UDC 541.145.4
DOI: 10.15587/2312-8372.2017.118648

Ludyn A.,
Reutskyy V.

IMPROVEMENT OF THE CYCLOHEXANE OXIDATION PROCESS

Розглянуто спосіб удосконалення процесу рідкофазного окиснення циклогексану. Встановлено позитивний вплив кисневмісної добавки – Біс-2 ціанетилового етеру – на основні техніко-економічні показники процесу – конверсію сировини, селективність за продуктами окиснення та співвідношення цільових продуктів. Досліджено оптимальне співвідношення компонентів бінарної каталітичної системи. Запропоновано комплексний метод використання продуктів окиснення циклогексану шляхом утилізації одержаних побічних кислот естерифікацією їх зі спиртами.

Ключові слова: *окиснення циклогексану, кисневмісна добавка, бінарна каталітична система, конверсія сировини.*

1. Introduction

Processes of homogeny-catalytic oxidation of hydrocarbons have important role in industry. Among those processes is oxidation of cyclohexane (CH) that results in obtaining of raw materials for manufacturing of polyamide fibers. Aim-products of CH oxidation are cyclohexanole (COL), cyclohexanone (CON), and cyclohexyl hydroperoxide (CHHP) that on later stages decomposes into COL and CON. Main by-products during CH oxidation are ethers, main quantity of which is dicyclohexyl adipinate, and acids, mainly, – adipic acid. Another important index of the process is ratio of aim-products CON/COL. Increase of CON quantity allows to increase production of valuable monomer – caprolactame.

Industrial processes of CH oxidation in the presence of catalyst – cobalt naphthenate – have certain features, among which – low indexes of selectivity for aim-products and low indexes for conversion of raw material. All of mentioned cause high energy consumption of production, mainly due to recirculation of unreacted raw material. Another important problem is inefficient use of by-products, that are mainly burned, and this causes increase of spending coefficients of manufacturing.

One of the ways of dealing with such problems is creation of technology of complex use of oxidation by-products based on new effective catalytic systems that allow increasing of selectivity of the process. Promising direction is research of catalytic systems based on organic salts of metals of variable valence (MVV) and their modification by additives with different nature. This is why task of creation of more effective catalytic systems, that allow increasing of technical-economical indexes of the processes, remains actual.

2. The object of research and its technological audit

Object of following research is process of CH oxidation. One of the most problematic spots in this process is low numbers of conversion of raw material and low selectivity of aim-products under conversions higher than 4 %. One of the main reasons for this is lack of modern effective catalytic systems that could increase mentioned indexes.

Successful direction in search of effective catalysts for CH oxidation is creation of binary catalytic systems that consist from active oxygen-containing additives and industrial catalyst – cobalt naphthenate. For research was used oxygen-CN-containing compound – bis-2 cyanoethyl ether (TC of Ukraine 6-09-3583-74), general chemical formula: $O(CH_2CH_2CN)_2$, shortened name – CEE.

For identification of features of impact of mentioned oxygen-containing additive, as a part of binary catalytic system, at CH oxidation process was made technological audit, with purpose of determination of raw material conversion, selectivity for aim products and ratio for created compounds.

Research was made at laboratory installation of CH oxidation, reactor of which was used under high temperatures and pressures and is made from steel AISI 430.

Scheme of experimental laboratory installation is shown in Fig. 1.

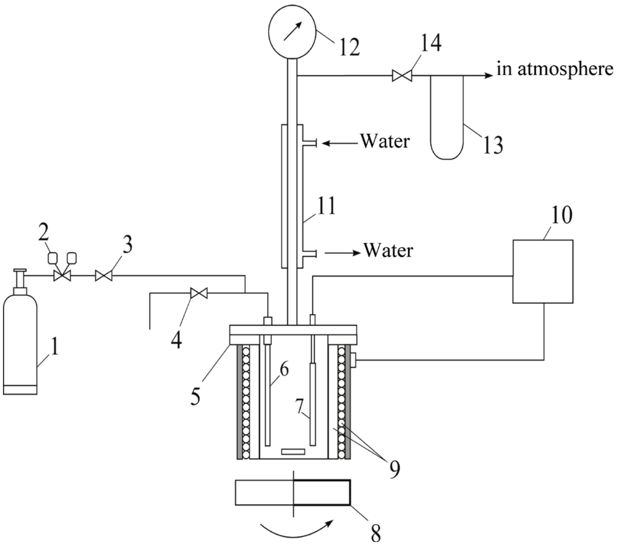

Fig. 1. Autoclave installation for cyclohexane oxidation:
1 – reservoir with oxygen; 2 – reducer; 3, 4, 14 – valves; 5 – reactor for cyclohexane oxidation; 6 – thermocouple; 7 – capillary for oxygen; 8 – magnetic mixer; 9 – oil shell and electrical heater; 10 – control-measuring instrument OVEN TRM-1; 11 – shell-and-tube heat exchanger; 12 – manometer; 13 – flowmeter for measurement of oxygen consumption

Installation works in following way. Technical oxygen from reservoir 1 through reducer 2 and valve 3 comes in reactor 5. Reactor contains previously loaded 100 cm^3 of CH. Heat is provided by electrical heater 9. Process of oxidation starts after reaching of needed technological indexes (temperature – 418 K, pressure – 1.0 MPa) in reactor.

Stable temperature regime is supported by silicone oil in shell of reactor. Reaction mixture is stirred by magnetic mixer and by intense bubbling of oxygen through capillary 6.

Temperature in reactor is measured by chrome-kopel thermocouple ChK-68 (Ukraine) 7 and is registered by control-measuring instrument OVEN TRM-1 (Ukraine) 10. Pressure in system is measured by manometer 12, and gas consumption at the exit from system by flowmeter 13.

Steam condensation is provided by return shell-and-pipe heat exchanger 11 with water cooling. Probe for analysis was taken with opened valve 4 and closed valve.

During process probes are periodically sampled for analysis of concentration of main products of liquid phase CH oxidation: CHHP, COL, CON, adipic acid (AA), and dicyclohexyl adipinate (DCA). Concentrations of CH oxidation by-products (CO, CO_2, lower dicarbonic and monocarbonic acids, cyclohexyl formate) are lower than analysis in accuracy and thus are not determined.

3. The aim and objectives of research

The aim of research is improvement of CH oxidation process by creation of binary catalytic system [CN:CEE] and complex use of all oxidation products.

In order to reach aim of research we need:

1. To investigate influence of oxygen-containing additive – CEE – in binary catalytic system on main technical-economical indexes of CH oxidation process: conversion of raw material, selectivity for oxidation products and ratio of aim-products.
2. To determine optimal ratio of components of binary catalytic system [CN:CEE].
3. To analyze impact of binary catalytic system [CN:CEE] at creation of by-products of CH oxidation process and propose method of utilization of those products.

4. Research of existing solutions of the problem

From literature is known method of laboratory CH oxidation by molecular oxygen in the presence of light and photochemicaly produced tert-butyl hydroperoxide [1]. Main disadvantage of mentioned process is its duration.

There is also a method of CH oxidation in presence of individual bis-oxovanadium complexes placed on silica gel. Oxidation goes under temperature 448 K and pressure 10 atm by molecular oxygen. Disadvantages of this method, even taking into account high selectivity for aim products, are low quantity of COL and CON and partial decrease of catalyst activity after 20 hours of working [2].

Catalysts based on cerium have certain specific features. One of such features during CH oxidation is creation of relatively big quantities of CHHP. But main product of CH oxidation in the presence of cerium salts is alcohol and ratio of [CON]/[COL] is 0.37–0.42 [3].

As catalysts are also used oxides of V, Mn, Ni, Cu, Zn, Mo, Zr and Ce [4]. There are researches of impact of titan oxide on photocatalytic CH oxidation [5, 6]. Those methods are ecologically clean and highly selective but also they are very complex for implementation in industry.

In the presence of Fe (III) complexes oxidation can be conducted with help of oxidizing reagents – hydrogen peroxides or tert-butyl peroxide [7]. After 24 hours process ratio of [COL]/[CON] for hydrogen peroxide oxidation was 1.5; for tert-butyl peroxide – 0.7–1.0. However main disadvantage of this process is its duration.

Cobalt is widely used as part of catalysts for CH oxidation. There is a known process in which as catalyst for CH oxidation are used cobalt salts of highly molecular oxyacids [8].

Also is known [9], that amin acids have positive impact on CH oxidation. Amin acids are showing features of two classes of compounds: carbonic acids and organic amines, due to the fact that they contain two functional groups.

Researches of binary catalysts of CH oxidation [10, 11] show that indexes of the process can be largely influenced by oxygen- and nitrogen-containing compounds, which in small quantities with catalyst are able to regulate selectivities of products via formation of intermediate complexes or associates. Use of catalytic systems that along with cobalt naphthenate (CN) contain oxygen-containing additives of different nature is effective method of influence on speed and selectivity of processes of oxidation of hydrocarbons of different nature [12].

Analysis of literature shows that for improvement of CH oxidation it is necessary to continue search of new effective catalytic systems.

5. Methods of research

In order to obtain legit results, that can be compared with literature data or with industrial indexes of CH oxidation, during research as base component of complex catalytic systems was used industrial catalyst – CN.

Due to the fact that effective CH oxidation goes under temperatures that are much higher than its boiling point (354.7 K), process of liquid phase CH oxidation should be performed after creation of high pressure that would keep substrate in liquid phase. Process of homogeny-catalytic CH oxidation was performed under conditions close to industrial: temperature – 418±2 K, pressure 1.0±0.05 MPa. Catalyst concentration was $5.0\cdot10^{-4}$ mol/l.

Analysis of aim products COL and CON was made at chromatograph LCM-80 (mod. 3, State standard 24313-80) with detector for heat conduction. Column from steel with length 2 m and diameter 3 mm was filled with filling that is made from 10 % polyethelenglycolsebacinate inflicted on Chromaton N-AW with grain 60–100 [13]. Concentration of COL and CON was determined by method of absolute calibration.

Concentration of CHHP was determined by iodinemetric method [13].

Carbonic acids, mainly adipic acid (95–97 %), should be determined titrometrically, because gas chromatography analysis of their concentration would have larger error. Concentration of acids recalculated to AA was determined by method described in [13].

Mid ether (dicyclohexyladipinate (DCA)) is highly soluble in CH and due to this during oxidation it accumulated in organic layer. Acid ether is far less soluble in CH and main quantity of it is in acid-water layer. Content of DCA is more than 95 % from total quantity of ethers. DCA was analyzed by return titration described in [13].

6. Research results

Results obtained during CH oxidation in presence of catalytic system [CN–CEE] were compared to results obtained during CH oxidation in the presence of individual CN under same conditions.

We determined influence of nature and surface activity of oxygen-containing additive on main technical-economical indexes of CH oxidation process – CH conversion, selectivity for aim-products (COL and CON) and for by-products (CHHP, AA, DCA). Notable influence of researched additive to industrial catalyst CN can be observed at conversion of raw material starting from $k \approx 2$ % (Table 1).

Results obtained at such conversion along side with data from deeper oxidation allow evaluate dynamics of the process and see trends of products accumulation.

Table 1

Impact of organic modifiers of industrial catalyst of CH oxidation process. $T = 418$ K, $P = 1$ MPa, $[CN] = 5 \cdot 10^{-4}$ mol/l, [CN]:[ADDITIVE] = 1:1

k, %	S(CHHP), %	S(AA), %	S(DCA), %	S(COL), %	S(CON), %	Sap total, %	[COL]/[CON]
CN							
2.0	18.53	12.48	11.58	40.72	16.69	79.79	2.44
CN–CEE							
1.8	23.74	10.64	9.97	36.47	19.18	82.71	1.90
CN							
4.6	5.11	18.58	22.08	36.91	17.32	73.69	2.13
CN–CEE							
5.3	6.81	18.81	7.53	41.55	25.29	76.16	1.64
CN							
4.6	5.11	18.58	22.08	36.91	17.32	73.69	2.13
CN–CEE							
7.3	1.06	20.30	9.99	35.71	32.94	73.04	1.08

Already at the starting stage of CH oxidation total selectivity for aim-products (S_{AP}) in the presence of researched additive was higher than same index at oxidation in the presence of industrial CN. If we will look at by-products at starting stage of oxidation we can observe reduce of formation of AA and DCA and increase of formation of CHHP, confirming that additive is involved in radical-chain transformations.

During deeper CH oxidation at conversion $k \approx 4$ % selectivity for aim-products at the presence of binary catalyst remain higher compared to selectivity at oxidation in the presence of industrial CN. At this stage of oxidation reduce of quantity of formed ether is very noticeable.

Very important result is that use of researched binary catalytic system allows, at conversions higher than industrial, remaining of high selectivity index for aim-products (not lower than 73 %). Thus at high conversion rates, 2 times (7.3) higher than industrial, in the presence of researched catalyst we observed rapid decrease of CHHP and DCA formation and increase of AA formation. Therefore industrial use of this additive causes the issue of acid utilization (Table. 1).

Research results show that ratio of COL/CON with growth of conversion significantly reduces at the presence of researched binary catalytic system compared to industrial catalyst.

On next stage we conducted research of impact of change of CEE additive concentration in catalytic system [CN–CEE] on indexes of CH homogeny-catalytic liquid phase oxidation. For determination of influence of change of catalytic system components ratio on process indexes we changed ratio in direction of abundance of additive as well as in direction of abundance of CN: [CN:CEE] = [1:1], [1:1.5], [1:3], [1:1/2], [1:1/4]. Obtained indexes of CH oxidation process at conversion of raw material $k \approx 4$ % are shown in Table 2.

Table 2

Influence of catalytic system components ratio at indexes of CH oxidation process. $T = 418$ K, $P = 1$ MPa, $[CN] = 5 \cdot 10^{-4}$ mol/l

k, %	C(CHHP), mol/l	C(AA), mol/l	C(DCA), mol/l	C(COL), mol/l	C(CON), mol/l	S_{AP}, %	[COL]/[CON]	$W \cdot 10^4$, mol/(l · sec)
CN								
4.7	0.042	0.029	0.067	0.106	0.057	73.7	2.13	2.29
[CN:CEE]=[1:1]								
5.3	0.034	0.093	0.012	0.206	0.125	76.2	1.64	5.4
[CN: CEE]=[1:1,5]								
2.8	0.029	0.027	0.033	0.048	0.055	63.9	0.89	2.28
[CN: CEE]=[1:3]								
3.6	0.031	0.055	0.034	0.073	0.067	62.4	1.10	4.17
[CN: CEE]=[1:1/2]								
3.8	0.030	0.066	0.020	0.086	0.072	66.2	1.20	4.51
[CN: CEE]=[1:1/4]								
3.6	0.025	0.040	0.050	0.062	0.054	57.9	1.15	2.94

From obtained experimental data (Table 2) we can see that change of ratio of [CN:CEE] in directions of increase and decrease of CEE content leads to decrease of selectivity for aim-products in comparison with ratio [CN:CEE] = [1:1]. What is more, increase of CEE content in catalytic system in 1.5 times leads to rapid decrease of selectivity for COL and CON at conversion close to industrial numbers. Based on this data we assume that ratio [CN:CEE] = [1:1] is optimal for researched catalytic system (Fig. 2).

Trends of acids accumulation in oxidate in presence of CEE compared to individual CN are alike. At low conversions ($k < 3$ %) we can't see significant differences. But after reaching of industrial values ($k \approx 4$ %) and higher – selectivities for acids are significantly different depending on ratio of catalytic system components.

We discovered that abundance of oxygen-containing additive CEE compared to CN leads to increase of acid formation (Fig. 2, curves 5, 6). Decrease of CEE content leads to decrease of selectivity for acids. However, this decrease has maximum that is found at ratio [CN:CEE] = [1:1/2]. That allows to suggest that binary catalytic system is optimal for formation of acid despite decrease of COL and CON content (Fig. 3).

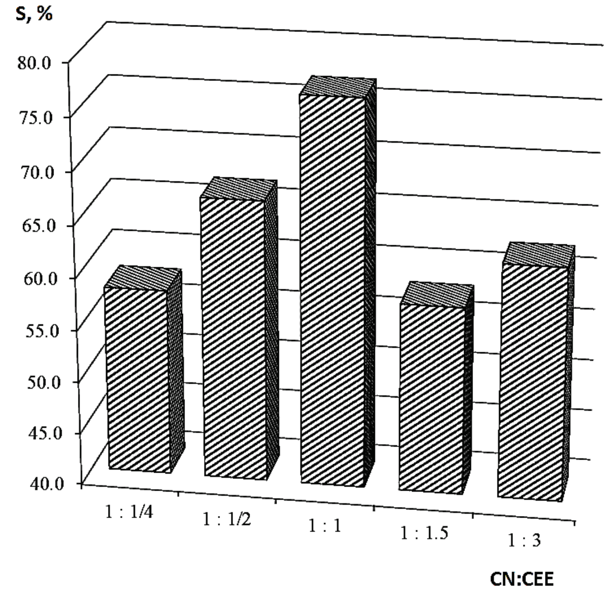

Fig. 2. Dependence of selectivity for aim-products from ratio of components of catalytic system [CN:CEE]. $T = 418$ K, $P = 1.0$ MPa, $k \approx 4$ %

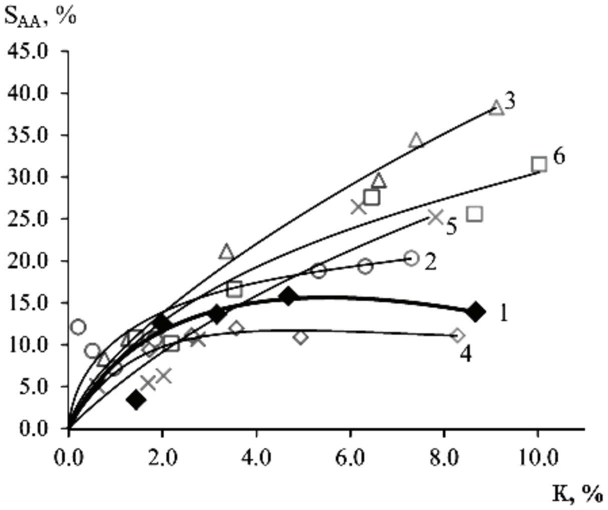

Fig. 3. Dependence of selectivity for acids from ratio of components in catalytic system [CN–CEE]. $T = 418$ K, $P = 1.0$ MPa.
1 – CN; 2 – [CN:CEE] = [1:1]; 3 – [CN:CEE] = [1:1/2];
4 – [CN:CEE] = [1:1/4]; 5 – [CN:CEE] = [1:1.5]; 6 – [CN:CEE] = [1:3]

During homogeny-catalytic CH oxidation in presence of CN acids are formed, however their quantities are low ($S_{AA} = 15.8$ at conversion $k = 4.6$ %), and because of it in industry they are neutralized by alkali compounds and burned.

In case of researched catalytic systems we obtain significantly larger volumes of acids ($S_{AA} = 20.3$ % at conversion $k = 7.3$ %). For improvement of this process and obtainment of additional valuable compounds is necessary using of complex method of using of CH oxidation products. This is reason for utilization of received acids.

One of methods of utilization of received acids is formation of ethers from acids by etherification with alcohol. Later received ethers could be used as plasticizers for polymers. In case of etherification with lower alcohols ethers can be divided by boiling temperature and used for receiving of individual acids. For etherification process we took oxidate received by CH oxidation in the presence of catalytic system [CN–CEE] (CN:CEE = 1:1). Composition of oxidation products is shown lower (Table 3).

Table 3

Composition of products received by CH oxidation in the presence of binary catalytic system CN–CEE. $T = 418$ K, $P = 1$ MPa, $[CN] = 5 \cdot 10^{-4}$ mol/l, [CN]:[CEE] = 1:1

k, %	C(CHHP), mol/l	C(AA), mol/l	C(DBA), mol/l	C(COL), mol/l	C(CON), mol/l	[COL]/[CON]
11.96	0.026	0.433	0.090	0.177	0.225	0.78
	S(CHHP), %	S(AA), %	S(DBA), %	S(COL), %	S(CON), %	
	0.24	39.15	8.09	15.98	20.37	

Received acids were divided from mixture of all products by water. Received water solution of organic acids was concentrated by evaporation of water. Composition of received acids solution is shown below (Table 4).

Table 4

Composition of water solution of acids

C(AA), mol/l	C(CHHP), mol/l	C(DCA), mol/l	C(COL), mol/l	C(CON), mol/l
0.476	0.001	0.023	0.009	0.014

Etherification of water acid layer was made in abundance of n-butanol with presence of ion exchange resin KU-2 under boiling of received azeotrope water – *n*-butanol $T = 365$ K.

After etherification we conducted distillation of water and untreated n-butanole Mass of received mixture of ethers is $m(\text{total}) = 4.467$ gr. Analysis of composition of received mixture can be found in Table 5. Yield of ethers is $n = 57.6$ %.

Table 5

Composition of received products mixture of etherification of adipic acid and *n*-butanol at $T = 365$ K

C(AA), mol/l	C(CHHP), mol/l	C(DBA), mol/l	C(COL), mol/l	C(CON), mol/l
0.090	0.000	0.668	0.000	0.000

For evaluation of efficiency of researched methods we used following calculation. Calculation consisted from determination of quantity of received products from 1000 kg of processed raw material. This index was compared to similar index for process of oxidation in presence of individual CN in case of neutralization of acids and burning of received adipates (Tables 6, 7).

Table 6

Quantities of received aim-products from 1 *t* of processed CH in presence of CN. $T = 418$ K, $P = 1$ MPA, $[CN] = 5 \cdot 10^{-4}$ mol/l

Compound	Used, kg	Received, kg
Cyclohexane	1000	–
n-butanol	–	–
Sodium hydroxide	228	–
COL + CON	–	863
Adipates	–	462
Dibutyl adipinate	–	–
Sum of aim-products (COL + CON)	–	863

Table 7

Quantities of received aim-products from 1 t of processed CH in presence of catalytic system CN–CEE. $T = 418$ K, $P = 1$ MPa, $[CN] = 5 \cdot 10^{-4}$ mol/l, CN:CEE = 1:1

Compound	Used, kg	Received, kg
Cyclohexane	1000	–
n-butanol	417	–
Sodium hydroxide	31	–
COL + CON	–	860
Adipates	–	69
Dibutyl adipinate	–	727
Sum of aim-products*	–	1587

Note: *– mixture of COL, CON and ether, received through etherification of adipic acid and n-butanol.

Therefore during oxidation of 1 t of CH, in presence of industrial catalyst – CN, was received m(COL,CON,AA) = = 863 kg of mixture of COL, CON and AA, that required m(NaOH) = 228 kg for neutralization (Table 6). And during CH oxidation in the presence of binary catalytic system CN–CEE (1:1) was received $m = 860$ kg of mixture of COL and CON, dibutyl adipinate (DBA) $m = 727$ kg and $m = 69$ kg of adipates (Table 7). Comparison of received data shows that quantity of received mixture of COL and CON in both cases is almost even. However in the presence of CN-CEE we receive more acids that were used as raw material for receiving of additional volume of aim-products (DBA).

This means that proposed method of complex use of CH oxidation products creates opportunity for receiving of additional quantities of aim-products via more useful processing of received acids that were traditionally neutralized and burned in industry.

7. SWOT analysis of results of research

Strengths. From strong points of this research we should note received results of search of optimal conditions of CH oxidation process in presence of new binary catalytic system based on existing industrial catalyst and active oxygen-containing additive. Use of received data will allow intensification of process through increase of compounds transformation depth. Proposed method of use of acids that in previous methods were burned is very important for etherification. This will allow receiving of additional quantities of CH oxidation products with their complex processing in national economy, and as a result will decrease spending coefficients for raw material and, therefore, cost of production.

Weaknesses. Weak points of this research are slight increase of number of apparatus in production and slight increase of purchase costs for additional raw materials for preparation of binary catalyst.

Opportunities. Additional opportunities that can help reaching of aim of research are searches of other active additives for creation of effective catalytic systems. There can be found a lot of other oxygen-containing compounds that might have more positive influence on CH oxidation process. Another possible direction of research is economical calculations of profit that can be reached in case of implementation of proposed oxidation method in industry.

Threats. Threats from implementation of obtained results can be related to two factors.

First – management of companies that are using such processes. Long stoppage of technological installations, investments in additional materials, absence of rapid high result might become braking factor for managers of such companies.

Second – unstable laws in economical sphere of Ukrainian industry.

8. Conclusions

1. Positive impact of oxygen-containing additive on main technical-economical indexes of CH oxidation process – selectivity for oxidation products and ratio of aim-products – was found. Selectivity for aim-products grows at 3–4 % in comparison with oxidation at industrial catalyst and stays maximal – 73 % under conversion that is two times higher than industrial – 7.3 %. During use of researched binary catalytic system, ratio of aim-products in comparison with industrial catalyst decreases from 2.44 to 1.08 in direction of COL formation.

2. It was found that ratio of binary catalytic system components [CN:CEE]=[1:1] is optimal for use in CH oxidation process.

3. It is determined that in presence of researched binary catalytic system at conversion higher than 4 % quantity of formed acids increases to 20.3 %. Therefore we propose method of utilization of formed acids by etherification with alcohol. Quantity of aim-products produced by this method is 1587 kg, while conventional method of CH oxidation results in 863 kg.

References

1. Li, G. Photooxidation of cyclohexane and cyclohexene in BaY [Text] / G. Li, M. Xu, S. C. Larsen, V. H. Grassian // Journal of Molecular Catalysis A: Chemical. – 2003. – Vol. 194, No. 1–2. – P. 169–180. doi:10.1016/s1381-1169(02)00518-6
2. Mishra, G. S. Selective single-pot oxidation of cyclohexane by molecular oxygen in presence of bis(maltolato)oxovanadium complexes covalently bonded to carbamated modified silica gel [Text] / G. S. Mishra, A. J. L. Pombeiro // Journal of Molecular Catalysis A: Chemical. – 2005. – Vol. 239, No. 1–2. – P. 96–102. doi:10.1016/j.molcata.2005.05.035
3. Yao, W. Liquid oxidation of cyclohexane to cyclohexanol over cerium-doped MCM-41 [Text] / W. Yao, Y. Chen, L. Min, H. Fang, Z. Yan, H. Wang, J. Wang // Journal of Molecular Catalysis A: Chemical. – 2006. – Vol. 246, No. 1–2. – P. 162–166. doi:10.1016/j.molcata.2005.10.029
4. Hettige, C. Cyclohexane oxidation and carbon deposition over metal oxide catalysts [Text] / C. Hettige, K. R. R. Mahanama, D. P. Dissanayake // Chemosphere. – 2001. – Vol. 43, No. 8. – P. 1079–1083. doi:10.1016/s0045-6535(00)00195-8
5. Du, P. Selective photo(catalytic)-oxidation of cyclohexane: Effect of wavelength and TiO2 structure on product yields [Text] / P. Du, J. Moulijn, G. Mul // Journal of Catalysis. – 2006. – Vol. 238, No. 2. – P. 342–352. doi:10.1016/j.jcat.2005.12.011
6. Teramura, K. Photo-oxidation of cyclohexane over alumina-supported vanadium oxide catalyst [Text] / K. Teramura, T. Tanaka, T. Yamamoto, T. Funabiki // Journal of Molecular Catalysis A: Chemical. – 2001. – Vol. 165, No. 1–2. – P. 299–301. doi:10.1016/s1381-1169(00)00417-9
7. Carvalho, N. Cyclohexane oxidation catalyzed by mononuclear iron(III) complexes [Text] / N. Carvalho, A. Hornjr, O. Antunes // Applied Catalysis A: General. – 2006. – Vol. 305, No. 2. – P. 140–145. doi:10.1016/j.apcata.2006.02.053

8. Nowotny, M. Increasing the ketone selectivity of the cobalt-catalyzed radical chain oxidation of cyclohexane [Text] / M. Nowotny, L. N. Pedersen, U. Hanefeld, T. Maschmeyer // Chemistry. – 2002. – Vol. 8, No. 16. – P. 3724–3731. doi:10.1002/1521-3765(20020816)8:16<3724::aid-chem3724>3.0.co;2-w
9. Ludyn, A. M. The impact of amino acids on cyclohexane oxidation [Text] / A. M. Ludyn, V. V. Reutskyy // Bulletin of the Lviv Polytechnic National University. Series of Chemistry, Materials Technology and Their Application. – 2016. – Vol. 841. – P. 108–112.
10. Reutskyy, V. Okysnennia tsykloheksanu v prysutnosti bahatoatomnykh spyrtiv [Text] / V. Reutskyy, O. Ivashchuk, S. Mudryi, O. Suprun // Materialy mizhnarodnoi naukovoi konferentsii, prysviachenoi 100-richchiu vid dnia narodzhennia profesora Dmytra Tolopka «Aktualni problemy khimii ta tekhnolohii orhanichnykh rechovyn (APCTOS)», Lviv, Ukraine, November 6–8, 2012. – Lviv: Vydavnytstvo Lvivskoi politekhniky, 2012. – P. 24.
11. Christopher, R. Oxidation of Cyclohexane by Transition Metal Oxides on Zeolites [Text] / R. Christopher, R. Riley, E. N. Montgomery, N. N. Megally, A. J. Gunn, L. S. Davis // The Open Catalysis Journal. – 2012. – Vol. 5, No. 1. – P. 8–13. doi:10.2174/1876214x01205010008
12. Novye kataliticheskie kompozitsii dlia selektivnogo okisleniia uglevodorodov na osnove soedinenii metalov peremennoi valentnosti i katalizatorov mezhfaznogo perenosa [Text] // Tezisy dokladov 7-go Neftehimicheskogo simpoziuma. – Kyiv, 1990. – 230 p.
13. Reutskyy, V. V. Kataliticheskoe okislenie tsiklogeksana v akusticheskom pole [Text]: PhD thesis / V. V. Reutskyy. – Lviv, 1988. – 119 p.

УСОВЕРШЕНСТВОВАНИЕ ПРОЦЕССА ОКИСЛЕНИЯ ЦИКЛОГЕКСАНА

Рассмотрен способ усовершенствования процесса жидкофазного окисления циклогексана. Определен положительный эффект кислородосодержащей добавки – Бис-2 цианетилового этера – на основные технико-экономические показатели процесса – конверсию сырья, селективность по продуктах окисления и соотношение целевых продуктов. Исследовано оптимальное соотношение компонентов бинарной каталитической системы. Предложен комплексный метод использования продуктов окисления циклогексана путем утилизации полученных побочных кислот эстерификацией их со спиртами.

Ключевые слова: окисление циклогексана, кислородосодержащая добавка, бинарная каталитическая система, конверсия сырья.

Ludyn Anatoly, *PhD, Associate Professor, Department of the Theory of Organic Products, National University «Lviv Polytechnic», Ukraine, e-mail: anatolii.m/ludyn@lpnu.ua, ORCID: https://orcid.org/0000-0002-5555-687X*

Reutskyy Viktor, *Doctor of Technical Sciences, Associate Professor, Department of the Theory of Organic Products, National University «Lviv Polytechnic», Ukraine, e-mail: reutskyy@polynet.lviv.ua, ORCID: https://orcid.org/0000-0002-7388-1115*

UDC 646.7:615:579.6
DOI: 10.15587/2312-8372.2017.119392

Tkachenko N.,
Vikul S.,
Sevastyanova E.,
Dets N.,
Honcharuk Ya.

SUBSTANTIATION OF THE COMPOSITION OF PROBIOTIC COSMETIC PRODUCTS FOR THE TONING OF OILY SKIN

Показана доцільність застосування пробіотиків у натуральній косметиці. Обґрунтовано оптимальні масові частки кислої сироватки та екстракту квітів Tagetes patula (59,98 та 40,02 % відповідно) як компонентів пробіотичного косметичного засобу для тонізації жирної шкіри. Доведено, що розроблений пробіотичний косметичний лосьйон натуральний, безпечний, характеризується високими органолептичними, нормованими фізико-хімічними показниками, покращеними мікробіологічними характеристиками.

Ключові слова: *пробіотична косметика, тонізація шкіри, Bifidobacterium, Lactobacillus, водно-спиртовий екстракт, Tagetes patula, кисла сироватка.*

1. Introduction

Skin is the largest organ in the human body, which is in constant work throughout life. The condition of the skin largely depends on age, nutrition and lifestyle. The main function of the skin is protection of the human body from external influences, creating a physical barrier. In addition, the skin also performs additional functions, which include: regulating body temperature, controlling sweating, feeling, keeping lipids and water. Acting as a barrier and a link between internal organs and the external environment, the skin is always in contact with various substances. A healthy and blooming skin is the result of well-being and constant care [1].

The face is the most open part of the skin of a person, his business card. This is the first thing that they pay attention to when they meet. In order for the face to remain beautiful, fresh and attractive, special care is needed. The skin of the face is constantly exposed to the negative effects of various external factors. In addition, it shows signs of fatigue, physical overload and stress. Over time, the skin loses its freshness, wrinkles appear on it, it dims and becomes less attractive [2].

Facial skin care involves a number of procedures: washing, cleansing, nutrition, moisturizing, toning. To care for a specific type of facial skin, it is necessary to choose the right cosmetic products. If the means for washing and moisturizing