# Information

# Cyclohexanone in the production of caprolactam. Problems and solutions

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This review presents data analysis on the impurities in cyclohexanone: pathways of their formation and the influence on the qualty of commercial caprolactam. The existing purification methods are described and their advantages and drawbacks are considered. Novel, increased throughput methods for alkaline hydrolysis of esters in the process of cyclohexanone production are proposed by the authors, based on their expertise.

**Key words:** cyclohexanone, caprolactame, alkaline hydrolysis, esters.

The development of modern domestic (Russian) large-scale production technologies requires thoughtful theoretical studies and cost optimization procedures, which would improve the position of these technologies on the global market. One the chemicals with a high added value is cyclohexanone. Over 95% of it is used in the production of ε-caprolactam, a monomer for polyamide materials, synthetic fibers, engineering plastics and thin films.[1] Russian caprolactam industry is export-oriented with more than 60% of the chemical produced being shipped abroad.

The production scheme for about 80% overall caprolactam in Russia is based on cyclohexane oxidation followed by the isolation of cyclohexanone, oximation and the further oxime rearrangement into caprolactam. The variety of chemical transformations and the low oxidation selectivity leads to large amounts of O-containing impurities (both saponifiable and non-saponifiable) at the first production step, which contaminate the final product and reduce the quality of polyamide.[2—5]

Modern production technologies include the removal of saponifiable impurities from cyclohexanone: esters are subjected to alkaline hydrolysis and the rest of the crude ketone is rectified in the presence of an alkali. An industrial installation with a productivity of 100 000 ton per year of cyclohexanone can yield esters up to 300 ton per year. The complexity of the problem lies in a great variety (more than 50 compounds with different reactivity) of the impurities, while their content in the oxidate to be subjected to saponification is low (1.5—2 wt.%). This impedes the choice of the optimal process conditions and does not allow the impurities to be efficiently removed and high purity cyclohexanone to be produced. All attempts to use harsh conditions (elevated temperature, pressure, longer contact of the reactants, higher alkali concentration and excessive amounts of it) result in an autocondensation of cyclohexanone which increases the product waste and the number of impurities. From the experience of the existing Russian production sites, it is possible to remove only 50—70% of the ester impurities

at the saponification step. The side reactions give high-boiling products ("dianones", "trianones", tar) with a total amount up to 50—100 kg per ton of the target product.

Thus, the necessity for theoretical studies aimed at the improvement of cyclohexanone production processes is quite obvious. Such theoretical basis could bring the produced cyclohexanone and caprolactam quality to worldwide standards.

This review contains data analysis on the mechanisms of the formation of caprolactame quality-determining impurities in cyclohexanone and information on the

**Scheme 1**



existing cyclohexanone reagent-based purification methods. The benefits and drawbacks of the methods are discussed and new saponification techniques are proposed, which could intensify alkaline ester hydrolysis and rectification processes in cyclohexanone production.

## Production of caprolactam by the oxidation protocol. Parameters of the impurities

As mentioned above, the major (>80%) caprolactam industrial production method utilizes the oxidation process (Scheme 1).[1,6,7]

Low selectivity is a drawback of the oxidation protocol[8,9]: the oxidation proceeds via the radical chain mechanism affording large amounts of side producs (Scheme 2).

There are data testifying that cyclohexyl hydroperoxide (CyOOH) is the major source of such side products.[10] The basic impurities in cyclohexanone are esters, aldehydes, ketones, alcohols, carboxylic acids and unsaturated compounds. The mechanisms of their formation had been thoroughly studied.[11—14] Mono- and dicarboxylic acids and their cyclohexyl esters can be formed in amounts as high as 20—25 kg per 100 kg of oxidized cyclohexane.[15]
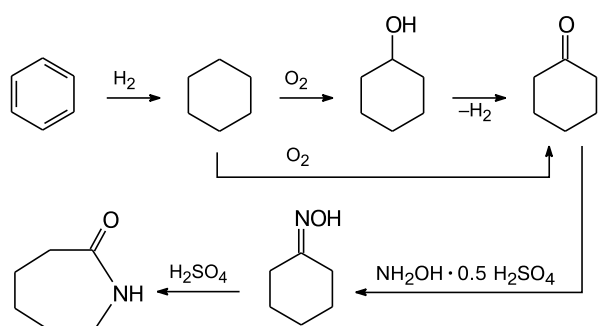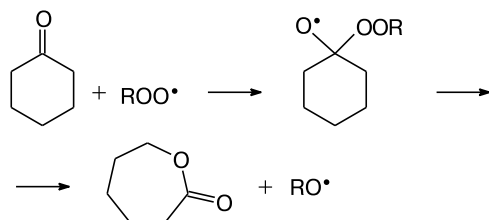
**Scheme 2**
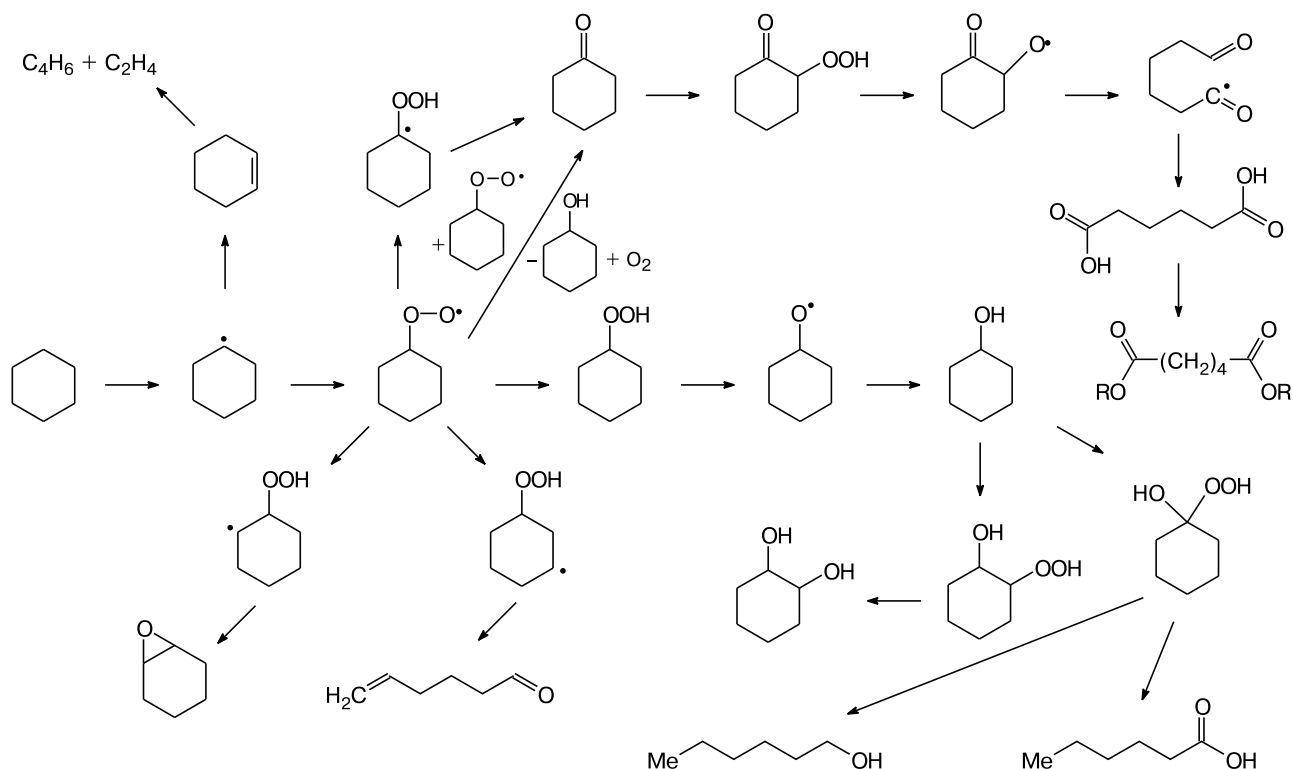
Addition of peroxide radicals to ketones (a free radical variation of the Bayer—Villiger reaction) can yield esters or lactones (Scheme 3).

**Scheme 3**



Most often, peroxide radicals attack the C—H-bond in position $\alpha$ to the carbonyl group, with the subsequent carbon chain cleavage (or ring opening) and oxidation to carboxylic acids (Scheme 4).

The mechanism of the formation of secondary alcohol esters (including cyclohexanol) during the oxidation has long been unknown. Early studies proposed these esters to be formed during the esterefication of carboxylic acids by alcohols. However, later[16,17] it was demonstrated that it is the reaction between alcohols and acid anhydrides that gives most of the secondary alcohol esters.

Transacylation of anhydrides with free acids leads to mixed anydrides. They react with alcohols and give esters containing acyl residues of the carboxylic acids involved in transacylation (Scheme 5).

At the examples of cyclohexane, cyclohexanol and cyclohexanone oxidation reactions, it was shown that mono- and dicarboxylic acid cyclohexyl esters or 2-oxocyclohexyl esters are formed with the involvement of adipic anhydride.[18,19]

The mechanism of the formation of such impurities as formic acid, $\gamma$-formylbutyric acid, $\delta$-formylvaleric acid, cyclohexyl formate, cyclohexyl $\delta$-formylvalerate was discussed earlier.[20,21] The authors determined the main pathway of the formation of formic acid under the conditions of industrial cyclohexane oxidation to involve oxidative transformations of $\delta$-formylvaleric acid that result in the formation of formic and $\gamma$-formylbutyric acids (Scheme 6).
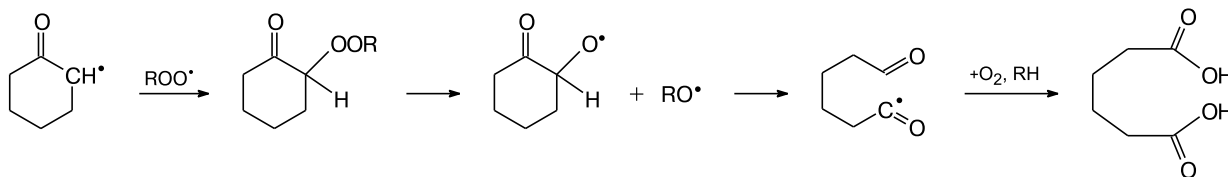
**Scheme 6**
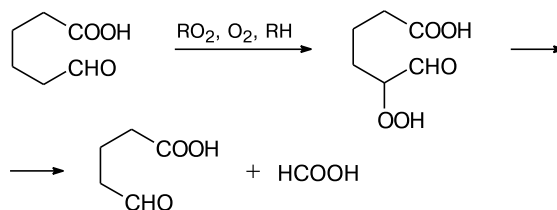


The elevated yield of cyclohexyl formate is the result of alcoholysis of mixed anhydrides containing formic acid residue. In a model experiment, the ratio of cyclohexyl ester to acid is almost by an order of magnitude higher for formic acid than for other ones (acetic, propionic and valeric).

### The influence of impurities on the quality of cyclohexanone and caprolactam

The quality of the manufactured cyclohexanone and caprolactam is evaluated by the permanganate index or permanganate number values. According to Russian standards, permanganate index is a quality control index which corresponds to the content of easily oxidized compounds in a produced substance. Optical density at

**Scheme 4**



**Scheme 5**
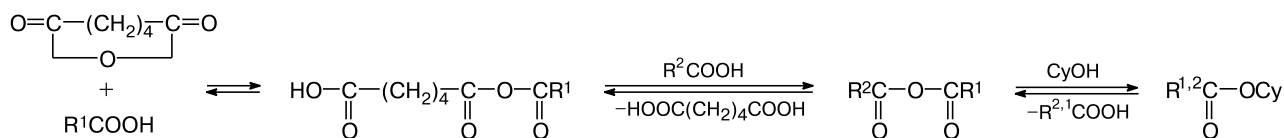
a certain wavelength of the test solution containing permanganate and the reference solution are measured after a certain time.[22] Permanganate number is time (in seconds) after which the solution of the product in water, combined with a certain amount of permanganate, obtains the color of the reference solution.[23]

The quality indexes of cyclohexanone and caprolactam must conform to the target specifications given in Table 1.

Permanganate number and the amount of volatile bases in caprolactam are known to correlate with the quality of cyclohexanone, while the intensity of color — with the quality of hydroxylamine sulfate used for oximation.[24] The quality of rectified cyclohexanone is in turn dependent on the efficiency of its purification.

Rectified cyclohexanone suitable for the production of high-quality caprolactam should have a permanganate number not lower than 10 000 (or permanganate index of 20 units).

Statistical analysis of caprolactam and cyclohexanone quality indicators allowed one to deduce the pair correlation coefficients[24] (Table 2). The pair correlation coefficient value lies between −1 and +1. Positive values represent a direct correlation while negative ones correspond to an inverse correlation. The values from 0 to 1 demonstrate the degree of approximation of the correlation to a functional relation for certain indicators.

Correlations between the following quality indicators of cyclohexanone and caprolactam should be noted: per-

**Table 1.** Quality indexes for cyclohexanone (CH) and caprolactam (CL)

| Index name | Russia | | Asia | | Europe | |
|---|---|---|---|---|---|---|
| | CH GOST 24615-81 | CL GOST 7850-86 | CH | CL | CH | CL |
| Cyclohexanone weight content, %, not less than | 99.8 | — | 99.8 | — | 99.9 | — |
| Overall impurities weight content, %, not greater than | 0.1 | — | — | — | 0.05 | — |
| Water weight content, %, not greater than | 0.1 | — | 0.08 | 0.1 | 0.05 | 0.05 |
| Permanganate index, units, not greater than | 20.0 | 4 | — | — | — | — |
| Permanganate index, s, not greater than | — | — | — | 10 000 | — | 28 000 |
| Optical density, not greater than | 0.10 | — | — | — | — | — |
| Acidity, %, not greater than | — | — | 0.01 | — | 0.01 | — |
| Acidity, mmol kg$^{-1}$, not greater than | — | — | — | 0.05 | — | — |
| Pt-Co color index, units, not greater than | — | — | 15 | — | 5 | — |
| Boiling point, °C (101.3 kPa) | — | — | 153—157 | — | 156.7 | — |
| Density at 20 °C, g cm$^3$ | — | — | 0.946—0.947 | — | 0.946±0.001 | — |
| Residue after evaporation, %, not greater than | — | — | — | — | 0.05 | — |
| Hazen color of 50% aqueous caprolactam solution, units, not greater than | — | 3.0 | — | 5 | — | 3.0 |
| Volatile bases content, mmol kg$^{-1}$, not greater than | — | 0.4 | — | 0.5 | — | 0.3 |
| Melting point, °C, not below | — | 68.8 | — | 68.8 | — | 69.0 |
| Iron weight content | — | 0.00002%, not greater than | — | 0.5 mg kg$^{-1}$ | — | 0.3 mg kg$^{-1}$ |
| Cyclohexanone oxime weight content | — | 0.002%, not greater than | — | 10 mg kg$^{-1}$, not greater than | — | 2 mg kg$^{-1}$, not greater than |
| Optical density of 50% caprolactame solution not greater than | — | 0.04 | — | 0.05 | — | 0.04 |
| Alkalinity, mmol kg$^{-1}$, not greater than | — | 0.1 | — | 0.1 | — | 0.05 |
| pH of a 20% aqueous solution | — | 6.7—7.3 | — | — | — | — |
| Ash content | — | — | — | — | — | 2 mg kg$^{-1}$, not greater than |

**Table 2.** Pair correlation coefficients of the quality indexes for caprolactam and cyclohexanone

| Correlation parameter | Coefficient |
|---|---|
| Caprolactam permanganate number — cyclohexanone permanganate number | +0.78 |
| Caprolactam volatile bases content — cyclohexanone ester number | +0.90 |
| Cyclohexanone permanganate number — cyclohexanone content in rectified cyclohexanone | −0.71 |
| Cyclohexenone content in cyclohexanone — cyclohexanone ester number | +0.78 |

**Scheme 7**
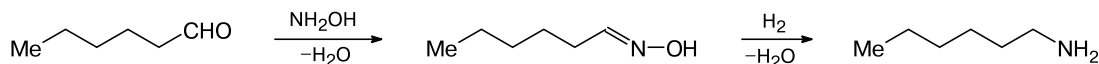
manganate number, ester number, and volatile base content.

According to many researchers, the most undersired impurities are pentanal, hexanal and cyclohex-2-enone.[25–27] Linear aldehydes are formed upon oxidation of *n*-pentane and *n*-hexane present in cyclohexane. Unsaturated cyclic ketones are formed both during the oxidation of cyclohexane and dehydration of cyclohexanol. If these compounds are present in cyclohexanone and therefore contaminate the material for further polyamide production steps (oximation, Beckmann rearrangement and polymerization), the mechanical performance of the polyamide fibers degrades below the minimal requirements due to the high amine content in caprolactam (Scheme 7).

At the oximation step, esters (generally the saponification-resistant esters of mono- and dicarboxylic acids) give hydroxamic acids. In micro-quantities these compounds can reach the distillation step and react with alkali to undergo Lossen rearrangement into amines (Scheme 8).

**Scheme 8**
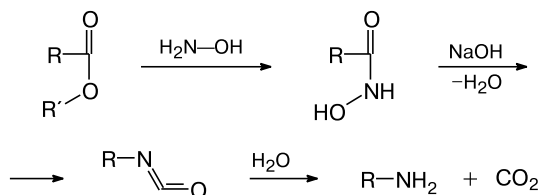
R — alkyl $C_1$—$C_4$; R′ — (cyclo)alkyl $C_1$—$C_6$

A direct correlation was shown in[28,29] between the content of aliphatic and aromatic amines, octahydrophenazine and some other nitrogen-containing compounds and such quality indicators as permanganate number (Fig. 1) and volatile amine content.

Similar results were demonstrated in Samara State Technical University, Chair of Technology of Organic and Petrochemical synthesis. Such impurities as 3- and 4-methylpyridine, 2,3-dimethylpyridine, cyclohex-2-enone, aniline, 3-ethyl-2-methyl-pyridine, and 2-butenylpiperidine were identified in study[30] and their significant negative influence on the quality of caprolactam and its derivatives was demonstrated.

The abovesaid testifies an important correlation between the content of impurities in cyclohexanone and the quality indicators of caprolactam.
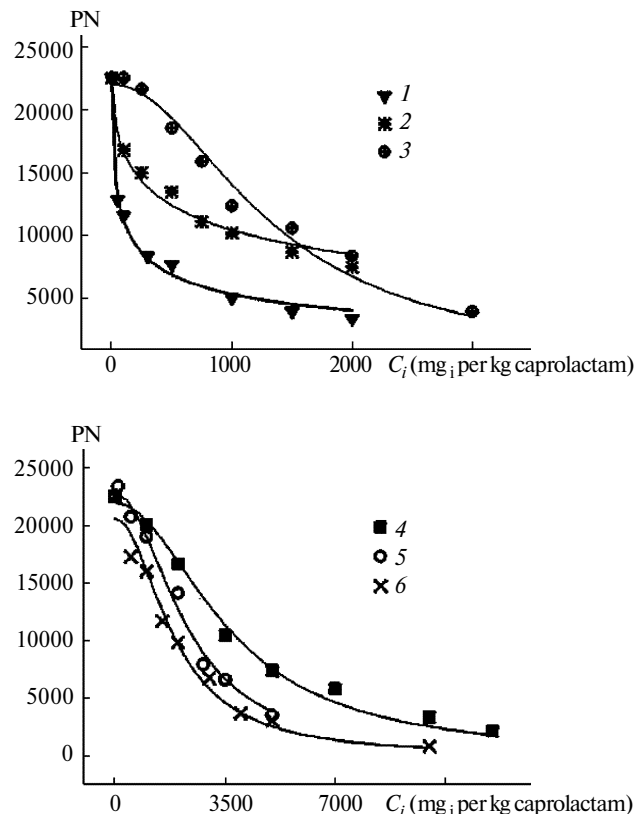
**FIg. 1.** The influence of the content of different caprolactam impurities on permanganate number (PN)[28]: *1*, octahydrophenazine, *2*, caprolactone, *3*, methylvalerolactam, *4*, 2-heptylamine, *5*, hexylamine, *6*, cyclohexylamine.

### The existing cyclohexanone impurities removal methods and their drawbacks

The basic procedure used to remove esters from the oxidate is saponification (alkaline hydrolysis). At the saponification step, which is conducted in the presence of aqueous alkali, the content of impurities is decreased due to the hydrolysis of mono- and dicarboxylic esters (Scheme 9).

Hydrolysis of esters can be also conducted in an acidic medium (in the presence of mineral acids). In some cyclohexanone industrial production processes, *e.g.* in CYCLOPOL-process[31], acidic hydrolysis (acidolysis) is used. However, alkaline hydrolysis is used most often, as it is faster and almost irreversible. The alkali concentration is usually 5—20%. The temperature is maintained at 80—

**Scheme 9**
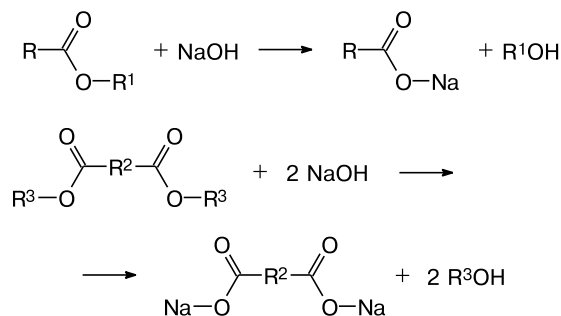


90 °C and the pressure is atmospheric. According to literature, though, such a temperature does not result in a

**Scheme 10**
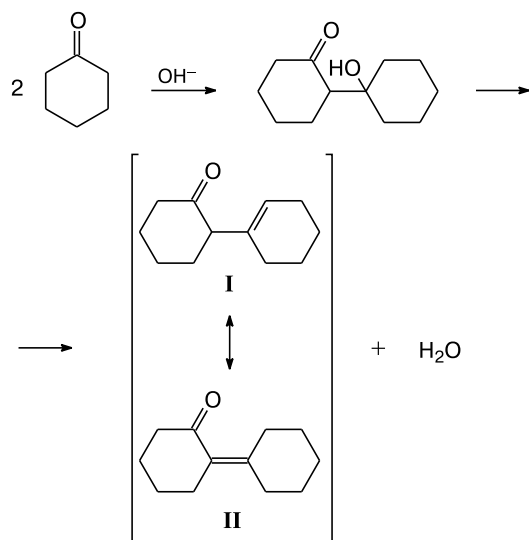


complete saponification, especially of saponification-resistant adipic acid esters.

The saponification rate depends considerably on the electronic and steric effects.[32—34] For esters of a general formula of RCOOR´ the hydrolysis rate is significantly different for various R- and R´: it is decreased 10- and 200-fold when a primary alcohol residue is replaced, respectively, by a secondary or a tertiary one. The activation energy is increased by 14.2 kJ mol$^{-1}$. Thus, esters of tertiary and secondary alcohols (including cyclohexanol) are most saponification-resistant under alkaline hydrolysis conditions.

It should be noted that an increase in both the temperature and the alkali concentration leads to an uncontrollable aldol condensation of cyclohexanone[35,36] giving new impurities (2-(1-cyclohexenyl)cyclohexanone (**I**) and 2-cyclohexylidenecyclohexanone (**II**)) and to losses of the target product (Scheme 10).

The self-condensation process can proceed with the formation of trimers of various structure, as well as high-boiling tarry products that are the main component of "X oil"[37,38] (Scheme 11).

The amount of wasted material can reach 50—100 kg per ton of cyclohexanone, so the impact of the alkali on cyclohexanone itself should be minimized. In some cases, using elevated temperatures for saponification requires to pressurize the equipment, which leads to high expenditures.

In our previous study[39] we demonstrated a significant influence of temperature, contact time and alkali concentration on the ester hydrolysis rate and the yield of cyclohexanone self-condensation products (Fig. 2). Calculations show that for $C_{KOH} = 0.025$ mol L$^{-1}$, which is equal to the concentration of impurities in crude cyclohexanone, 99% conversion at 110 °C (the average rectification column temperature for cyclohexanone) is reached after 22.5 min and the yield of the condensation products
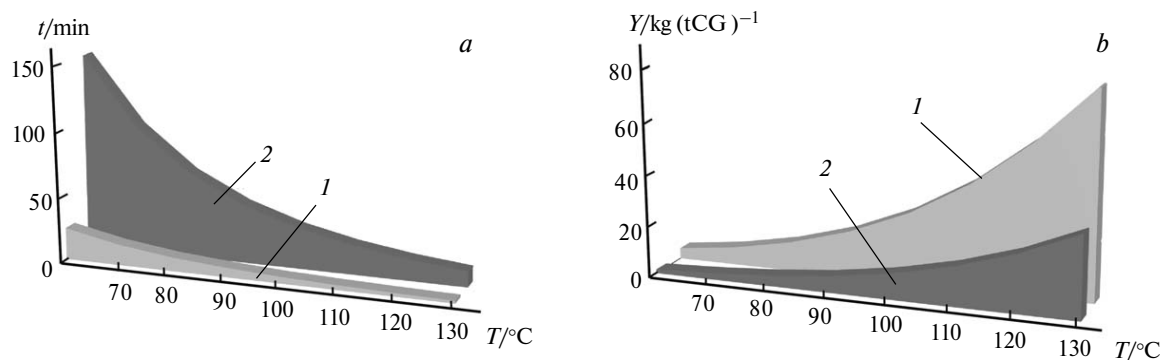
**Scheme 11**
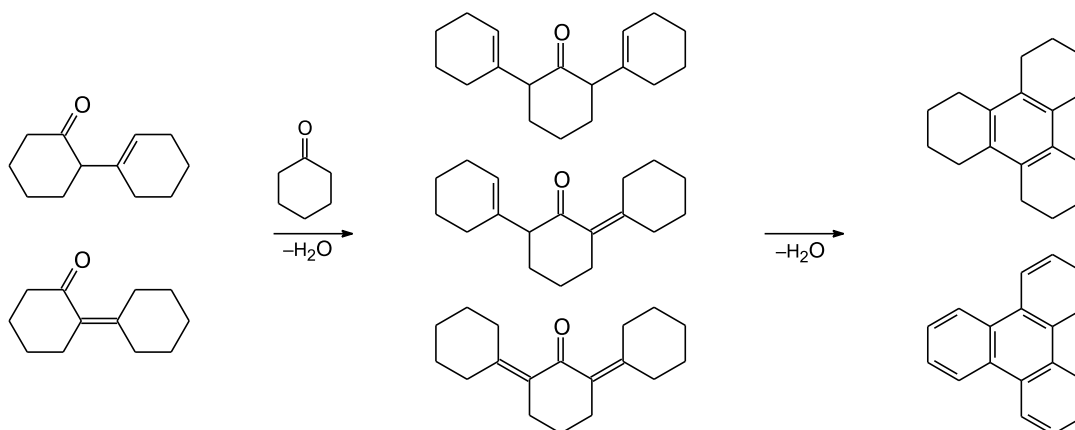
**Fig. 2.** The dependency of time required for quantitative ester hydrolysis (99% conversion) (*a*) and the cyclohexanone condensation product yield (*b*) from the temperature at different alkali concentrations: $C_{KOH}/C_{est.gr} = 2$ (*1*), 1 (*2*). Condotions: $C_{est.gr} = 0.025$ mol $L^{-1}$, $C_{CH} = 4.85$ mol $L^{-1}$.

is 15.3 kg per ton of cyclohexanone. When, at the same temperature, the concentration of alkali is doubled ($C_{KOH} = 0.05$ mol $L^{-1}$), the conversion time for esters is shortened to 3.5 min, while the condensation product yield is increased almost threefold.

There are several techniques that allow one to raise the permanganate number and reduce the ester number of cyclohexanone at the rectification step.

In a early work[40] solid alkaline compounds (alkaline and alkaline earth metal hydroxides, carbonates, alcoholates, phenolates and naphthenates) were added to crude cyclohexanone in the amount of 0.01—1 wt.%. This mixutre is then fraction distilled in three subsequent columns, one of which operates at atmospheric pressure while the other two at vacuum. Such a procedure is efficient for the removal of unsaturated ketones which are known to undergo condensation at elevated temperatures in the presence of alkaline compounds (Scheme 12).

**Scheme 12**
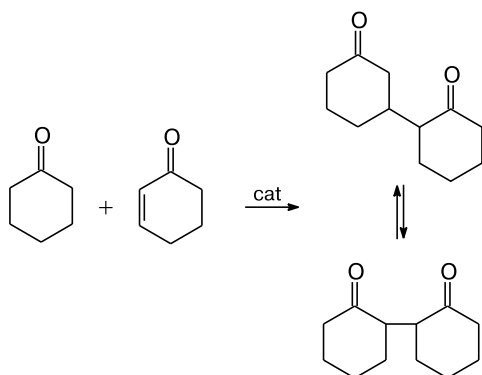


When a small amount of an aqueous alkali solution (preferably KOH as it is more soluble in cyclohexanone) is introduced to the bottoms of one of the rectification columns used to separate the alcoholic fraction, and at temperatures higher then generally used at the saponification step, volatile esters which can contaminate the distilled cyclohexanone are cleaved.

In a later work[41] crude cycloalkanone, containing $C_5—C_{12}$ aldehydes and cycloalkyl esters of $\geq C_4$ acids, was treated with an aqueous alkali or a strong acid solution. In this case, at least 80% of the aldehydes undergo condensation and ~20% cyclohexyl esters are saponified. A general drawback of the described purification methods utilizing an alkali is the instability of quality indexes and the uncontrollable formation of high-boiling impurities, as well as the high alkali consumption rate.

A number of works suggest purification of cyclohexanone with acidic or basic ion exchange resins.[42] However, these processes are difficult to implement, the resins must be often replaced and much of cyclohexanone is lost.

Some methods utilize liquid- or gas-phase hydrogenation of cyclohexanone imputities.[43] The conversion of unsaturated compounds can reach 99%. Other impurities are formed though, and they also need removal. Moreover, considerable energy and capital investments are required.

A method to decrease the concentrations of hexanal and pentanal in their mixtures with cyclohexanone was proposed[44]. This method utilizes the reaction shown in Scheme 13.

The mixture is rectified in the presence of an alkaline compound (alkaline metal hydroxide or carbonate) which is fed to the bottoms of the rectification column at anhydrous conditions. The alkali concentration should not exceed 50 ppm, else cyclohexanone self-condensation is accelerated.

Above that, several techniques were proposed that allow one to avoid the use of basic compounds for the purification of cyclohexanone. One of them involves the addition of amines to the reaction mixture, which react with aldehydes with the formation of heavier products which are then separated.[45]

**Table 3.** Rectification parameters for crude cyclohexanone, different methods of feeding alkali to the column

| Batch of rectification experiments | Requirements to rectified cyclohexanone (specifications) | I | II | III | IV |
|---|---|---|---|---|---|
| Weight content of cyclohexanone in the distillate, wt.% | >99.9 | 99.71 | 99.52 | 97.20 | 99.92 |
| PI units | 20 | 120 | 10 | 71 | 18 |
| $C_{es} \cdot 10^5$, mol es. groups $g^{-1}$ | — | 0.41 | 0.25 | 0.28 | 0.17 |
| Tar yield on the basis of rectified cyclohexanone, kg per ton | — | 6.3 | 28.3 | 8.2 | 9.3 |

*Notice:* I, no alkali; II, the alkali is fed to the column feedstock material, $C_{KOH} = 2.57 \cdot 10^{-5}$ mol $g^{-1}$; III, rectification with the feed of alkali to the reflux, $C_{KOH} = 0.43 \cdot 10^{-5}$ mol $g^{-1}$; IV, "divided" column with the feed of alkali to the reflux of the first column, $C_{KOH} = 0.43 \cdot 10^{-5}$ mol $g^{-1}$.

**Scheme 13**
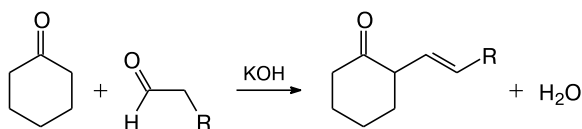


R = alkyl $C_3$, $C_4$

In a study[46] the authors subjected the mixture of cyclohexanone and cyclohexanol from the process of cyclohexane oxidation to dehydrogenation. Cyclohexanol is transformed into cyclohexanone and such impurities as α,β-cyclopentene/cyclopentane-1-carbaldehyde — into compounds which can be separated from cyclohexanone by fractional distillation.

The overall analysis of the available data demonstrates:

— esters formed in the process of cyclohexane oxidation, persisting in cyclohexanone, influence the quality of the target product — caprolactam, decreasing its permanganate number (increasing the permanganate index) and increasing the content of volatile bases in it;

— there is currently no highly efficient method for the purification of cyclohexanone that could afford a high-quality product: the drawbacks of the existing methods are the instability of the quality indexes and the uncontrolled formation of high-boiling components.

We performed an evaluation of the scientific basis of alkaline ester hydrolysis present in cyclohexane oxidation products both in homophase and heterophase systems, in the presence and absence of phase transfer catalysts, kinetic models were constructed.[47,48] Highly lipophilic catalysts: tetrabutylammonium bromide and methyl(trioctyl)ammonium chloride demonstrated the highest hydrolysis rate increase (three times compared to the non-catalytic process). The experimental data were used to deduce optimal conditions for heterophase alkaline hydrolysis of ester impurities in the presence of methyl(trioctyl)ammonium chloride: concentration of the catalyst of 0.015—0.02 mol $L^{-1}$, 80—90 °C, 90—120 min reaction time. The ester conversion is 90—95% (while being 50—70% for the currently used technology).

Post-treatment of industrial grade crude cyclohexanone by rectification in the presence of alkali was studied.[49,50] As the column height at which the alkali is introduced influences the contact time with the material, changing the feeding height can be used to reach an optimal combination of both maximizing the ester hydrolysis efficiency and minimizing the amount of condensation products. The following experiments were conducted: without an alkali, with the feeding of a suspension of powdered alkali in cyclohexanone to the reflux, with the use of a two-column system (a "divided" column) where an alkaline cyclohexanolic solution is fed to the reflux of the first column.

After each experiment the composition (by GC) of the distillates was determined, their permanganate indexes (PI) and the content of esters ($C_{es}$) were measured. The bottom residues were analyzed for tar content. The results are summed in Table 3.

Rectification on a double column in the presence of KOH being fed as a solution to the reflux of the first column was found to be most efficient. It provides high purity of rectified cyclohexanone and high quality indexes (99.92% purity, 18 units PI) while the cyclohexanone condensation product level is maintained at a minimum (less than 10 kg per ton of cyclohexanone), all of which conforms to the target product specifications.

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