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CARBOXYLIC ACIDS ELECTROOXIDATION ON SHUNGITE ELECTRODE

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Abstract

Purpose: *This article discusses the electrochemical method of directional conversion of carboxylic acids, which are the most aggressive hydrocarbons oxidation products back into the corresponding hydrocarbons. Existing methods for the regeneration of waste petroleum oils have significant drawbacks, which include the formation of new hard-reclaimed waste and loss of a significant part of the oil during regeneration.* ***Methods:*** *Electrooxidation processes of carboxylic acid on various electrode materials: platinum, graphite and shungite anodes were studied.* ***Results:*** *Potentiostatic polarization curves with simultaneous measurement of near-electrode solution pH showed differences in the process on these anode materials: dimer yield for Kolbe is decreased under the transition from platinum to shungite. At potentials higher than 2.0 v, carboxylic acid has a higher adsorbability compared to water. Therefore Faraday's side-process of water oxidation doesn't almost occur, which contributes to high yield of expected product according to current. Electrolysis of carboxylic acids solutions under controlled potential (2.0 and 2.4 V) and chromatographic analysis of the formed products showed that along with the dimeric structures formation for Kolbe reaction, the occurrence of a hydrocarbons mixture takes place, which may be the result of disproportionation of hydrocarbon radicals (alkane and alkene) and hydrocarbons of isomeric structure, by further oxidation of the hydrocarbon radical to carbocation and its subsequent transformation into the corresponding saturated and unsaturated isomers. Such statement is not supported by conception of the process of one- and two-electron carboxylic acid oxidation.* ***Discussion:*** *General carboxylic acid oxidation scheme according to one-electron mechanism (dimerization and disproportionation of the radical) and two-electron mechanism (formation and carbocation rearrangement) is proposed. The formation of hydrocarbons under carboxylic acid electrooxidation of waste oils during their regeneration can promote the increase of oil yield without formation of dangerous by-products.*

Keywords: electro-oxidation; carboxylic acid; regeneration; shungite; waste oils.

1. Introduction.

The annual world usage of petroleum oils became widespread. In 2014, annual production reached 38.6 million tones. It is predicted that in 2019 the needs in oil will increase up to 42.8 million tones, which corresponds to 2.1% increase. Mineral oils make up 90% of total world production, while the synthetic oils – only 10%. At the same time the market of synthetic oils is developing more actively. Automotive oils make up 56.0% of the total oil production, industrial oils – 26.2%, processing oils – 9.4%, cutting oils – 5.3%, and grease – 3.1% [1].

Use of oils is accompanied by triggering of additives, accumulation of wear products, water, solids, and the progress of hydrocarbons oxidation. Hydrocarbons oxidation occurs according to radical chain mechanism through the stages of hydro- and dehydroperoxide formation, aldehydes and ketones are some of the degradation products. The last in their turn experiences further oxidation with the formation of carboxylic acids the content of which can be up to 1% by oil weight. They negatively affect the quality of oil and significantly increase its corrosivity. Due to mentioned above transformations oils no longer satisfy quality characteristics, especially such as the kinematic viscosity, acid number, flash point, base number, lubricating ability and require replacement, leading to formation of large quantities of hazardous waste – waste oils. [2]

There are several ways of disposing of waste oils the most promising one is the regeneration. Most of regeneration methods are based on oils adsorption and oils cleaning processes with sulfuric acid. These methods are rather effective but cause the formation of new and high difficultly recyclable waste [3]. Therefore the development of new methods for waste oils regeneration is a promising and topical task.

This work is dedicated to the research of electrochemical methods of carboxylic acid waste oils regeneration by means of electrochemical anodic oxidation up to hydrocarbons and to search for new effective electrode materials.

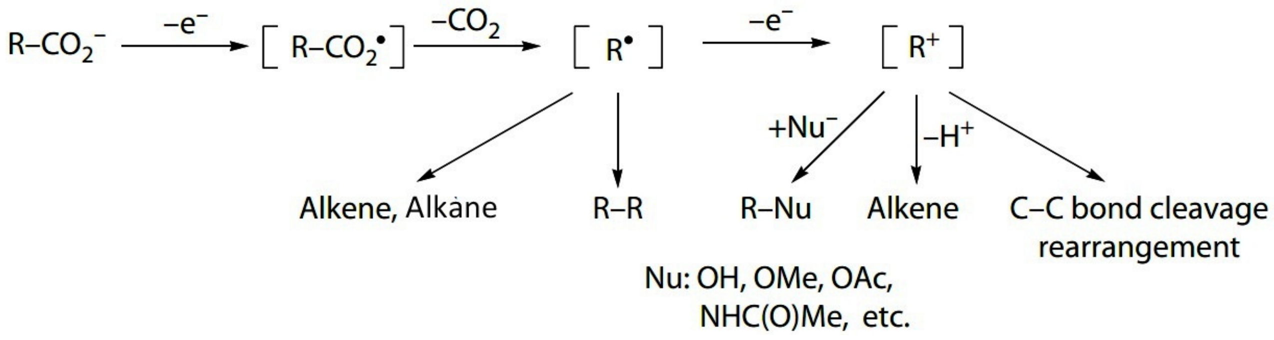
2. Analysis of the latest research

Kolbe reaction or anodic condensation process includes the electrochemical oxidation of carboxylic acids up to hydrocarbons which contain twice the number of carbon atoms relative to the initial acid. Kolbe electro-synthesis example is the formation of ethane and carbon dioxide by the electrolysis of acetate aqueous solutions [4].

$$2CH_3COO^- - 2e^- \longrightarrow 2CH_3COO^\bullet \longrightarrow$$

$$2CH_3^\bullet + 2CO_2 \longrightarrow CH_3CH_3$$

The reaction mechanism of the anode decarboxylation of carboxylic acids includes the step of forming a carboxylate radical which in its turn can be oxidized further to carbocation that depending on the conditions of the electrolysis process and an anode material leads to the following products [5]:



A typical anode, on which many of the researches are performed, is smooth platinum. But the use of platinum in industry is extremely expensive and is accompanied by a gradual removal of metal from an electrode. Therefore, the search for new electrode materials for anodic oxidation of the carboxyl compounds is an important scientific and technical challenge.

There are directions [4] for the implementation of Kolbe reaction on graphite anodes and at the same time yields in these cases are much lower than for platinum. Use of platinum is caused by having high overvoltage of water oxidation and corrosion resistance even at high positive potentials. For example, under electro-oxidation of sodium acetate aqueous solution, current output of dimeric product has made up: for a smooth Pt - 89%; for platinized Pt - 3%; for Au, Ni, PbO_2 - 0%; for retort coal - 21%; for graphite - 4.0%. One of the byproducts of the anode reaction are alcohols, although in some cases they are in fact the only product of the conversion, it is observed in alkaline media where the probability of encountering a hydrocarbon radical with hydroxide radical is significantly higher than with the hydrocarbon radical to form the dimeric structure of hydrocarbons. [4] In addition, in [4 - 6] works the optimum conditions for increasing the yields of products are not determined, namely the influence of the medium pH on the product nature and the ratio of their yields under electrolysis, and the possibility of reaction spreading from the alkali metal acetates to carboxylic acids of higher molecular weight.

A disadvantage of graphite anodes is large porosity and low mechanical resistance, due to that during electrolysis, electrode material is partially destroyed [7]. This thing prompted us to search for alternative electrode materials on which the process of anodic decarboxylation (Kolbe reaction) would pass satisfactorily and it would have high mechanical resistance. Our choice was focused on a natural mineral - shungite. Shungite is the final stage of natural graphite formation. It has high electrical conductivity and mechanical stability (Table. 1), making it perspective for use as a new electrode material.

3. Purpose

The focus of this paper is given to comparative research of course mechanisms of carboxylic acid electro-oxidation on various materials – platinum, graphite, shungite, to determine the possibility of applying for such processes shungite anodes and search for conditions of their performance in the transformation direction of the carboxyl compounds back into hydrocarbons, i.e. in the direction opposite to petroleum oil oxidation processes under their operation.

4. Experimental

Major world deposits of shungite are in the Republic of Karelia (Russia), and total about 1 billion tons. Main shungite mining is produced on Shungskom, Maksovo, Zazhoginskom, Nigozerskom, Myagrozerskom and Turastamozerskom deposits. There are known deposits on Kamchatka too. Mining is also underway on Koksuyskom deposit (49 million tons) in Kazakhstan. Small deposits of shungite are known in Austria, India and the Democratic Republic of Congo [8].

Comparison of the physical properties of natural graphite and shungite is shown in Table 1. [9-10].

Table 1

Physical properties of natural graphite and shungite

Index	Graphite	Shungite
Density, g/cm^3	1,9 - 2,6	2,1 – 2,4
Electric current resistivity, Ohm•m	5-30·10^{-6}	32,9 – 3,53·10^{-3}
Thermal conductivity, W/m•K	3,55	3,8
Thermal conductivity coefficient, W/m•K	10,87	5
Melting point (at P = 0.9 - 1 atm), °C	3845 - 3890	—
Boiling point, °C	4200	—
Combustion heat, kJ/kg	32769 - 32869	31380
Magnetic properties	diamagnetic	diamagnetic
Specific heat capacity (298,15 K), kJ/(kg•K)	0,79-0,81	0,98
Ultimate tensile strength, MPa	9,8 - 14,7	17534,6
Flexural strength, MPa	6,9 – 100	13062,2
Compressive strength, MPa	20 – 200	10054,75
Hardness according to Mohs scale	1 - 2	3 – 4
Porosity, %	30 - 32	0,5 - 5
Elasticity modulus (E), MPa	8 – 15·10^3	31 · 10^3
Conductivity, S/m	125 · 10^6	(1 - 3) · 10^3
Average temperature coefficient of thermal expansion, 1/°C	1,2 – 8,2·10^{-6}	12·10^{-6}

From Table 1it is seen that shungite is an electrically conductive material but in comparison with the graphite it has a higher resistivity and lower electric current conductivity. At the same time, it has much less porous and substantially higher ultimate tensile strength, bending and compression. These shungite properties indicate the possibility of its use as an anode material instead of mechanically less stable graphite and especially expensive platinum.

Differences of graphite from shungite are explained by their nature and origin conditions and element characteristics and chemical composition (Tables 2 and 3). Unlike of graphite it has considerably lower carbon content, but contains more silicon, which is in the form of polymeric oxide SiO_2, and oxides of many metals that provide high mechanical stability [11].

Table 2

The main element composition of shungite and natural graphite

Element	Content, % (wt.)	
	graphite	shungite
F*	0,03060	—
Cl*	0,00200	—
Na*	0,00300	0,27000
Mg*	0,01980	0,34000
Al*	0,02060	1,46000
Si*	0,13000	17,01000
P*	0,00040	0,02000
S*	0,07270	0,37000
K*	0,00170	0,51000
Ca*	0,02130	0,09000
Ti*	0,00080	0,14000
V	0,00030	0,01500
Cr	0,00010	0,00720
Mn	0,00060	0,09000
Fe	0,09360	0,91000
Co	0,00010	0,00014
Ni	0,00140	0,00850
Cu	0,00350	0,00370
Mo	0,00080	0,00310
Ba	0,00090	0,32000
As	0,00001	0,00035
Pb	0,00010	0,02250
Zn	0,00020	0,00670

C	matrix	26,26000

* for these elements in shungite, content is calculated on the basis of their oxide contents

Table 3

Averaged chemical composition of oxides in shungite

Components	Content, % (wt.)
SiO_2	18,793
TiO_2	0,457
Al_2O_3	4,287
Fe_2O_3	3,67
FeO	0,34
MnO	0,006
MgO	1,193
CaO	0,293
Na_2O	0,14
K_2O	1,723
(H_2O)	2,05
P_2O_5	0,07
Cr_2O_3	0,02
V_2O_5	0,256
CoO	0,002
NiO	0,021
CuO	0,007
ZnO	0,01
S_{3ar}.	2,833
Wastes under decrepitation	68,4

For experimental researches of carboxylic acid electro-oxidation, we used natural shungite, the chemical content of which was determined by X-ray spectroscopy (Table 4). The carbon content in the graphite anode, which was used for comparative electrochemical measurement was 91.5% (Table 5).

Table 4

The chemical composition of natural shungite used as an electrode material for electrochemical measurements in this paper.

Components	Content, % (wt.)
SiO_2	51,6
TiO_2	0,18
Al_2O_3	3,04
Fe_2O_3	1,07
MnO	-
MgO	0,6
CaO	0,66
Na_2O	-
K_2O	1,27
P_2O_5	0,87
Cr_2O_3	-
V_2O_5	0,019
Co_3O_4	-
NiO	0,028
CuO	-
ZnO	0,012
SO_3	5,4
BaO	0,026
Au	0,011
ZrO_2	0,012
Cl	0,2
C	35
Lanthanides	0,004

Table 5

Physical and chemical properties of natural graphite used for experimental researches

Index	Value
Specific electric resistance, Ohm·mm^2/m, more	150
Flexural strength, MPa Compressive strength, MPa	200 500
Rockwell hardness under a load of 60 kg, HRB	50-75

As a model substance which contains a carboxyl group we used chemically pure hexanoic acid: $CH_3CH_2CH_2CH_2CH_2COOH$, M = 116.16 g/mole, t_{mel} = - 3.4°C, t_{boil} = 202°C. Solution neutral pH of output media was put with NaOH.

Polarization measurements were performed on a potentiostat P-5827M, where we used three electrode thermostated chamber (10 °C) with a working electrode made of natural shungite, graphite and platinum, a platinum wire separated from the working electrode with a porous glass septum was an auxiliary electrode, potentials were measured against a silver chloride electrode, and enumerated according to a normal hydrogen scale. At the same time pre-anode layer pH (pH-meter pH-150MI) was measured during the measuring of anodic polarization.

Preparative electrolysis of hexanoic acid solution under concentration of 0.5 mol/L we carried out under controlled potential (potentiostat) of shungite, graphite and platinum electrodes (E_{work} = 2.0 - 2.4 V (HBE)), the current of the electrochemical process was measured by milli-ammeter M2020 with a scale of 1 micron uA.

To determine the products of electrooxidation carboxylic acid – the analyte – was subjected to isooctane extraction followed by chromatographic analysis (gas chromatograph Crystal 5000.2 with capillary columns and temperature programming device). To identify the peaks we used standard samples of substances.

5. Results discussion

Fig. 1 shows the potentiostatic polarization curves of shungite, graphite and platinum in the background solution and Fig. 2 shows the corresponding curves of pH dependence on potential during measuring of potentiostatic polarization curves.

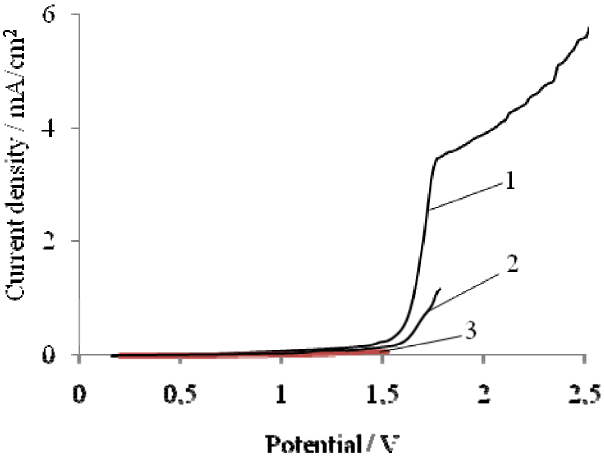


Fig. 1 Potentiostatic polarization curves of various anodes in the aqueous neutral background solution: 1–platinum; 2 – shungite; 3 – graphite.

According to potentiostatic polarization curves (Fig 1.) we can see areas of water oxidation, which exist under potentials higher than 1.23 V in neutral solutions according to an electrode reaction, which causes acidification of analyte (Fig. 2):

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

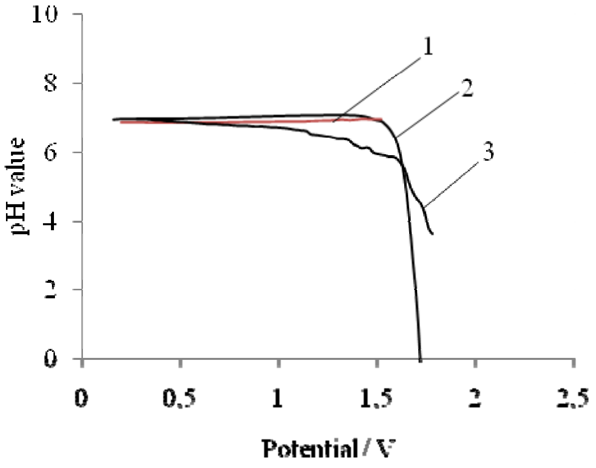


Fig. 2. The pH value dependence on potential during measuring potentiostatic polarization curves in the aqueous background solution at various anodes: 1 – graphite; 2 – platinum; 3 – shungite.

Fig. 3, 4 show potentiostatic polarization curves of shungite, graphite and platinum correspondingly in 0.5 mol/l hexanoic acid solution and the analyte pH change when receiving the curves.

Only one area of the limiting current can be seen on the polarization curves, which corresponds to the process of hexanoic acid oxidation:

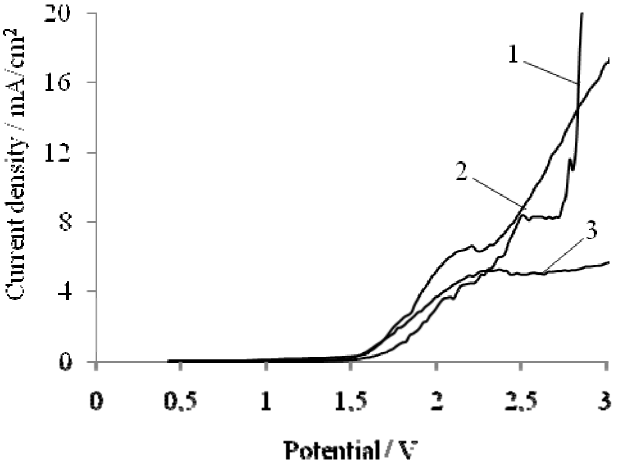


Fig. 3 Potentiostatic polarization curves of various anodes in 0.5 mol/l hexanoic acid solution: 1 – platinum; 2 – shungite; 3 – graphite.

$$RCOO^- \xrightarrow{-e^-} R\bullet + CO_2$$

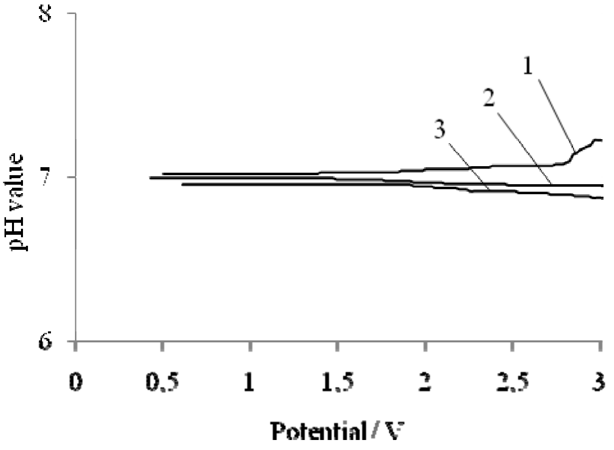


Fig. 4 Dependence of pH value of 0.5 mol/l hexanoic acid aqueous solutions on the potentials of various anodes while receiving potentiostatic polarization curves: 1 – platinum; 2 – graphite; 3 – shungite.

Fig. 4 shows that when reaching potentials of water oxidation the process of its oxidation on the anode does not proceed and curves pH – E are linear and there is no acidification of the solution, that indicates organic acid adsorption and the course of its only oxidation process.

To evaluate the electrooxidation velocity of carboxylic acid solutions we carried out preparative electrolysis of its solution under controlled potentials of 2.0 V and 2.4 V (HBE). Fig. 5 shows the current fall of hexanoic acid electrooxidation according to time at carrying out electrolysis under the potential of 2.0 V on various anode materials. The current decreases regularly in the process of electrolysis, which indicates a decrease of the explored organic acid concentration at the expense of its oxidation process, and this reaction occurs quickly enough.

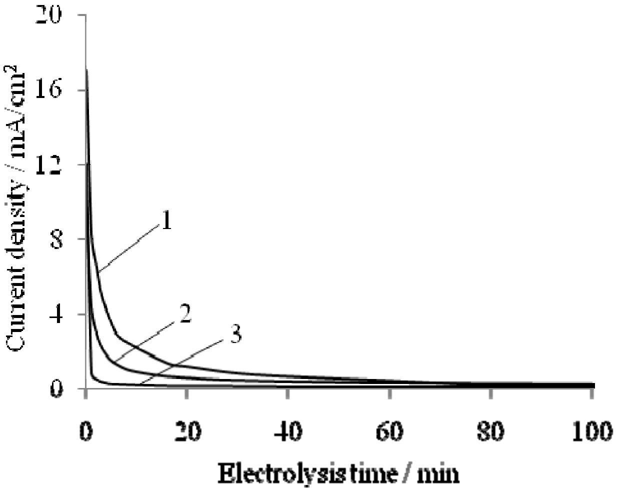


Fig. 5 Dependence of electrooxidation current of hexanoic acid on different anodes according to time under the potential of 2.0 V (pH=7): 1 – graphite; 2 – shungite; 3 – platinum.

During the electrolysis of hexanoic acid solution, adsorption and correspondingly water electrooxidation process on the anodes does not nearly occur, as evidenced by the almost constant pH (Fig. 6).

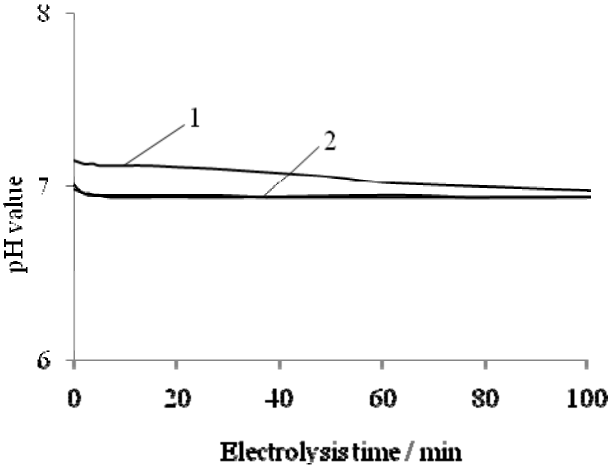


Fig. 6 The dependence of pH on electrolysis carrying out time of 0.5 mol/l hexanoic acid solution on the anodes: 1 – platinum; 2 – graphite and shungite.

Chromatographic analysis of the reaction mass after the electrolysis (Fig. 7) showed that the product of hexanoic acid electrooxidation in aqueous neutral solution on shungite anode is a mixture of hydrocarbons. Similar results were obtained with extracts chromatography after hexanoic acid solution electrolysis on the graphite and platinum anodes.

Formation of products obtained by acid electrooxidation conforms to the reaction course mechanism, proposed for process on a platinum anode [12-19].

According to the one-electron mechanism (dimerization and disproportionation of hydrocarbon radical) these representations are reflected by the scheme 1.

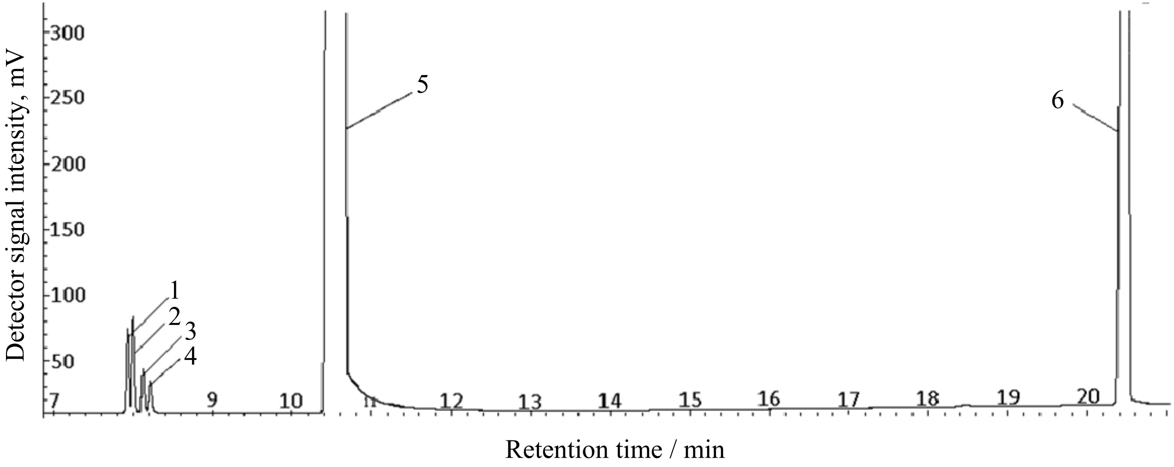
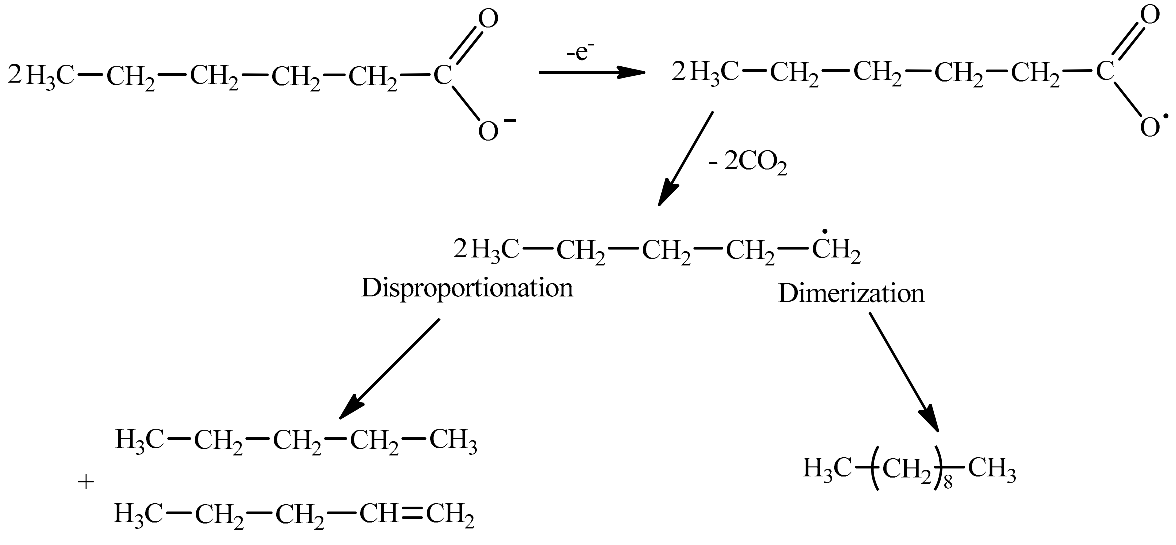


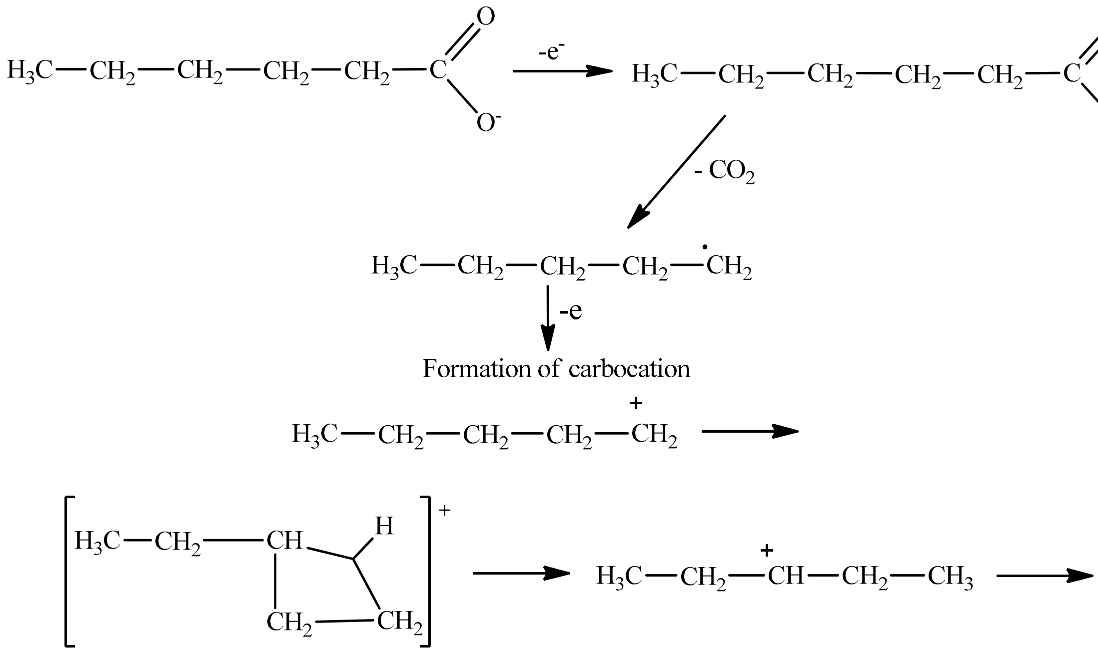
Fig. 7 Chromatogram of products extract of 0.5 mol/l hexanoic acid electrooxidation on shungite electrode under 2.4 V: 1 – n-pentane; 2 – pentene; 3 – isopentane; 4 – 2-methyl-2-butene; 5 – iso-octane (solvent-extractant); 6 – n-decane.

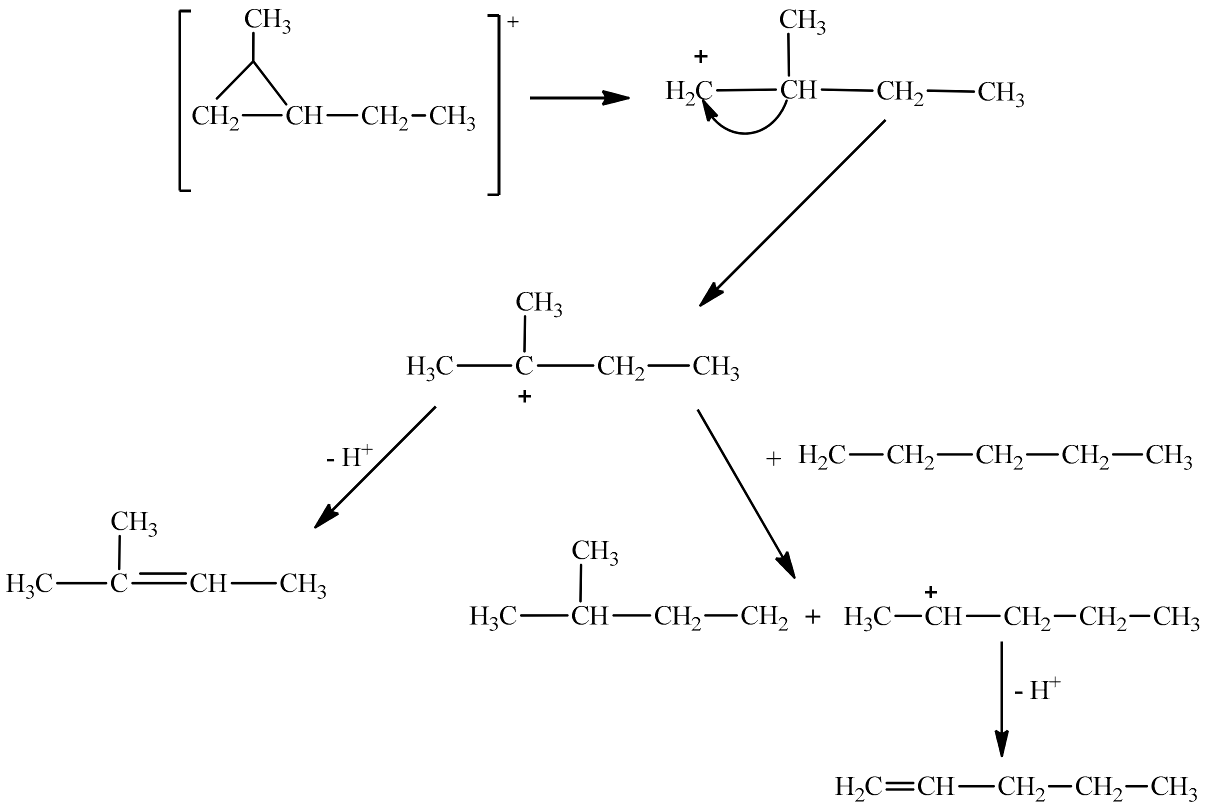


Scheme 1. One-electron oxidation mechanism hexanoic acid.

This scheme does not fully reflect all electrochemical processes occurring on the anode in aqueous solutions of carboxylic acids under pH close to neutral. The totality of electrolysis products defined in this paper can be explained on the basis of representation of two-electronic circuit, which provides electrochemical oxidation of the initially generated alkyl radical into carbocation, and its subsequent transformation into the corresponding saturated and unsaturated hydrocarbons of normal and isomeric structure. This point of view corresponds to the general concepts of organic chemistry in relation to the rearrangement of hyper-coordinated carbon atom in thermo-catalytic processes [12].

The general mechanism of carboxylic acids electro conversion under their anodic oxidation in close to neutral media can be submitted by the following scheme 2.





Scheme 2. Two-electron oxidation mechanism hexanoic acid

The proposed mechanism explains the formation together with the products of one-electron anode reaction also the substances emergence which can be explained by two-electron mechanism of the process course involving carbocations.

Fig. 8 shows a percentage ratio between the mentioned above substances in electrolysis products of 0.5 mol/l hexanoic acid solution under the potential of 2.4 V on various electrode materials.

Fig. 8 shows that the ratio of product yield under the same anodic potential (2.4 V) depends on an electrode material, that is the evidence of their electro-catalytic effect. The formation of products of carboxylic acid anodic oxidation (pentane, pentene and decane) on the selected anodes can be explained by one-electron acid anion oxidation course, and isopentane and 2-methyl-2-butene is explained by two-electron oxidation course.

The main product of the anodic hexanoic acid oxidation is a dimer (n-decane) – a product of Kolbe reaction. On platinum which is a typical anode material for Kolbe process, products formation through the stage of forming carbocation did not practically observed.

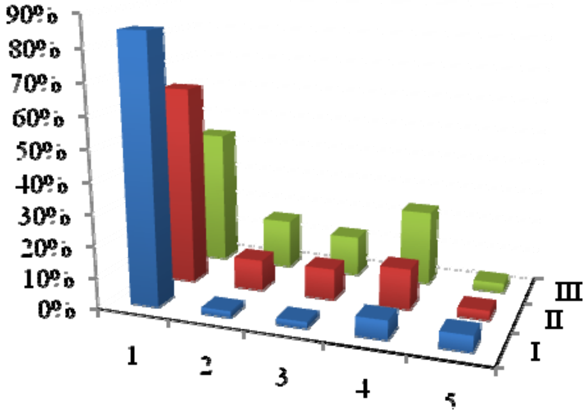


Fig.8 Product yields ratio during electrooxidation process of 0.5 mol/l hexanoic acid solution (pH = 7) on platinum (I), graphite (II), shungite (III) anodes under the potential of 2.4 V: 1 – decane (dimer); 2 – 2-methyl-2-butene; 3 – isopentane; 4 – pentene; 5 – pentane.

6. Conclusions

Based on the comparison of the physicochemical properties of natural shungite with graphite and platinum, we show that the application of a shungite electrode material in technology of electrochemical carboxylic acids oxidation into hydrocarbons is perspective for oxidized hydrocarbons regenerating, including waste petroleum oils. We show that shungite allows satisfactorily and with a high yield to oxidize carboxylic acids up to a mixture of hydrocarbons, the main of which is a dimer formed by Kolbe reaction. Anode material reveals electro-catalytic effect causing a comparative decrease in dimer yield under the transition from platinum to shungite.

According to one-electron mechanism of an anode reaction decarboxylation of carboxylic acid occurs, followed by disproportionation of hydrocarbon radical into saturated and unsaturated hydrocarbons.

Electrooxidation of carboxylic acids under high anodic potentials we explain by conceptions of the intermediate forms formation – hydrocarbon radical and subsequent carbocation.

To explain this mechanism we propose the general scheme, which allows the formation and rearrangement of hyper-coordinate carbon atom, resulting in the formation from hexanoic acid, besides the product of Kolbe condensation, also saturated and unsaturated hydrocarbons of pentane series.

Due to the high adsorption of carboxylic acid on the anode under operating potentials of 2.0 V or even higher, the Faraday by-product water oxidation process is not almost observed, which contributes to high yield of expected product according to current.

Comparative evaluation of anode materials including shungite showed the possibility of application of different electrode materials to perform process of carboxylic acids electro-oxidation.

The formation of hydrocarbons during carboxylic acid electrooxidation is aimed at improving existing technologies of waste oils regeneration and increasing their yield.

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Електроокиснення карбонових кислот на шунгітовому електроді

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Мета: Стаття розглядає електрохімічний метод спрямованого перетворення карбонових кислот, як найагресивніших продуктів окиснення вуглеводнів, назад у відповідні вуглеводні. Існуючі методи регенерації відпрацьованих нафтових олив мають суттєві недоліки, до яких належить утворення нових важкоутилізованих відходів та втрата значної частини оливи під час регенерації. **Методи:** Дослідженні процеси електроокиснення карбонової кислоти на різних електродних матеріалах: платиновому, графітовому та шунгітовому анодах. **Результати:** Потенціостатичні поляризаційні криві з одночасним вимірюванням pH приелектродного розчину показали відмінності перебігу процесу на даних анодних матеріалах: вихід димеру за реакцією Кольбе зменшується при переході від платини до шунгіту. За потенціалів, вищих за 2,0 В, карбонова кислота має більш високу адсорбційну здатність порівняно з водою. Тому побічного фарадеївського процесу окиснення води майже не спостерігається, що сприяє високому виходу за струмом цільового продукту. Електролізом розчинів карбонових кислот при контрольованому потенціалі (2,0 та 2,4 В) та хроматографічним аналізом утворених продуктів показано, що разом з утворенням димерних структур за реакцією Кольбе, спостерігається виникнення суміші вуглеводнів, які можуть бути результатом диспропорціонування вуглеводневого радикалу (алкан та алкен), та вуглеводнів ізомерної структури, за рахунок подальшого окиснення вуглеводневого радикалу до карбкатіону і його подальші трансформації у відповідні насичені та ненасичені ізомери. Таке твердження не підтверджується уявленням про перебіг одно- та двох-електронного окиснення карбонової кислоти. **Обговорення:** Запропонована загальна схема окиснення карбонової кислоти за одно-електронним механізмом (димеризація та диспропорціонування радикалу) і двох-електронним механізмом (утворення та перегрупування карбкатіону). Утворення вуглеводнів при електроокисненні карбонових кислот відпрацьованих олив при їх регенерації, може сприяти збільшенню виходу оливи без утворення побічних небезпечних продуктів.

Ключові слова: відпрацьована олива; електроокиснення; карбонова кислота; регенерація; шунгіт.

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Цель: Данная статья рассматривает электрохимический метод направленного преобразования карбоновых кислот, как агрессивных продуктов окисления углеводородов, обратно в соответствующие углеводороды. Существующие методы регенерации отработанных нефтяных масел имеют существенные недостатки, к которым относится образование новых тяжело утилизированных отходов и потеря значительной части масла при регенерации. **Методы:** Исследовании процессы электроокисления карбоновой кислоты на различных электродных материалах: платиновом, графитовом и шунгитовом анодах. **Результаты:** потенциостатические поляризационные кривые с одновременным измерением pH приелектродного раствора показали различия течения процесса на данных анодных материалах: выход димера за реакцией Кольбе уменьшается при переходе от платины до шунгита. При потенциалах, превышающих 2,0 В, карбоновая кислота имеет более высокую адсорбционную способность по сравнению с водой. Поэтому побочного фарадеивського процесса окисления воды почти не наблюдается, что способствует высокому выходу по току целевого продукта. Электролизом растворов карбоновых кислот при контролируемом потенциале (2,0 и 2,4 В) и хроматографическим анализом образованных продуктов показано, что вместе с образованием димерних структур за реакцией Кольбе, наблюдается возникновение смеси углеводородов, которые могут быть результатом диспропорционирования углеводородного радикала (алкан и алкен) и углеводородов изомерной структуры, за счет дальнейшего окисления углеводородного радикала в карбкатион и его дальнейшие трансформации в соответствующие насыщенные и ненасыщенные изомеры. Такое утверждение не подтверждается представлением о ходе одно- и двух-электронного окисления карбоновой кислоты. **Обсуждение:** Предложенная общая схема окисления карбоновой кислоты с одно- электронным механизмом (димеризация и диспропорционирования радикала) и двух-электронным механизмом (образование и перегруппировки карбкатиона). Образование углеводородов при электроокислении карбоновых кислот отработанных масел при их регенерации, может способствовать увеличению выхода масла без образования побочных опасных продуктов.

Ключевые слова: карбоновая кислота; отработанное масло; регенерация; шунгит; электроокисление.

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