50 ˚ C and above oxidation get accelerated significantly.

Temperature coefficient (γ) in Van't Hoff plot equation, that shows by how many times the rate of reaction increases under increased temperature per each 10 ˚ C, for oxidation of hydrocarbons under temperature of 140-150 ˚ C is $\gamma = 2$.

It is vastly higher for the temperatures lower than 140 ˚ C and lower for the temperatures higher than 150 ˚ [11].

When operating machinery the initial products of oil oxidation undergo further chemical transformations to acids, resins, coke substance, that causes darkening of oils and undesirable deterioration of their physical and chemical properties: an increase in viscosity and media's corrosive power, increasing their susceptibility to fouling, varnishes, sediments, etc.

4. Electroreduction of carbonyl compounds

Organic carbonyl substances, which include aldehydes and ketones, can undergo reduction at their solutions electrolysis cathodic process.

Carbonyl group in the molecules of these compounds is a polar group, due to displacement of valence electrons to the most electronegative oxygen: the atoms gain partial effective charges - positive on carbon and negative on oxygen.

During electrolysis, the presence of positively polarized carbon atom determines the possibility of their adsorption on the negatively charged cathode surface [7].

Metals with high hydrogen overvoltage are used for electroreduction of carbonyl compounds.

In this case the electrons are transferred onto reducing substance in acidic mediums is previously subjected to protonation, which makes the course of electrochemical reactions easier [7, 11].

So on cadmium cathode propionic aldehyde was reduced to propane, methylpropylketone and diethylketon to pentane.

For reduction of carbonyl compounds to secondary alcohols the most suitable electrode materials were mercury and lead, for the products of hydrodimeryzation like pinakone those werewas zinc, mercury and lead.

Elevation of such values as cathode potential, solution pH, temperature and conducting of electrolysis at high cathode current density leads to the reduction of carbonyl compounds into hydrocarbons while lowering of these values - to alcohols and hydrodimers.

The specified testifies to perspective of development of the electrochemical stages for the processes of regeneration of used oils.

The maiden attempts to applyelectrolysis by imposition of wide difference of potentials on used oils, showed some improvement of their descriptions, as an acid number and viscosity.

5. Experimental

Research of electroreduction of aliphatic aldehydes was performed for a case of isovaleric aldehyde $CH_3CH(CH_3)CH_2CHO$, M = 86,13 g/mol, m.p. = = -51˚C, b.p. = 92,5˚C..

Polarization measurements were performed using potentiostat P-5727 M in potentiostatic mode.

We used termostatic 3x-electrode cell with a porous glass divided partition cathode and anode volumes.

Auxiliary electrode was Pt, potentials of the working electrode (Cd), were measured against comparison chlorine-silver electrode and recalculated onto the standard hydrogen scale.

Cathode polarization curves for cadmium were measured after installation of stationary potential.

Background solution composition was: 920 cm^3 of isopropyl alcohol, 19.8 cm^3 of sulfuric acid, 22.4 cm^3 of distilled water.

Preparative electroreduction process for aldehyde was performed by electrolysis at controlled potential which corresponded to limiting current of substance electroreduction.

Products of electrochemical conversion of substances were studied by chromatographic method [12] using gas-liquid chromatograph LHM-8MD.

6. Results and discussion

Fig. 1 shows the potentiostatic polarization curve of cadmium cathodic polarization in the background solution.

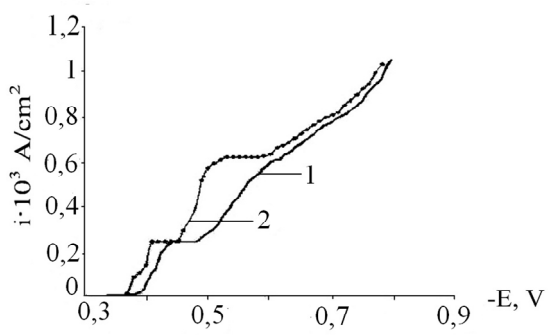


Fig. 1. Polarization curves of cadmium:
1 – in background solution;
2 – in presence of 0.5 mol/l of isovaleric aldehyde

The curve has one wave of electroreduction, which corresponds to the limiting diffusion current of dissolved oxygen reduction at electrode reaction:

$$O_2 + 4H^+ + 4e = 2H_2O.$$

The polarization curve for Cd electrode in the solution of aliphatic aldehyde had two waves of reduction and is characterized by two areas corresponding to limiting current of oxygen and organic matter diffusion (Fig. 1).

These observations are consistent with literature data concerning the possibility of cathodic reduction of carbonyl compounds in dilute acid solutions.

The equation for the density limit diffusion current for a flat electrode takes the form [1]:

$$i = nFc\sqrt{\frac{D}{\pi\tau}},$$

where n – the number of electrons participating in potential forming reaction stage;

F – Faraday number; c is molar concentration of depolarizer, mol/dm^3;

D – diffusion coefficient of the substance; τ is time of electrolysis.

From equation it is seen that the diffusion current density should vary inversely proportional to the electrolysis time square root.

We have used this dependence to control the process of electroreduction of carbonyl compounds.

In Fig. 2 we can see that the curve of threshold current declines at controlled potential of aldehyde electroreduction quite rapidly, it is evidenced by reduction of the diffusion limiting current, which is determined by the fall of aldehyde concentration in solution.

In static solution it takes about 20-25 min for the process to complete.

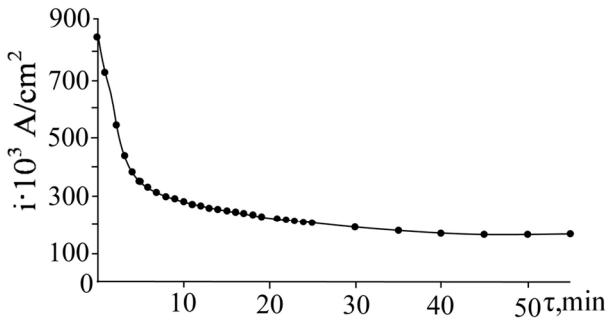


Fig. 2. The dependence of the limiting current density of isovaleric aldehyde recovery in sulfuric acid-water-alcohol solution

To determine the products of electrochemical reduction of aldehyde reaction solution was transferred into a flask for the distillation with deflegmator.

At the beginning some 3-4 cm^3 of distillate was sampled for chromatographic analysis in view of possible formation of saturated hydrocarbon isopentane, boiling point (b.p.= 27.8 ˚C) of which is lower than that of isopropyl alcohol solvent (b.p. = 82.4 ˚C) which has to come out before the solvent at chromatography [1].

At the subsequent distillation of the reaction mass an azeotrop -isopropanol-water - was removed. It contains 87. 9% of ethanol boils at 81˚C.

Consequently water is removed together with isopropyl alcohol.

A small residual solution was subjected to chromatographic analysis.

Chromatogram of isovaleric aldehyde electroreduction products is shown in Fig. 3.

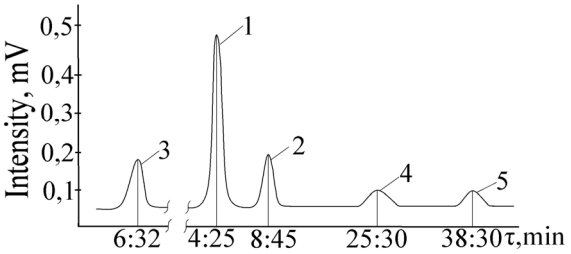
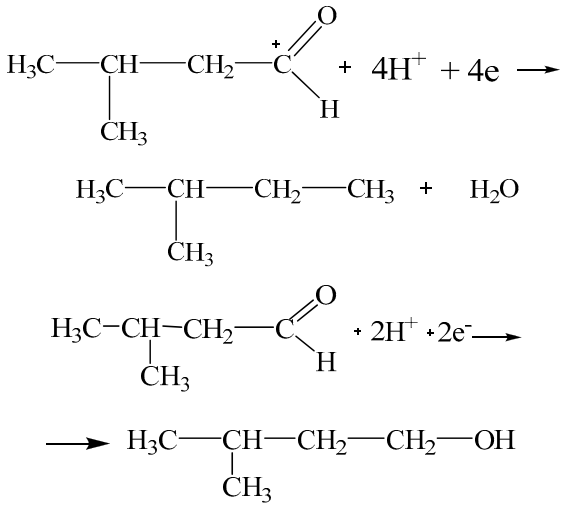
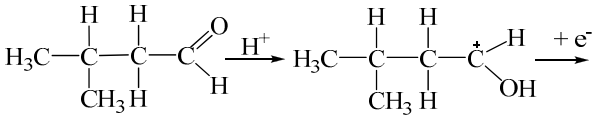
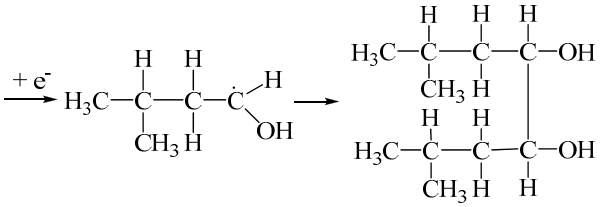


Fig. 3. Chromatographic analysis of isovaleric aldehyde electroreduction products on Cd – electrode in sulfuric acid-, water-alcohol solution:
1 – isopropanol (solvent);
2 – isopenthanol;
3 – isopentane;
4, 5 – side products

The formation of the substances listed in Fig. 3, can be explained with the following equations:







We can assume that one of the side products is substituted glycol 2-isobutyl-4-metylpentanal.

The formation of this type of compounds is characteristic of carbonyl compounds electroreduction in typical metals with high hydrogen overpotential.

7. Conclusions

Electroreduction of aliphatic aldehydes on Cd-electrode with high overvoltage of hydrogen in acidic media proceeds with a significant rate and leads to the formation of hydrocarbons, alcohols and substituted glycols,

2. It is shown that the electrochemical reduction of oxygen-containing compounds into safe and corrosion-inactive substances may be appropriate for the use in the regeneration of used motor oils.

References

[1] *Antropov, L. I.* Theoretical electrochemistry. Kyiv, Lybed. 1993. 542 p. (in Ukrainian).

[2] *Chayka, O.G.; Chayka, Y.A.*. Comparative analysis of methods for purification used oils in Ukraine and outside. Proceedings Scientifical works. Lviv, Lviv Polytechnic. 2009. P. 224 – 228 (in Ukrainian).

[3] *Chayka, O.G.; Kovalchuk, O.Z.; Chayka Y.A.* Monitoring the formation of waste oils. Proceedings Scientifical works. Lviv, Lviv Polytechnic. 2009. P. 221-224 (in Ukrainian).

[4] *Gureev, A. A.; Fuks, I.G.; Lashhy, V.L.*. Himmotology. Moscow, Chemistry. 1986. 368 p. (in Russian).

[5] *Ivanov, K. I.* Intermediates products and intermediate auto-oxidation reactions of hydrocarbons. Moscow, Gostoptekhizdat. 1949. 246 p. (in Russian).

[6] *Nogaret, S.D.; Dzhuvet, R.S.* Gas-liquid chromatography. Theory and Practice. Leningrad, Nedra. 1966. 472 p. (in Russian).

[7] *Rakin, J.F.; Samuylov, A.V.* Change the engine oil characteristics in service, of automotive engines. Proceedings of the Institute of SKHPR NovSU. 2006. Vol. 1. 302 p. (in Russian).

[8] *Rybakov, K.V.; Kovalenko, V.P.* Regeneration of used oils and their reuse. Survey information. Moscow, AgroNIITEIITO. 1989. 86 p. (in Russian).

[9] *Shashkin, P.I.; Bri, I.V.* Regeneration of waste petroleum oils. Moscow, Chemistry. 1970. 303 p. (in Russian).

[10] *Shkolnikov, V.M.; Gordukalov, A.A.; Yuzefovich, V.I.; Petrosova, M.A.* Analysis of foreign approaches to the problem of disposing of waste oil. World of oil products. 2004. N 1. P. 36-39 (in Russian).

[11] *Tomilov, A.P.; Mayranovsky, S.G.; Fioshin, M.J.; Smirnov, V.A.* Electrochemistry of organic compounds. Leningrad, Chemistry 1968. 592 p. (in Russian).

[12] *Venzel, S.V.*. The use of lubricating oil in engines of internal burning. Moscow, Chemistry. 1979. 240 p. (in Russian).

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В.М. Ледовських[1], О.М. Давиденко[2], Є.О. Рогова[3]. Катодне відновлення аліфатичних альдегідів на кадмієвому електроді для регенерації відпрацьованих моторних олив

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Наведено результати досліджень електровідновлення аліфатичних альдегідів як продуктів окиснення моторних олив на кадмієвому катоді в сульфатно-кислому водно-спиртовому середовищі. Потенціостатичними поляризаційними вимірюваннями визначено дифузійний механізм катодного процесу та умови його перебігу. Електролізом розчину альдегіду при контрольованому потенціалі показано, що катодний процес відновлення перебігає швидко з глибоким перетворенням вихідної речовини. Хроматографічним аналізом виявлено основні продукти електровідновлення альдегіду – відповідний спирт та вуглеводень. Висунуто припущення щодо утворення сполук типу пінакону.

Ключові слова: альдегіди; вуглеводні; електровідновлення; карбонільні сполуки; окиснення; олива; регенерація; сульфатно-кислий водно-спиртовий розчин; хроматографія.

В. М. Ледовских[1], А. Н. Давыденко[2], Е.А. Рогова[3]. Катодное возобновление алифатических альдегидов на кадмиевом электроде для регенерации отработанных моторных масел

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Приведены результаты исследований электровосстановления алифатических альдегидов как продуктов окисления моторных масел на кадмиевом катоде в сульфатно-кислой водно-спиртовой среде. Потенциостатическими поляризационными измерениями определены диффузионный механизм катодного процесса и условия его проведения. Электролизом раствора альдегида при контролируемом потенциале показано, что катодный процесс возобновления протекает быстро с глубоким превращением исходного вещества. Хроматографическим анализом выявлены основные продукты электровосстановления альдегида - соответствующий спирт и углеводород. Выдвинуто предположение относительно образования соединений типа пинакона.

Ключевые слова: альдегиды; карбонильные соединения; масло; окисление; регенерация; сульфатно-кислый водно-спиртовой раствор; углеводороды; хроматография; электровосстановление.

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