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New technological solutions in the production of high quality cyclohexanone

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Objectives. *The intensification of modern large-tonnage Russian technologies requires a deep investigation into the theoretical foundations of these processes and searching for ways that would significantly reduce the time and cost of their development, as well as to ensure the access of high-quality products on the world market. The aim of the work was to study the options regarding technological changes in the process of obtaining cyclohexanone at two stages: 1) oxidate (cyclohexane oxidation product after the stage of neutralization and removal of the main amount of unreacted cyclohexane) saponification and 2) end product rectification. The changes should ensure the high quality of the product without requiring significant energy and investment costs.*

Methods. *Studies of heterophase alkaline hydrolysis with NaOH solutions were carried out at 30–80 °C in the presence of and without a phase transfer catalyst (PTC) (saponification conditions in the industry are 70 °C). The homophase process was studied in the presence of KOH at 120 °C (industrial conditions for raw cyclohexanone rectification are 90–130 °C) on artificial mixtures based on industrial samples of the oxidate with the addition of model substances (oxygen-containing impurities with a main substance content of no less than 95%). Analysis of the initial and obtained products was carried out using gas-liquid chromatography and chromatography-mass spectrometry.*

Results. *The totality of the obtained data provides theoretical justification for the fact: 50–70% of esters and unsaponifiable impurities can be removed by using heterophase alkaline saponification in industrial environments. The post-treatment of crude cyclohexanone by rectification in the presence of KOH decreases the ester number by a factor of 3–5, however, the number of cyclohexanone condensation products in the bottom sharply increases. The amount of these substances varies from 10 to 20 kg/t of cyclohexanone depending on compliance with the conditions. In the presence of PTC, the conversion of esters at the saponification stage is 95–100%, aldehydes 100%, and unsaturated ketones 80%.*

Conclusions. *If the proposed technology for saponification in the presence of PTC is adopted there will be no need to use an alkali during the process of cyclohexanone rectification. This makes the process more stable, reduces the losses of cyclohexanone, reduces the amount of tars, and normalized indicators of cyclohexanone quality are attained.*

Keywords: *caprolactam, cyclohexanone, purification, impurities, phase-transfer catalysis.*

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Новые технологические решения в производстве циклогексанона высокого качества

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Цели. *Интенсификация современных многотоннажных отечественных технологий требует глубокой проработки теоретических основ этих процессов и поиска путей, которые позволили бы существенно сократить сроки и затраты на их освоение и обеспечить выход на мировой рынок продукции высокого качества. Цель работы заключалась в исследовании вариантов технологических изменений процесса получения циклогексанона на стадиях омыления оксидата (продукта окисления циклогексана после отгонки основной части непрореагировавшего циклогексана) и ректификации целевого продукта, обеспечивающих его высокое качество, не требующих значительных энергетических и инвестиционных затрат.*

Методы. *Исследования гетерофазного щелочного гидролиза водными растворами NaOH проводили в интервале температур 30–80 °C в присутствии и без катализатора межфазного переноса (КМФП) (режим омыления в промышленности 70 °C); гомофазный процесс изучали в присутствии KOH при температуре 120 °C (промышленный режим ректификации циклогексанона-сырца 90–130 °C) на искусственных смесях, составленных на основе промышленных образцов оксидата с добавлением модельных веществ (кислородсодержащих примесей с содержанием основного вещества не менее 95%). Анализ исходных и полученных продуктов проводили с использованием газо-жидкостной хроматографии и хромато-масс-спектрометрии.*

Результаты. *Совокупность полученных данных дает теоретическое обоснование реальному факту: при гетерофазном щелочном омылении в промышленных условиях сложные эфиры и неомыляемые примеси могут быть удалены на 50–70%. Доочистка сырого циклогексанона при ректификации в присутствии KOH в 3–5 раз уменьшает эфирное число, однако в кубе резко возрастает количество продуктов конденсации циклогексанона, которое в зависимости от соблюдения режимов колеблется от 10 до 20 кг/т циклогексанона. В присутствии КМФП конверсия эфиров на стадии омыления составляет 95–100%, альдегидов 100%, непредельных кетонов 80%.*

Заключение. *В случае внедрения предложенной технологии омыления оксидата в присутствии КМФП отпадает необходимость использования щелочи в процессе ректификации сырого циклогексанона, что делает процесс более стабильным, сокращаются потери циклогексанона, уменьшается количество смол и достигаются нормированные показатели качества циклогексанона.*

Ключевые слова: *капролактам, циклогексанон, очистка, примеси, межфазный катализ.*

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Introduction

The intensification of modern large-tonnage Russian technologies requires an in-depth study of the theoretical basis of these processes, as well as a search for methods that would allow for a considerable reduction in the time and costs of their development and allow high-quality products to enter the world market [1–3].

The complexity of the situation regarding the production of caprolactam is that, as we know, when oxidizing cyclohexane, a large amount (more than 50) of oxygen-containing compounds (saponifiable and non-saponifiable) belonging to different classes and having different reactivity are formed. These are aldehydes, alcohols, ketones, peroxides, carboxylic acids, as well as their aliphatic and cyclohexyl esters [4–7].

The state of cyclohexanone and caprolactam can be evaluated by generally accepted quality indicators, which while rather sensitively, yet conditionally, indicate the presence of impurities of another chemical nature. This is the permanganate index (PI) – an indicator of cyclohexanone and caprolactam quality characterizing the content of easily oxidizable compounds in the target product. For rectified cyclohexanone that meet the requirements of international standards, the permanganate index should be no more than 20 units[1] [2]. The quality of marketable caprolactam (PI: 4–5 units) directly depends on the quality of cyclohexanone. The purification of the latter in the production process has been attracting the attention of chemists and technology experts from around the world over the course of several decades with varying degrees of success [2, 8–21].

The Russian industrial production of cyclohexanone includes several successive stages to purify the oxidate obtained by cyclohexane liquid-phase oxidation in the presence of cobalt naphthenate: aqueous or aqueous-alkaline washing to remove acids, saponification (hydrolysis) of esters, and rectification of crude cyclohexanone in the presence of potassium hydroxide (0.01–1% wt. per reaction mass). The main disadvantage of the industrial purification methods is the lack of stable indicators and of control of the resulting high-boiling by-products, as well as high alkali consumption and the loss of the target product [2].

We have provided reasons about the possible options to make changes at the stage of oxidate saponification and cyclohexanone rectification to ensure its high quality. The suggested changes are based on an analysis of the available literature, from our previous studies [2, 3, 14, 17–19] and results obtained in this work. These changes do not require significant power consumption and investment expenditures.

Materials and Methods

An industrial sample of the reaction mass from the cyclohexane oxidation process obtained after the neutralization stage and removal of the basic amount of unreacted cyclohexane was used for the study, % wt.: cyclohexane – 38.8; cyclohexanone – 35.5; cyclohexanol – 24.0; impurities – 1.7.

The following compounds were chosen as models for the study: hexanal and cyclohexen-2-one as research objects among aldehydic and unsaturated/carbonyl impurities, respectively; dibutyl adipate (DBA) and dicyclohexyl adipate (DCHA), among other compounds. The latter was chosen as an ester that is most difficult to saponify.

Dibutyl adipate (DBA) of at least 96% wt. purity produced by *Acros Organics* is a colorless transparent liquid, bp = 305 °C, $\rho^{20} = 0.965$ g/cm^3.

Dicyclohexyl adipate (DCHA) was obtained by the esterification of adipic acid (analytical grade) with cyclohexyl alcohol (chemically pure). The resulting product is a white powder, mp = 35.5 °C, bp = 324 °C, $\rho^{20} = 1.037$ g/cm^3. The purity of the obtained ester was at least 99.8% according to GLC.

Cyclohexen-2-ol was synthesized by cyclohexene bromination with N-bromosuccinimide followed by saponification with sodium bicarbonate according to the procedure [22]. The final product was of more than 85% wt. purity according to GLC, bp = 164–165 °C.

Cyclohexen-2-one and hexanal manufactured by *Sigma-Aldrich* were of at least 95.0 and 98.0% wt. purity, respectively.

The phase transfer catalyst, trioctylmethylammonium chloride (trade name: Aliquat-336) produced by *Acros Organics*, is a heavy, viscous, colorless liquid of more than 97.0% purity. Potassium and sodium hydroxides used in the work were chemically pure and of an analytical grade, respectively.

Artificial mixtures based on industrial samples of the oxidate with the addition of the studied objects in the temperature range of 30–90 °C (temperature close to the conditions of the saponification stage) in the presence of and without the phase transfer catalysts (PTC) were used in the studies.

The oxidate was analyzed chromatographically. The oxidation products were identified by chromatography-mass spectrometry. Analysis conditions: Shimadzu GCMS QP2010 Ultra apparatus, DB-1ms capillary column, 30 m × 0.25 mm; temperature control mode: 60 °C (5 min) – 10 °C/min – 260 °C; carrier gas: helium; split injection 1/100. The majority of impurities in the oxidate were identified on the basis of mass spectra available in the NIST database [23], while other components were identified according to the rules of molecular ion fragmentation [24].

Results and Discussion

The alkali-catalyzed hydrolysis of esters is irreversible. Due to this, it is widely used in industrial organic synthesis. Most esters are water-insoluble. So, hydrolysis with aqueous solutions of alkalis in a two-phase system proceeds very slowly, especially in the case of dicyclohexyl esters of dicarboxylic acids [5, 25].

The stage of ester saponification with 5–20% aqueous alkali solutions is as follows:

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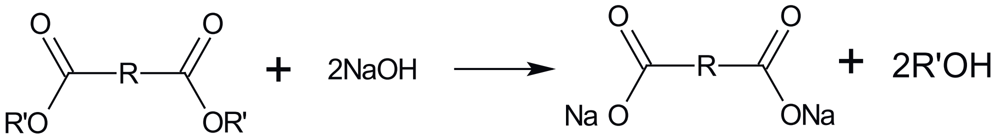
[1] State Standard GOST 26743.7-86. Caprolactam. Method for determination of permanganate index. Moscow, Standartov Publ., 1981. 6 p. (in Russ.).

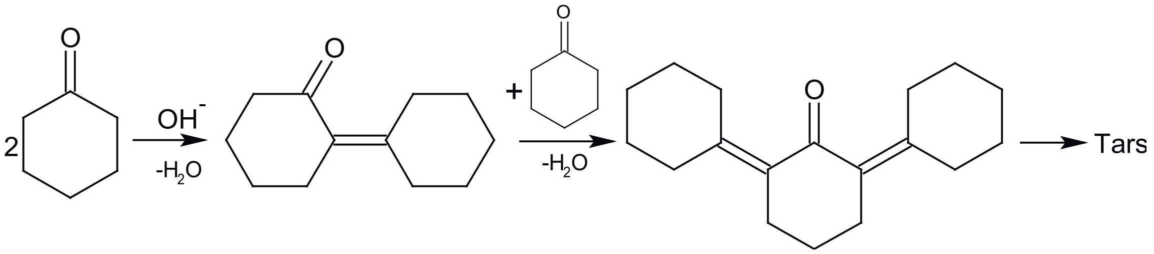


(1)

As shown by studies of industrial samples, esters can be removed at the saponification stage by only 50–70%, indicating its low efficiency. The non-catalytic reaction in the heterophase aqueous alkaline system has limitations due to the limit of the substrate solubility in the aqueous phase, which is inversely proportional to the concentration of the alkaline solution used [26]. It was assumed that the effect of the substrate dissolution in water-alkaline reactions increases, which is fundamental for intensifying the process in a perfect mixing reactor. We considered several options for a possible solution to the problem.

1) Changing the process's temperature conditions

It was shown in [17] that increasing the saponification temperature allows esters to be removed more completely. However, this results in the formation of cyclohexanone condensation products:



(2)

It was established that as the temperature increases from 30 to 120 °C, the amount of condensation products (tars) increases 10-fold.

An increase in temperature results in the need to carry out the process under pressure. This requires a change in the implementation process and, accordingly, high capital costs.

2) Reaction medium homogenization

The transition from a heterophase system to a homophase system when carrying out the process in a water-alcohol alkali solution results in a significant increase in the esters' hydrolysis rate even at lower temperatures (0–20 °C). The rate constants increase by 2–3 orders of magnitude [17]. So, the time to attain a 95% conversion of dicyclohexyl adipate (DCHA) in the case of heterophase hydrolysis is 6 hours, and in the case of homogeneous hydrolysis, 1 min. However, a disadvantage of this method is the use of a solvent for homogenization, which results in a change in the current technology and significant costs for the solvent's regeneration. Therefore, it is necessary to look for other ways of intensifying the process.

3) Using phase transfer catalysts

Phase-transfer catalysis is known to be a recognized method of intensifying heterophase processes including the saponification of esters [27, 28]. Our studies have shown [17] that the greatest increase in esters' hydrolysis rate was observed when using trioctylmethylammonium chloride $[N(C_8H_{17})_3CH_3]Cl$ (TOMAC) as a catalyst. In the concentration range of 0.2–1.4% wt. (optimally 0.5% wt.) it can be attributed to the class of phase-transfer catalysts not blocking the phase interface. When increasing concentration to more than 1.5% mass., tarring is observed. Using PTC increases the rate of esters' hydrolysis: the time to attain a 95% conversion of dicyclohexyl esters is 2 hours versus 6 hours in a non-catalytic process; the quantitative conversion of dibutyl adipate (DBA) is achieved in just a few minutes.

As mentioned above, the oxidate contains unsaponifiable impurities in addition to saponifiable products: about 6% mass. of the total amount of impurities. Among these, 3.1% are compounds containing an aldehyde group, 1.5% are compounds containing a keto group, 1.1% are hydrocarbons, and 0.1% are unsaturated compounds [18]. Under the conditions of nucleophilic catalysis, all of these compounds, except hydrocarbons, can theoretically undergo condensation and disproportionation reactions forming high-boiling by-products. The latter should be removed from crude cyclohexanone.

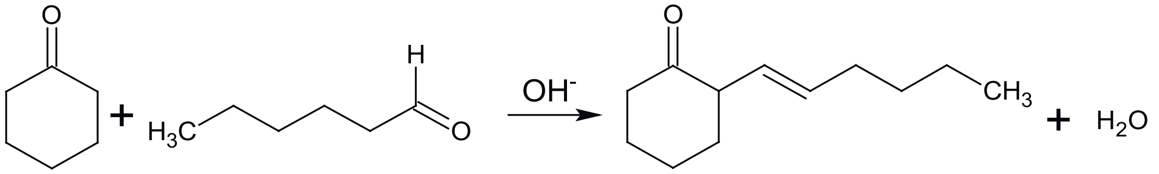
In [18], competing condensation reactions of cyclohexanone with unsaponifiable impurities were studied on model systems close to industrial conditions.

The studies were carried out under the conditions of heterophase alkaline hydrolysis with aqueous NaOH solutions in a temperature range of 30–80 °C in the presence of and without PTC (saponification mode is 70 °C), and also under homophase conditions in the presence of KOH at 120 °C (crude cyclohexanone rectification mode is 90–130 °C).

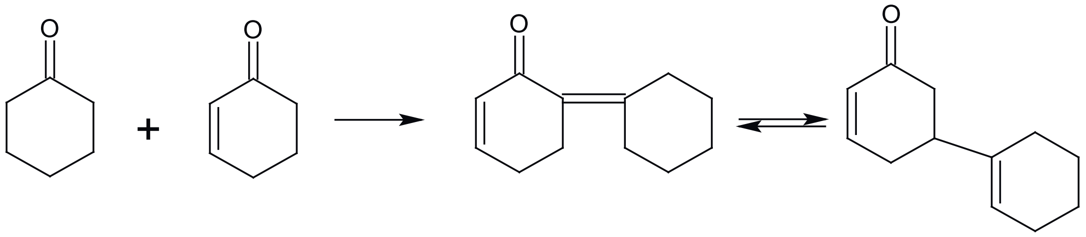
The results obtained allow us to draw the following conclusions:

– Linear aldehydes with a boiling point of 75–130 °C interact with cyclohexanone (reaction 3) under the conditions of alkaline catalysis with a conversion of 30–40% in the temperature range of 30–70 °C (saponification mode). In the presence of a PTC, the rate increases 2-fold, and the conversion reaches more than 80%.

– Unsaturated cyclic ketones behave similarly. Due to the presence of an active carbonyl group they interact with cyclohexanone at 50–70 °C. In the presence of a PTC at 70 °C, the reaction proceeds almost quantitatively (reaction 4).



(3)



(4)

The totality of the data obtained provides a theoretical justification for one fact: esters and unsaponifiable impurities cannot be completely removed under the conditions of oxidate saponification without a PTC. The oxidate PI before saponification is 350–400 units; after saponification, 80–130 units.

The further purification of crude cyclohexanone under industrial conditions is carried out by rectification in a plate column in the presence of potassium hydroxide (up to 1% wt. per reaction mass) at 90–130 °C (average temperature in the column). The reaction mixture residence time in the column is 2–2.5 hours. As shown in [14, 19, 29], the purity of crude cyclohexanone during rectification without alkali is 99.7–99.8%, the PI remains at a level of 80–100 units, and the content of readily oxidizable impurities averages $(0.3–0.5)\cdot10^{-5}$ mol of ester groups/g. If the alkali solution is supplied to the rectification column simultaneously with the feed in an amount equivalent to the content of readily oxidized impurities, then the PI will decrease to 10–20 units, and the ester number will decrease 3–5-fold $(0.1–0.3)\cdot10^{-5}$ mol of ester groups/g). However, the quantity of cyclohexanone condensation products – its dimers and trimers – dramatically increases in the rectifying still (up to 20–50 kg/t). Cyclohexanone dimers appear in the distillate and reduce the concentration of marketable cyclohexanone to 99.1–99.4%. To obtain normalized quality indicators, it is required to install an additional package or an additional rectification column [29]. However, in this case one will have to put up with the constant formation of heavy products. Their amount depends on compliance with rectification indicators (temperature, supplied alkali amounts, and hydrodynamic regimes in the column) and varies from 10 to 100 kg/t of cyclohexanone.

As the problem analysis shows, using PTC opens up a real opportunity to optimize the saponification stage, and there is no need to change the implementation process [18].

During the course of this study, a control experiment was carried out at the industrial oxidate saponification stage in the presence of and without a

PTC under the recommended conditions on the basis of kinetic studies [18]. The GLC and GC-MS analyses of reaction masses were performed before and after hydrolysis. The results are presented in the table. It can be seen that the conversion of esters including those difficult to saponify is 95–100%, aldehydes – 100%, and unsaturated ketones – 80%. In this case, rectification can be carried out without alkali.

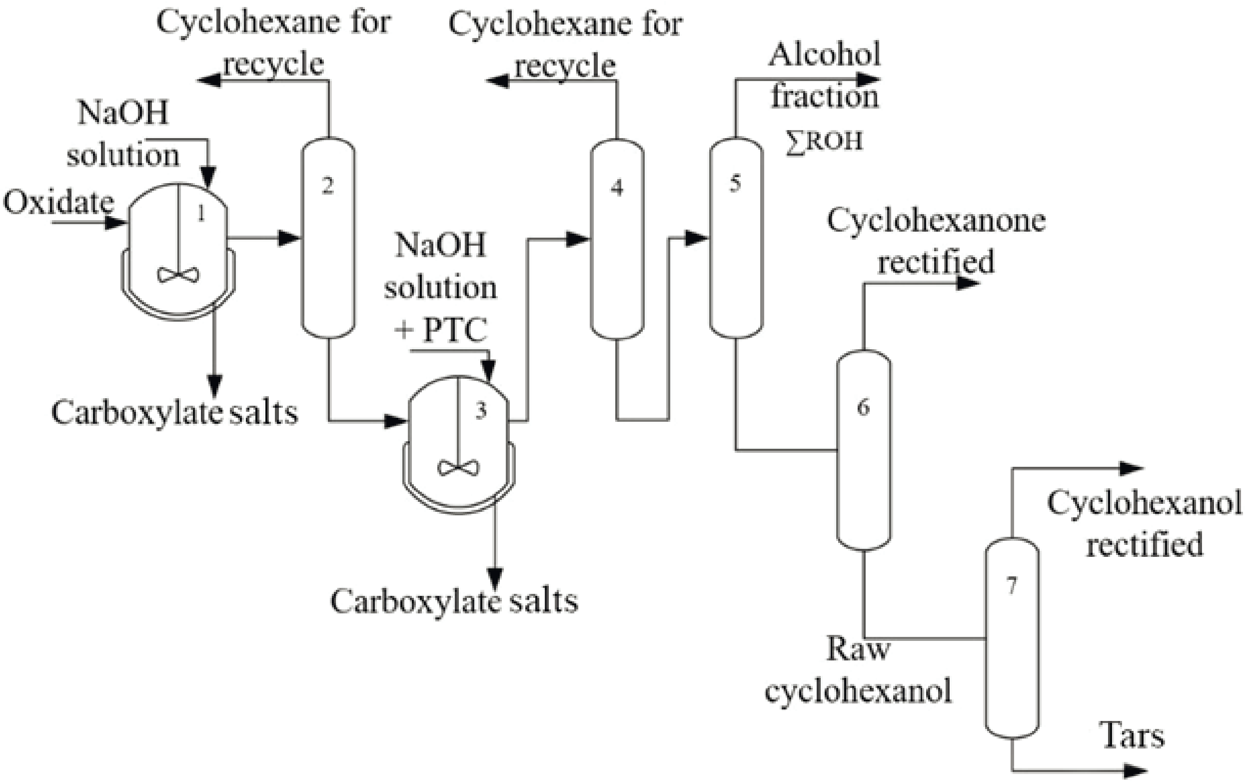
Results of the oxidate analysis before and after alkaline hydrolysis of esters under the conditions of phase-transfer catalysis

No.	Compound name	Concentration*, %	
		Before hydrolysis	After hydrolysis
1	**Ethanoic acid propyl ester**	**0.51**	**0.00**
2	Methylcyclohexane	1.38	0.82
3	Ethylcyclopentane	0.39	0.40
4	1-Pentanol	11.90	12.36
5	Toluene	1.03	1.14
6	Cyclopentanol	2.00	2.64
7	Hexanal	8.19	0.00
8	1,2-Epoxycyclohexane	4.58	1.49
9	2-Cyclohexen-1-one	3.33	0.00
10	**Methanoic acid cyclohexyl ester**	**0.39**	**0.00**
11	Hexanoic acid	0.43	0.00
12	1,5-Pentadiol	3.01	1.19
13	**Ethanoic acid cyclohexyl ester**	**1.01**	**0.00**
14	1,2-Cyclohexanediol	4.00	3.97
15	1,3-Cyclohexanediol	7.53	3.13
16	2-Ethylidenecyclohexanone	0.74	1.20
17	**Propanoic acid cyclohexyl ester**	**1.23**	**0.00**
18	**Pentanoic acid hexyl ester** **Hexanoic acid pentyl ester**	**0.63**	**0.00**
19	**Pentanoic acid cyclohexyl ester**	**0.66**	**0.00**
20	Hexadial-1,6	2.52	1.86
21	**Pentanoic acid cyclohexyl ester**	**4.19**	**0.00**
22	Hexylcyclohexyl ether	0.62	0.57
23	Dicyclohexyl ether	6.45	6.70
24	**Hexanedioic acid pentyl ester**	**0.62**	**0.00**
25	**Hexane acid cyclohexyl ester**	**0.83**	**0.00**
26	2-(1-Hydroxy-1-hexyl)cyclohexanone	13.74	7.70
27	2-Cyclohexenylcyclohexanol	0.72	2.82
28	[1,1’-Bicyclohexyl]-2-one	1.22	0.96
29	**Pentanedioc acid cyclohexyl ester**	**1.37**	**0.00**
30	2-Cyclohexylidenecyclohexanone	0.74	2.15
31	1,5-Octahydro-4a-methylnaphthalenedione-1,5	1.48	2.13
32	**Cyclopentanecarboxylic acid pentyl ester**	**1.08**	**0.00**
33	**Butanedioic acid dicyclohexyl ester**	**1.79**	**0.00**
34	1’-Hydroxy-[1,1’-bicyclohexyl]-one-2	0.92	40.42
35	1,2’-Dihydroxy-[1,1’-bicyclohexyl]	1.16	0.00
36	Bicyclohexyl-2,3’-dione	0.62	1.01
37	**Cyclopentanecarboxylic acid cyclohexyl ester**	**1.27**	**0.00**

Table. Continued

No.	Compound name	Concentration*, %	
		Before hydrolysis	After hydrolysis
		2.41	5.33
39	**Hexanedioic acid dibutyl ester**	**1.28**	**0.00**
40	**Hexanedioic acid dicyclohexyl ester**	**2.01**	**0.00**
Σ		**100.0**	**100.0**

* The content is presented as a percentage of the total impurity content equal to 1.7%.



Scheme of an industrial process for cyclohexanone isolation and purification with the suggested optimization options.

The Figure shows a block diagram of an industrial process for cyclohexanone isolation and purification with the suggested optimization options at the oxidate saponification and crude cyclohexanone rectification stage.

After cyclohexane oxidation, the oxidate goes to the neutralization stage, where it is mixed with an aqueous alkali solution in a cascade of mixing apparatuses (item 1) at a temperature of 140–160 °C and a pressure of 1.3–1.65 MPa. The neutralization of organic acids and the partial hydrolysis of esters occur. Next, the organic layer enters the distillation column (item 2), where the bulk of the unreacted cyclohexane is distilled off. The distillation residue enters a cascade of apparatuses with stirrers (saponification reactors), where an aqueous solution of alkali with added PTC is supplied (item 3). The temperature in the reactors rises sequentially from 60 °C, and in the last reactor it reaches 90 °C. Under these conditions, the quantitative decomposition of non-readily saponifiable esters and the condensation of saturated and unsaturated aldehydes occur. After saponification, the organic layer is sent to column 4 for residual cyclohexane removal. Along with other by-products, the reaction mixture contains alcohols: amyl alcohol, butyl alcohol, cyclopentanol, ketones, etc. (the alcohol fraction). They are distilled off in column 5 (a top pressure of no more than 0.01 MPa, the top temperature of the column is no more than 160 °C).

Distillation columns 6 and 7 are designed for the separation of cyclohexanone (bp = 155 °C) and cyclohexanol (bp = 160 °C). It was suggested on the basis of the study results to exclude alkali supply to column 6. Columns 6 and 7 operate under a vacuum at a column top pressure of no more than 10 kPa and 6.67 kPa, respectively. For rectified cyclohexanone distillation, the column's top temperature is no more than 90 °C, and the rectifying still temperature is no more than 125 °C. In column 7, rectified cyclohexanol is separated from high-boiling components (tars). The column's top temperature is 74–88 °C, and the rectifying still temperature is no more than 175 °C.

Conclusions

On the basis of the analysis, relevant Russian and foreign information, and our own research it was found that in the operation of existing industrial plants for cyclohexanone production:

1. The main disadvantage of industrial methods for cyclohexanone purification is the lack of stability indicators and of control over the resultant high-boiling by-products, high alkali consumption and target product loss.
2. The use of PTC makes it possible to optimize the saponification stage with no need to change the implementation process and no additional investment costs: the conversion of non-readily saponifiable esters increases 3–4-fold (up to 90–96%), and the carbonyl impurities condensation rate increases 2-fold.
3. This, in turn, enables one to avoid using alkali in crude cyclohexanone rectification, reduces the target product loss, and decreases the amount of tars 1.5–2-fold. The standard indicators of cyclohexanone quality are attained: purity more than 99.9% and PI 18–20 units.

Acknowledgments

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The authors declare no conflict of interest.

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