CHEMMOTOLOGY AND CHEMICAL TECHNOLOGY

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Volodymyr Ledovskykh[1]
Oleksandr Davydenko[2]

ELECTROREDUCTION OF ALIPHATIC ALDEHYDES ON ALUMINUM CATHODE

[1,2]National Aviation University
1, Kosmonavta Komarova avenue, Kyiv, 03680, Ukraine
E-mails: [1]uchneftexim@bigmir.net; [2]dom237@ukr.net

Abstract. *The article represents the results of the research on the reduction of aliphatic aldehydes on aluminum in aqueous-alcohol solutions. They show that relatively high overpotential of hydrogen on aluminum cathode promotes effective processes of conversion of carbonyl compounds into the corresponding saturated and unsaturated hydrocarbons, moreover saturated products output of electrolysis increases with negative values of the operative potential of the cathode. According to the data under controlled potential of electrolysis processes occur fast at high products output, that makes them perspective for the regeneration of used oxidized engine petroleum oils.*

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

1. Introduction

The use of petroleum products including oils has become very important. During application petroleum oils (especially motor oils) are exposed by physical and chemical transformations, caused by oxidation of hydrocarbons, resulting in the loss of their operating characteristics and needs replacement. [1]. As a result, large amounts of used oils are formed that create hazardous waste. At the same time they act as an important source of fresh oil production by regeneration oil and adding a required additive package. Therefore, development, improvement and cheapening of regeneration processes are relevant and important task [2].

Oxidation of hydrocarbons oils occurs under chain mechanism through intermediate stages of formation of organic hydroperoxides as a result of oxygen addition to the C-H bond. Later, they are exposed to decomposition into groups of compounds, the first of which includes aldehydes, ketones, acids, hydroxy acids, and asphaltenes acid, the second includes neutral products, phenols, resins, asphaltenes, carbenes [3].

2. Analysis of research and publications

In the previous research it was shown that carbonyl compounds could be reproduced electrochemically mainly in corresponding alcohol at electrolysis processes when used as cathode materials of metals, which are characterized by high hydrogen overtension: Pb, Cd, Hg, Zn and some others [4]. This thing makes possible to include the electrochemical processes to prospective methods of used oils regeneration [5]. At the same time, mentioned cathode metals belong to toxic substances, which are able to act as potential polluters of environment, and major products of cathode electroreduction reactions of carbonyl compounds are alcohols. This leads to search for and research of new electrode metals that would not be toxic and also contribute to a high output of hydrocarbons, which is important in used motor oils regeneration.

The purpose of this research is reduction of aliphatic aldehydes on aluminum cathode, analysis of formed substances, and determination of possibility of electrochemical method application for the cathode reduction of such carbonyl oxidation products of petroleum engine oils back into hydrocarbons under regeneration processes.

3. Electroreduction of carbonyl compounds

Reduction of organic compounds by electrolysis indicates the selectivity of processes course, depending on the cathode metal: on the cathodes of metals, characterized by a low hydrogen overpotential, which include d-elements of by-subgroup of eighth group of the periodic system (Pt, Ni, Fe, etc.), and some other refractory metals (W, Re), mostly double bonds of unsaturated hydrocarbons are reproduced and on the metals with high overpotential of hydrogen (Hg, Pb, Cd, Zn, Tl) carbonyl groups are reproduced. Moreover, the selective reduction happens according to specified regularities, if the organic compound contains both types of groups. [4, 6-8].

According to L.I. Antropov, concepts cathode metals form two extreme groups which differ not only by the hydrogen overpotential but also by the reaction mechanism of hydrogen electroreduction process and the character of its slow stage [4].

Cathode metals of Electrochemical Group I are characterized by high energy adsorption of hydrogen atoms on them, and their high surface concentrations. This group includes "hard" metals of platinum and iron subgroup. Under electrolysis, their surface is filled by adsorbed hydrogen atoms and slow stage of cathode reduction of H+–ions is catalytic:

$$H_{ads} + H_{ads} = H_2,$$

or electrochemical desorption:

$$H_{ads} + H^+ + e^- = H_2.$$

Surplus of hydrogen adatoms appears on metals of I group and they stand out as restoring agents. The most probable reduction of low-polar compounds such as unsaturated hydrocarbons (olefins) is possible on them by hydrogen hydrogenation to create fully hydrogenated product of electrode reaction.

Metals which are characterized by high hydrogen overpotential and low energy of hydrogen atoms adsorption (soft metals of d-elements) belong to the metals of II electrochemical group. They don't almost adsorb hydrogen atoms and kinetics of electroreduction of H^+-ions at cathode electrode polarization is determined by the slow stage of charge transfer: $H^+ + e^- = H_{ads}$ and its removal stage is not restrictive. Concentration of atomic hydrogen is insignificant on such metals and therefore, reduction of organic compounds is unlikely. Reduction of unsaturated organic compounds of hydrogen adatoms cannot occur on such cathode metals because they are practically absent on the cathode surface. Compounds are reproduced on them as a result of electrochemical process under direct transition of an electron to their molecule with following protonisaion: $R + e^- = R^-$, $R^- + H^+ = RH$. Such conditions promote adsorption and electroreduction of polar groups, which include the carbonyl groups. Lack of hydrogen adatoms on the cathode surface allows them to adsorb and reproduce with predominant formation of corresponding alcohols, and in some cases also hydrocarbons [4].

We assume that environmentally safe aluminum can serve as cathode metal for electroreduction of carbonyl compounds of used petroleum oil when regenerating. Aluminum in aqueous solutions of acids is characterized by relatively high hydrogen overpotential, though it is inferior to typical metals of II electrochemical group in these indicators. In previous research, it was shown the reduction of acetone to isopropyl alcohol and propane on this cathode metal [7].

In order to solve the issue of regeneration of used petroleum oils in this paper, the main attention is paid to the research of general regularities of cathode processes course and search of conditions of their performance in the direction of transformation of carbonyl compounds back into saturated hydrocarbons, i.e. in the direction opposite to oxidation oils processes during their application. The primary focus in this paper is devoted to the search of conditions for carrying out reduction processes towards conversion of carbonyl compounds primarily back into saturated hydrocarbons, i.e. in the reverse direction of petroleum oils oxidation processes during their operation.

4. Experimental

Chemically pure isovaleric aldehyde $(CH_3)_2CHCH_2CHO$, M = 86,13 g/mol, tpl = -51°C, tboil = 92,5°C was used as a model substance containing the carbonyl group.

Polarization measurements were performed on a P-5827M potentiostat, we used three electrode thermo-stated electrode (25 °C) cell with operating aluminum electrode UpA99 mark under purity 99,99 % Al; a platinum wire served as an auxiliary electrode separated from the working electrode with porous glass partition; potentials were measured against chlorine silver electrode and counted to the normal hydrogen scale. Composition of background sulfuric acid-aqueous-alcohol (isopropanol) solution was as follows : 920 ml of isopropyl alcohol, 56 ml of distilled deionised aqua, 24 ml of concentrated (98 %) sulfuric acid (pH = 2,98). During research under pH 7,98...1 % (10 g/l) Na_2SO_4 was added to the aqueous-alcohol medium instead of sulfuric acid. Preparative electrolysis of solutions of isovaleric aldehyde under concentration of 0,5 mol/l was performed at controlled potential (potentiostat) of aluminum electrode (E_{work} = -0,75 V), current of electrochemical process was measured by milliammeter M2020 with a scale division of 1 μA.

To analyze the products of aldehyde electroreduction, cationit was neutralized with alkali and was repeatedly dried with roasted absorb aqua reagent $CaCl_2$. After filtration, the solution of electrolysis products in isopropyl alcohol was subjected to analysis according to component composition at chromatography LHM-8MD mark while using nitrogen bearer gas of high purity (gas feed rate was 30 mL/min at the input of a device) Inerton Super was used as adsorbent which applied liquid fixed phase 5 % Apiezon L.

5. Results Discussion

Fig. 1 shows the potentiostatic polarization curves of aluminum in the background sulfuric acid-aqueous-alcohol solution. For comparison, the curve of a typical II electrochemical metal group with high hydrogen overpotential in the same medium (Cd) is also applied. In both cases, the curves have the limiting diffusion current wave of electroreduction of oxygen which corresponds to the equation in acidic solutions:

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

Limiting diffusion current density of oxygen in the tranquil aqueous-alcohol solution made up $O_2 i_d = 360$ A/cm^2, which much exceeds its value for aqueous solutions where $O_2 i_d \approx 5 \cdot 10^{-5}$ A/cm^2. This is explained by high growth of solubility of molecular oxygen in aqueous-alcohol solutions.

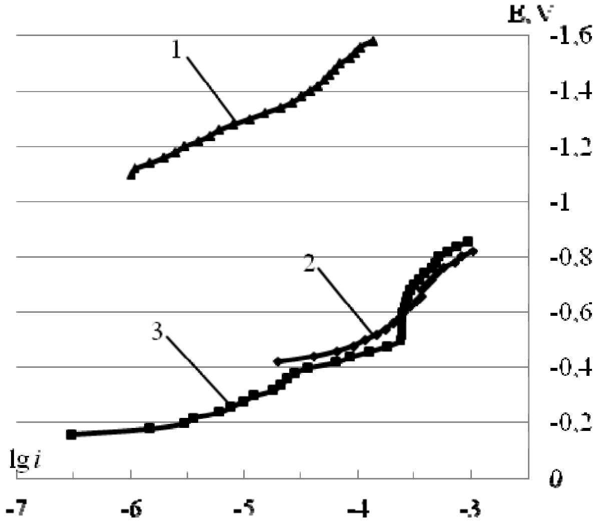


Fig. 1. Potentiostatic polarization curves of metals (25 °C): *1* – aluminum in aqueous-alcohol solution of 10 g/l Na_2SO_4 (pH = 7,98), *2* – aluminum – and *3* cadmium in sulfuric acid-aqueous-alcohol solution (pH = 2,98)

The united arrangement of curves 2 and 3 (fig. 1) shows that Al is characterized by less high overpotential of hydrogen than Cd. At the same time it much exceeds this indicator of typical metal of I electrochemical group, in which the hydrogen overpotential is very low.

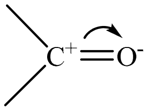
The foregoing conforms to results on the application of Tafel equation for rectilinear plots of polarization curves of metals Al and Cd in acidic and alkaline aqueous solutions $\eta = a + b\lg i$ (Table 1) [3].

Table 1. The values of constants a and b in Tafel equation for cathode evolution of hydrogen on different metals [3]

Metal	Acidic aqueous solutions		Alkaline aqueous solutions	
	-a	-b	-a	-b
Al	1,00	0,10	0,64	0,14
Cd	1,40	0,12	1,05	0,16
Pb	1,56	0,11	1,36	0,25
Pt	0,10	0,03	0,31	0,10

Usually the range of constants variation values (a) is from – 0,1 for platinum to – 1,5 V for plumbum. It is determined by surface state of electrode material. The value of b varies in range from – 0,03 to – 0,12 and sometimes it has higher values for oxidized metals. Low b values are typical for metals that have the lowest overpotential(with a minimum value), such as platinum. In the case of metals with high overpotentialb is about – 0,12, and a value is minus 1,4–1,5.

The Table 1 data show relatively high hydrogen overpotential on aluminum electrode and surmise the possibility of reduction course of carbonyl compounds in Al-cathode. This also conforms to structure peculiarities and electron distribution in the carbonyl groupings of organic substances. The functional group of such compounds is polar at the expense of displacement of valence electrons bond to the most electronegative oxygen. Therefore partial charges arise on atoms (positive on carbon and negative on oxygen):



The presence of positively polarized carbon atom determines the probability of carbonyl compounds absorption on the negatively charged surface of the cathode during electrolysis.

The foregoing is confirmed by the results of polarization measurements on aluminum and cadmium, for comparison, [5] electrodes in aqueous-alcohol solutions of carbonyl substances with the addition of sulfuric acid (fig. 2).

Each of the polarization curves (fig. 2) has two waves of substances reduction, the first of which corresponds to the reduction of molecular oxygen, the second – isovaleric aldehyde. According to this the electrolysis of acidic aqueous-alcohol solutions of isovaleric aldehyde under an aluminum cathode potential – 0,75 V showed rapid decrease in time of limiting current density of electroreduction of carbonyl compounds. A similar case was observed by us earlier when using Cd-cathode [5].

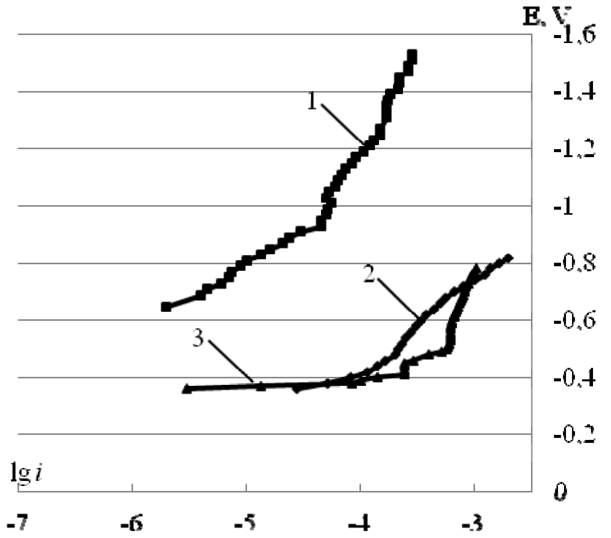


Fig. 2. Potentiostatic polarization curves in 0,5 mol/l solutions of isovaleric aldehyde (25 °C): *1* – aluminum in aqueous – alcoholic solution of 10 g/l Na_2SO_4 (pH = 7,98), *2* – aluminum and *3* – cadmium electrodes in sulfuric acid-aqueous-alcohol solution (pH = 2,98)

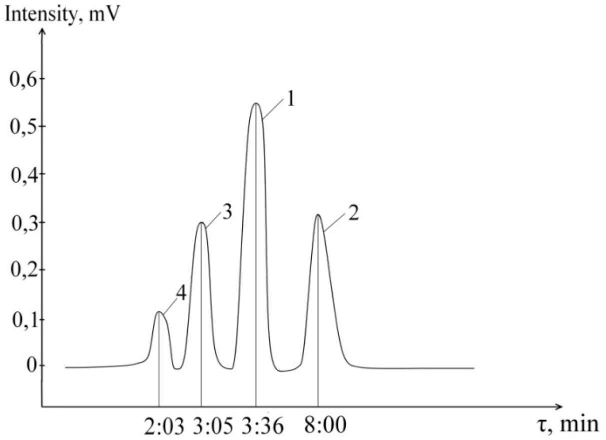


Fig. 3. The chromatogram of electroreduction products of isovaleric aldehyde in sulfuric acid-aqueous-alcohol solution under regular controlled potential (E = -0,7V): *1* – isopropyl alcohol (solvent), *2* – isovaleric aldehyde, *3* – isopentane, *4* – isopenten

The chromatographic analysis of the reaction mass after electrolysis showed that the major product of aldehyde reduction on the aluminum cathode in acidic medium is the corresponding hydrocarbon and only under negative potentials decrease the formation of some amount of unsaturated hydrocarbons is additionally observed (fig. 3–4).

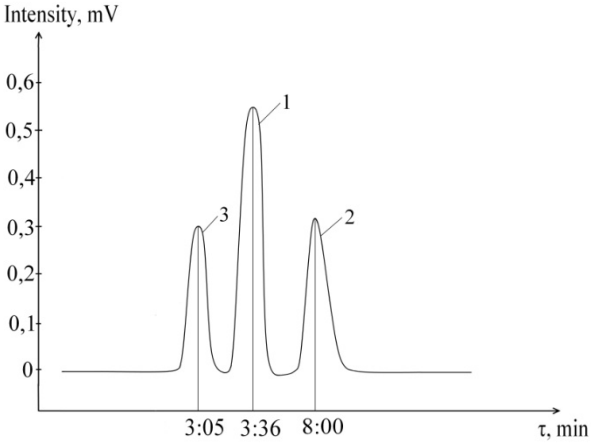
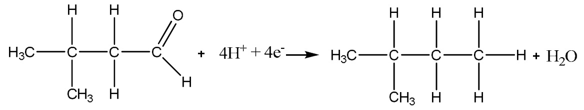


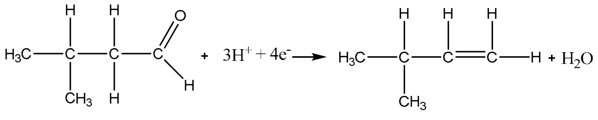
Fig. 4. The chromatogram of electroreduction products of isovaleric aldehyde in sulfuric acid-aqueous-alcohol solution under regular controlled potential (E = -0,75V): *1* – isopropyl alcohol (solvent), *2* – isovaleric aldehyde, *3* – isopentane

The formation of saturated hydrocarbons by electrochemical mechanism can be submitted as follows:



$$H_3C-CH(CH_3)-CH_2-CHO + 4H^+ + 4e^- \longrightarrow H_3C-CH(CH_3)-CH_2-CH_2-H + H_2O$$

and unsaturated hydrocarbons as follows:



$$H_3C-CH(CH_3)-CH_2-CHO + 3H^+ + 4e^- \longrightarrow H_3C-CH(CH_3)-CH=CH-H + H_2O$$

6. Conclusions

This paper demonstrates the possibility of using aluminum as safe from ecological point of view electrode material for the processes of cathode reduction of aldehydes to the corresponding hydrocarbons in processes of waste petroleum oils regeneration.

It is shown that in contrast to typical metals with high hydrogen overpotential (Hg, Cd, Pb, Zn), where the corresponding mixtures of hydrocarbons, alcohols and hydrodimers (pinacol type compounds) are formed at reduction, the reduction on aluminum occurs with formation of saturated hydrocarbons i.e.

the complete regeneration of oxidation products occurs back into the hydrocarbons from which petroleum oils consist of.

Only at lower negative potential of the cathode, a small amount of unsaturated hydrocarbons is formed. It is this fact that electrocatalytic effect is revealed at application of different cathode metals.

Working parameters of performing aldehydes electroreduction are determined.

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В. М. Ледовських[1], О. М. Давиденко[2] . Електровідновлення аліфатичних альдегідів на алюмінієвому катоді.

[1,2]Національний авіаційний університет, просп. Космонавта Комарова, 1, Київ, Україна, 03680
E-mails: [1]uchneftexim@bigmir.net; [2]dom237@ukr.net

Наведено результати по дослідження відновлення альдегідів аліфатичного ряду на алюмінії у водно-спиртових розчинах. Показано, що відносно висока перенапруга водню на алюмінієвому катоді сприяє ефективному перебігу процесів перетворення карбонільних сполук у відповідні насичені і ненасичені вуглеводні, причому вихід насичених продуктів електролізу зростає зі збільшенням від'ємних значень робочого потенціалу катода. За даними електролізів при контрольованому потенціалі процеси відбуваються швидко з високим виходом продуктів, що робить їх перспективними для регенерації відпрацьованих окиснених моторних нафтових олив.

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

В. М. Ледовских[1], А Н. Давыденко[2] Электровосстановления алифатических альдегидов на алюминиевом катоде.

[1,2]Национальный авиационный университет, просп. Космонавта Комарова, 1, Киев, Украина, 03680
E-mails: [1]uchneftexim@bigmir.net; [2]dom237@ukr.net

Приведены результаты по исследованию восстановления альдегидов алифатического ряда на алюминии в водно-спиртовых растворах. Показано, что относительно высокое перенапряжение водорода на алюминиевом катоде способствует эффективному протекания процессов преобразования карбонильных соединений в соответствующие насыщенные и ненасыщенные углеводороды, причем выход насыщенных продуктов электролиза возрастает с увеличением отрицательных значений рабочего потенциала катода. По данным электролизов при контролируемом потенциале процессы происходят быстро с высоким выходом продуктов, что делает их перспективными для регенерации отработанных окисленных моторных нефтяных масел.

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

Ledovskykh Volodymyr. Doctor of chemical sciences. Professor.
Chemistry and chemical technology Department, National Aviation University, Kyiv, Ukraine.
Education: Kyiv Polytechnic Institute, Kyiv, Ukraine (1962).
Research area: corrosion and defence of metals, purposeful development of PAIRS for retrofitting of oil and oil products, processes of electrochemical regeneration of oxidation of hydrocarbons and general chemistry.
Publications: 152.
E-mail: uchneftexim@bigmir.net

Davydenko Oleksandr. Graduate student.
Department of Chemistry and Chemical Technology, National Aviation University, Kyiv, Ukraine.
Education: National Aviation University, Kyiv, Ukraine (2013).
Research area: processes of electrochemical regeneration of used oils.
Publications: 6.
E-mail: dom237@ukr.net