

## ВДОСКОНАЛЕННЯ ГОМОГЕННО-КАТАЛІТИЧНОГО ПРОЦЕСУ ОКИСНЕННЯ АЛКІЛ АРОМАТИЧНИХ СПОЛУК ЗА ДОПОМОГОЮ ПОЄДНАННЯ БІНАРНИХ КАТАЛІТИЧНИХ СИСТЕМ І УЛЬТРАЗВУКОВОГО ОБРОБЛЕННЯ

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Досліджено вплив сумісного застосування каталітичних систем на основі промислових каталізаторів окиснення та поверхнево-активних речовин різної природи (йонно- та нейонногенних) і ультразвукового оброблення реакційної суміші на процес рідиннофазного окиснення алкілароматичних сполук. Одержані результати дають змогу стверджувати, що сумісне застосування каталітичних систем та ультразвукового оброблення впливає на окиснення етилбензолу. Створені каталітичні системи не лише збільшують продуктивність реакційного обладнання за цільовими продуктами, але й здатні змінювати селективність процесу в бік утворення необхідного продукту.

**Ключові слова:** окиснення, етилбензол, поверхнево-активні сполуки, каталітичні системи, гідропероксид етилбензолу, ацетофенон, ультразвук.

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## IMPROVEMENT OF HOMOGENEOUS CATALYTIC PROCESS OF OXIDATION OF ALKYLAROMATIC COMPOUNDS BY COMBINATION OF BINARY CATALYTIC SYSTEMS AND ULTRASOUND TREATMENT

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Article is devoted to research of impact of combined use of catalytic systems based on industrial oxidation catalysts and surface-active compounds of different nature (ion- and non-ionogenic) with ultrasonic treatment of reaction mixture at alkylaromatic compounds liquid-phase oxidation process. Obtained results showed that combined use of catalytic system and ultrasound has impact on ethylbenzene oxidation. Created catalytic systems not only increase productivity of reaction volume (for aim products), but also allow to shift process selectivity towards creation of desired product.

**Key words:** oxidation, ethylbenzene, surface active compounds, catalytic systems, hydroperoxide of ethylbenzene, acetophenone, ultrasound.

**Introduction.** The practical significance of oxidation processes in the production of basic organic and petrochemical synthesis is overemphasized. Their primary role is based on following reasons:

1. Great value of compounds derived by oxidation (alcohols, aldehydes, ketones, carboxylic acids and their anhydride, a-oxides, nitrils, etc.) and intermediates, solvents, monomers and precursors for the production of polymers, plasticizers, etc.

2. Wide variety of oxidation reactions, which are possible for many organic compounds, including hydrocarbons of all classes. This allows to use oxidation processes for primary processing of hydrocarbons and to receive large number of substances on their basis.

3. Accessibility and low cost of most oxidative agents, among which most dominant is air oxygen. This defines a higher efficiency of synthesis methods of oxidation of certain products over other possible methods of their preparation.

Oxidation processes are widely used in organic synthesis, often replacing less economical ways to produce many products.

However alongside advantages processes of oxidation have few significant minuses. The most important disadvantage is low control of formation of aim and by-products on deeper stages of oxidation. Due to this fact conversion of oxidation processes is usually limited; therefore technologically process becomes more complicated through big recycle of raw material.

This problem can be solved by search and use of new effective catalytic systems and combination of such systems with physical methods of process intensification.

**Analysis of published data and problem definition.** In order to achieve high production values and relatively high speed of oxidation processes of hydrocarbons liquid-phase oxidation traditionally are preformed in the presence of catalysts. The most used homogeneous catalysts for such processes are salts of variable valence metal (VVM). Catalytic activity of homogeneous catalysts in processes of liquid-phase oxidation is mainly associated with two factors: 1) selective acceleration (braking) of the individual elementary reactions; 2) creation of new ways for chemical transformations. VVM participation in all the elementary stages of the process – origin, continuing, degenerate branching and chain termination determines their effect on the rate and selectivity of oxidation process. Main effectiveness of the presence of the salts of VVM is associated with their participation in the elementary stages of the formation and chain-transfer of free radicals [1–5, 7, 9].

Creation and chain-transfer of the radicals in the presence of VVM salts is going through stages of formation of an intermediate complex with charge transfer between the catalyst and hydroperoxide molecule or oxygen, and activation of reacting molecules. On the stages of the creation of radicals effectiveness of catalyst primarily depends on the redox potential of the metal cation and its ability to give and receive electrons. Creation of the chain reaction (in the presence of catalyst) is supposed to go as direct interaction between VVM cation in higher oxidative form and substrate molecules. Such scheme of oxygen and hydrocarbon phased activation in some cases allows satisfactorily explain patterns of catalytic initiation of oxidation reaction, but majority of theoretical and experimental data shows presence of simultaneous activation of molecular oxygen and hydrocarbon at VVM cation, as reaction center [1, 2, 9, 10].

It is also worth mentioning that organic compounds, able to be coordinated on a metal ion, may impact activation of molecular oxygen in the reaction mixture.

Taking into account the possibility of free radicals creation by direct reaction between starting compounds and VVM salts, main initiating action of mentioned catalysts is primarily associated with their participation in acceleration of peroxide compounds decomposition, as well as the interaction of VVM ion in a higher oxidative state with products that contain oxygen.

Liquid-phase oxidation of ethylbenzene is a classic version of the homogeneous radical-chain oxidation process [3]. This means low conversion of raw materials and complexity of managing of selectivity of the aim products. In industry this process can reach values of conversion up to 10–15 %. Such value can be reached because the process is carried out in multiple (up to 6) consecutive reactors with intermediate removal of ethylbenzene hydroperoxide (HPEB). In one reactor conversion is 3–4 %. In the literature there is data on achieving ethylbenzene conversion up to 80 % and selectivity for HPEB up to 90 % [8–10], but in these researches received hydroperoxide is immediately bonded and thus taken out from the oxidation reaction. Further processing of bounded HPEB is very hard and, in some cases, impossible. The average length of oxidation in mentioned processes is about 30 hours, and such length significantly reduces the reaction equipment productivity.

In the literature can be also found data on the use of bi-component catalytic systems, that along with VVM salt have inorganic salts of sodium, potassium and calcium [5–7]. Usage of these salts enhanced the conversion process of oxidation and also increases selectivity for HPEB.

Ultrasonic cavitation has positive influence on processes of auto-oxidation of aromatic hydrocarbons, and on process of their catalytic oxidation. Use of ultrasonic treatment (UST) during cyclohexane oxidation in

presence of VVM salts increases the oxidation speed in 1.2 – 2 times (depending on nature of catalyst). There is also change in selectivities for aim products – we can observe increase of CON formation [11].

**Purpose and objectives of the work** Previous work showed the influence of complex catalytic systems [surface-active compounds (SAC) – industrial catalyst] on the processes of liquid-phase oxidation of hydrocarbons, that is why it was appropriate to study the combine impact of catalytic additives and UST on liquid-phase oxidation of ethylbenzene.

**Methods of experiments** Patterns of liquid phase oxidation of ethylbenzene in the presence of industrial catalysts [NC and ACK] were studied at 403 K and a pressure 0–0.45 MPa. The concentration of VVM salt was  $1.0 \cdot 10^{-3}$  mol/L.

Patterns of liquid phase oxidation of ethylbenzene in the presence of catalytic systems [VVM salt – SAC] were studied at 403 K and a pressure 0.4–0.45 MPa. The concentration of VVM salt was  $1.0 \cdot 10^{-3}$  mol / L. The mass ratio of VVM salt / SAC was 1/1. As VVM salts were used industrial catalysts – cobalt naphthenate (NC) and cobalt acetate (AC).

The results obtained in the oxidation of ethylbenzene in the presence of catalytic systems [NC – SAC; AK – SAC] were compared with those indicators that have been achieved in the oxidation of ethylbenzene in the presence of individual industrial catalyst under the same conditions. As SAC were used : polyethylene glycol (PG), chromoxane (Ch) HPEB concentration was determined tytremetrycly, concentration of acetophenone (AP) and metylphenylcarbinol (MPC) – by gas-liquid chromatography.

**Results and Discussion** Basing on previous research we decided to investigate influence of ultrasound on NC based catalytic systems. Obtained results are shown in table 1.

Table 1

**Oxidation of EB in presence of NC-based catalytic systems and UST of reaction mixture. P=4–4,5 MPa, T=403 K**

Catalyst	time, min	C (HPEB), mol/l	C (AP), mol/l	C (MPC), mol/l	K EB	S (AP)	S (MPC)	S (HPEB)
NC	10	0.006	0.011	0.003	0.24	54.93	16.84	28.23
	60	0.028	0.030	0.011	0.85	43.12	16.5	40.38
	120	0.048	0.067	0.016	1.62	51.09	12.36	36.55
	180	0.068	0.089	0.018	2.15	50.87	10.42	38.71
	210	0.068	0.113	0.021	2.48	55.86	10.43	33.71
	240	0.067	0.131	0.026	2.75	58.47	11.56	29.97
NC+UST	10	0.0115	0.0107	0.003	0.31	42.46	11.9	45.63
	60	0.026	0.061	0.012	1.22	61.62	12.12	26.26
	120	0.047	0.093	0.035	2.15	53.14	20.00	26.86
	180	0.066	0.111	0.057	2.88	47.44	24.36	28.21
	210	0.079	0.155	0.079	3.85	49.52	25.24	25.24
	240	0.083	0.283	0.083	5.52	63.03	18.49	18.49
NC+PG+UST	10	0.012	0.0107	0.003	0.32	41.63	11.67	46.69
	60	0.051	0.056	0.009	1.43	48.28	7.76	43.97
	120	0.073	0.094	0.018	2.28	50.81	9.73	39.46
	180	0.102	0.132	0.027	3.21	50.57	10.34	39.08
	210	0.112	0.159	0.031	3.71	52.65	10.26	37.09
	240	0.116	0.168	0.036	3.94	52.50	11.25	36.25
NC+Ch+UST	10	0.011	0.014	0.003	0.34	50.00	10.71	39.29
	60	0.022	0.081	0.004	1.32	75.70	3.74	20.56
	120	0.043	0.162	0.005	2.58	77.14	2.38	20.48
	180	0.054	0.218	0.005	3.41	78.70	1.81	19.49
	210	0.059	0.235	0.005	3.68	78.60	1.67	19.73
	240	0.06	0.254	0.005	3.92	79.62	1.57	18.81

Data showed in Table 1 shows that in comparison with use of individual NC UST of reaction mixture influences oxidation of EB.

Data on formation of HPEB shows that UST increases HPEB formation on later stages of oxidation. Such effect can be explained by influence of concentrated cavitation energy on stages of creation and transfer of radical chain. However increase of HPEB formation under combined influence of catalytic system [NC – PG] and UST is smaller compared to use of only catalytic system. This means that cavitation is also influencing stability and formation of highly active intermediate complexes [NC-PG-substrate] leading to its faster decomposition into secondary products of EB oxidation – MPC and AP.

Also it is worth mentioning that use of UST combined with industrial catalyst NC leads to increase of EB conversion (K) on more than 100 %, compared with use of individual NC. Such increase is achieved by increase in formation of secondary oxidation products – mainly AP – and decrease in concentration of HPEB. Such result proves influence of cavitation through faster decomposition of intermediate particles and less stable HPEB.

Use of UST combined with catalytic system allows increase of EB conversion up to 35 % and reach selectivity for AP up to 80 %. This also proves proposed mechanism of cavitation influence – concentrated energy of cavitation allows faster decomposition of intermediate complexes and formation of secondary products of EB oxidation.

Table 2

**Oxidation of EB in presence of AC-based catalytic systems  
and UST of reaction mixture. P = 4–4,5 MPa, T = 403 K**

Catalyst	time, min	C (HPEB), mol/l	C (AP), mol/l	C (MPC), mol/l	K EB	S (AP)	S (MPC)	S (HPEB)
AC	10	0,007	0,0146	0,00184	0,29	62,29	7,85	29,86
	60	0,009	0,6025	0,1908	9,87	75,1	23,78	1,12
	120	0,0205	0,7225	0,162	11,13	79,83	17,9	2,27
	180	0,017	0,8745	0,1236	12,49	86,15	12,18	1,67
	210	0,019	1,2105	0,1236	16,64	89,46	9,13	1,4
	240	0,019	1,2745	0,1492	17,75	88,34	10,34	1,32
AC+UST	10	0,006	0,017	0,00064	0,29	71,91	2,71	25,38
	60	0,0113	0,9234	0,0987	12,71	89,36	9,55	1,09
	120	0,0245	1,387	0,1356	19,03	89,65	8,76	1,58
	180	0,03	1,7205	0,1748	23,68	89,36	9,08	1,56
	210	0,034	1,7225	0,1748	23,76	89,19	9,05	1,76
	240	0,038	1,7231	0,1748	23,81	89,01	9,03	1,96
AC+PG+UST	10	0,0075	0,0119	0,00064	0,25	59,38	3,19	37,43
	60	0,017	0,6346	0,0985	9,23	84,60	13,13	2,27
	120	0,023	0,9866	0,1232	13,93	87,09	10,88	2,03
	180	0,031	1,1945	0,1428	16,83	87,30	10,44	2,27
	210	0,033	1,2185	0,1428	17,15	87,39	10,24	2,37
	240	0,037	1,2267	0,1429	17,30	87,21	10,16	2,63
AC+CH+UST	10	0,007	0,014	0,001	0,27	63,64	4,55	31,82
	60	0,016	0,693	0,156	10,64	80,12	18,03	1,85
	120	0,018	0,796	0,177	12,19	80,32	17,86	1,82
	180	0,021	1,126	0,195	16,51	83,90	14,53	1,56
	210	0,022	1,263	0,207	18,35	84,65	13,87	1,47
	240	0,022	1,383	0,214	19,91	85,42	13,22	1,36

Another influence of UST is its impact on ratio between reduced and oxidized forms of catalyst. Cavitation leads to faster formation of oxidized form of catalyst metal –  $\text{Co}^{3+}$ .  $\text{Co}^{3+}$ -based catalytic

complexes allows straight oxidation of EB into AP without intermediate formation of HPEB, as the most energetically favorable route of reaction.

Taking into account influence of UST on formation of secondary products of EB oxidation next logical step of research was investigation of UST influence with combined use with catalytic systems based on AC.

Industrial catalyst AC improves formation of secondary products of oxidation – mainly AP – and basically promotes speed of energetically favorable routes of reaction.

Previous research showed that catalytic systems based on AC increases speed of EB oxidation, in comparison with use of individual AC, and increases selectivity for AP and MPC.

UST of reaction mixture was conducted during 1 hour by ultrasound generator UZG5-22.

Data obtained during research is presented in Table 2.

Obtained data shows, that in comparison with use of individual AC, UST increases speed of oxidation and conversion of EB in all cases, with exclusion of use of system [AC-PG-UST].

PG as catalytic additive leads to increase of formation of HPEB. This trend remains even under use of UST. Such results can be explained by impact of PG as SAC. PG increases solubility of oxygen in reaction mixture and therefore increases speed of HPEB formation.

In all other cases UST increases conversion of EB but concentrated cavitation energy influences speed of formation and decomposition of intermediate catalytic complexes [AC-additive-substrate] and this leads to increase of selectivity for MPC.

**Conclusions.** On the basis of the research the following conclusions and assumptions can be made: UST of reaction mixture influences process of EB oxidation. Concentrated cavitation energy increases number of reactions of creation and transfer of radical chain. Use of UST proves assumption of formation of intermediate catalytic complexes [catalyst-additive-substrate]. Use of UST changes curves of accumulation of reaction products and decreases influence of additives on oxidation speed. Combined use of AC and UST allows to increase EB conversion 6 % in 1 reactor and achieve selectivity for AP up to 89 %. Obtained results allow to recommend combine use of AC and UST in industrial process of AP formation.

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