CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES

ХИМИЯ И ТЕХНОЛОГИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ

ISSN 2686-7575 (Online)
https://doi.org/10.32362/2410-6593-2023-18-3-189-218
UDC 661.7+006.065.2+504.062

RESEARCH ARTICLE

Assessment of resource-saving technologies in low-tonnage chemical industries for compliance with best available technologies principles

Natalia A. Kostikova✉, Elena N. Glukhan, Pavel V. Kazakov, Maria M. Antonova, Dmitry I. Klimov

GosNIIOKhT, State Scientific Center of the Russian Federation, Moscow, 111024 Russia
✉Corresponding author, e-mail: kutkin@gosniiokht.ru

Abstract

Objectives. *To develop a methodology for the quantitative assessment of new technologies in accordance with the principles of best available technologies (BAT). To evaluate the developed technologies of low-tonnage chemical production of tetramethylthiuram disulfide, N-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthohen disulfide, and N-phenyl-2-naphthylamine for compliance with BAT principles and compare with alternative (implemented, known) technologies in terms of environmental impact.*
Methods. A methodology for the quantitative assessment of new technologies for the production of organic substances in accordance with BAT principles was used.
Results. The developed methodology for the quantitative assessment of new technologies in accordance with BAT principles based on the calculation of comprehensive comparison indicators with alternative technologies for technological and environmental indicators allowed us to determine the level of implemented technologies for the production of tetramethylthiuram disulfide, N-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthohen disulfide, and N-phenyl-2-naphthylamine to minimize the impact on the environmental, including through the development of special technological solutions for resource conservation and waste reduction, and to conduct a quantitative assessment of the achieved environmental outcome. It is established that the

considered new technologies of low-tonnage chemical production comply with BAT principles and are more environmentally advanced compared to alternative ones previously implemented in the USSR.
Conclusions. For the first time, a methodology for quantifying new technologies in accordance with BAT principles is proposed. The possibility of its use at the stage of making basic technological decisions on the implemented production method in order to ensure compliance with legislative requirements for technologies in the field of environmental safety to achieve environmental protection goals is shown on the example of low-tonnage technologies for the production of tetramethylthiuram disulfide, N-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthohen disulfide, and N-phenyl-2-naphthylamine created in GosNIIOKhT.

Keywords: *low-tonnage chemical production technologies, quantitative assessment methodology, best available technologies (BAT) principles, tetramethylthiuram disulfide, N-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthogen disulfide, N-phenyl-2-naphthylamine*

For citation: Kostikova N.A., Glukhan E.N., Kazakov P.V., Antonova M.M., Klimov D.I. Assessment of resource-saving technologies in low-tonnage chemical industries for compliance with best available technologies principles. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2023;18(3):187–218 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2023-18-3-187-218

НАУЧНАЯ СТАТЬЯ

Оценка ресурсосберегающих технологий малотоннажных химических производств на соответствие принципам наилучших доступных технологий

Н.А. Костикова✉, Е.Н. Глухан, П.В. Казаков, М.М. Антонова, Д.И. Климов

Государственный научно-исследовательский институт органической химии и технологии, Москва, 111024 Россия
✉*Автор для переписки, e-mail: kutkin@gosniiokht.ru*

Аннотация

Цели. *Разработать методику количественной оценки новых технологий в соответствии с принципами наилучших доступных технологий (НДТ). Провести оценку разработанных технологий малотоннажных химических производств тетраметилтиурамдисульфида, N-циклогексил-2-бензотиазолилсульфенамида, диизопропилксантогендисульфида и N-фенил-2-нафтиламина на соответствие принципам НДТ и сравнить с альтернативными (реализованными, известными) технологиями по уровню воздействия на окружающую среду (ОС).*
Методы. *Методика количественной оценки новых технологий производства органических веществ в соответствии с принципами НДТ.*
Результаты. *Разработанная методика количественной оценки новых технологий в соответствии с принципами НДТ на основании расчета комплексных индексов сравнения с альтернативными технологиями по технологическим и экологическим показателям позволила определить уровень внедряемых технологий получения тетраметилтиурамдисульфида, N-циклогексил-2-бензотиазолилсульфенамида, диизопропилксантогендисульфида и N-фенил-2-нафтиламина по минимизации воздействия на ОС, в том числе*

за счет разработки специальных технологических решений по ресурсосбережению и снижению отходности, и провести количественную оценку достигаемого экологического результата. Установлено, что рассмотренные новые технологии малотоннажных химических производств соответствуют принципам НДТ и являются более экологически совершенными по сравнению с альтернативными, ранее реализованными в СССР.
Выводы. *Впервые предложена методика количественной оценки новых технологий в соответствии с принципами НДТ и показана возможность ее использования на этапе принятия основных технологических решений по внедряемому способу производства для обеспечения выполнения законодательных требований к технологиям в сфере э кологической безопасности по достижению целей охраны ОС на примере созданных во ФГУП «ГосНИИОХТ» малотоннажных технологий производства тетраметилтиурамдисульфида, N-циклогексил-2-бензотиазолилсульфенамида, диизопропилксантогендисульфида и N-фенил-2-нафтиламина.*

Ключевые слова: *стехнологии малотоннажных химических производств, методика количественной оценки, принципы наилучших доступных технологий, НДТ, тетраметилтиурамдисульфид, N-циклогексил-2-бензотиазолилсульфенамид, диизопропилксантогендисульфид, N-фенил-2-нафтиламин*

Для цитирования: Костикова Н.А., Глухан Е.Н., Казаков П.В., Антонова М.М., Климов Д.И. Оценка ресурсосберегающих технологий малотоннажных химических производств на соответствие принципам наилучших доступных технологий. *Тонкие химические технологии*. 2023;18(3):187–218. https://doi.org/10.32362/2410-6593-2023-18-3-187-218

INTRODUCTION

One of the tasks of state industrial policy in the field of production consists in the introduction of resource-saving and environmentally friendly technologies according to the provisions of the Federal Law of December 31, 2014 No. 488-FL "On Industrial Policy in the Russian Federation". The implementation of this policy is carried out by abandoning the use of outdated and inefficient technologies according to best available technologies (BAT) principles. BAT criteria are legally defined for evaluating technologies in terms of their environmental impact. Currently, the selection of BAT is carried out on the basis of expert assessments[1]. However, in order to substantiate BAT [1], present the BAT selection process [2], and identify technologies as BAT-compliant [3], various models are proposed based on a systematic approach and the use of mathematical tools, as well as on conducting environmental and economic BAT analysis. In the context of the state reform of the environmental regulation system and in accordance with the concept of introducing BAT as the primary mechanism for implementing state policy in the field of environmental safety at the stage of new technology development, special attention should be paid to addressing issues involved in determining the level of harmful effects on the environment and the minimization of such harmful effects to standard BAT values. This becomes all the more relevant due to the legal assignment of the production of basic organic

[1] Decree of the Government of the Russian Federation of December 23, 2014, No. 1458 "On the procedure for determining technology as the best available technology, as well as the development, updating and publication of information and technical reference books on the best available technologies" (as amended by Decrees of the Government of the Russian Federation of September 9, 2015, No. 954; dated December 28, 2016, No. 1508; dated March 09, 2019, No. 250). URL: http://www.consultant.ru/. Accessed February 13, 2022 (in Russ.).

chemicals to areas of BAT application[2] and objects of category I (significant) in terms of their negative impact on the environment[3].

These factors determine the relevance of conducting a preliminary assessment of new technologies to determine their compliance with modern environmental requirements. However, there is currently no methodological basis for such an assessment. The development and implementation of highly efficient resource-saving technologies for obtaining materials that are in demand by the industrial complex of the Russian Federation under conditions of low-tonnage industrial production is one of the main directions of scientific and practical activities of *GosNIIOKhT*. Ensuring the current level of implemented technologies to minimize the impact on the environment is achieved, among other things, by developing special technological solutions for resource saving and waste reduction. To assess the achieved environmental outcome, we have developed the "Methodology for the quantitative assessment of new technologies for the production of organic substances in accordance with BAT principles" [4].

Compliance with the approach for evaluating new technologies is determined on the basis of BAT principles by calculating comprehensive indicators of comparison with alternative (already implemented or known) technologies in terms of technological (amount of waste, emissions, and discharges) and environmental indicators (degree of use of raw materials and waste and the effectiveness of measures for the treatment of gas emissions and discharges into water bodies).

The evaluation of new technologies for compliance with environmental protection goals is a necessary but insufficient development element, since one of the key targets is achieving a high level of efficiency. The "Methodology for the quantitative assessment of new technologies for the production of organic substances in accordance with economic and environmental efficiency criteria" developed in our previous work [5] can be used to determine the most effective option for organizing production based on the calculation of comparative economic and environmental efficiency coefficients. The comparative economic efficiency coefficient includes an assessment of the cost of raw materials and instrumentation of a technological process. The comparative environmental efficiency ratio reflects the achieved level of minimization of the negative impact on the environment during the implementation of the technology, as well as the cost effectiveness of ensuring this environmental outcome. At the same time, the assessment of the economic efficiency of environmental costs makes it possible to exclude unreasonably costly options in comparison with the obtained environmental outcome and ensure that the developed technological solutions comply with the BAT criteria.

This article discusses new technologies for the production of tetramethylthiuram disulfide, *N*-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthogen disulfide, and *N*-phenyl-2-naphthylamine developed at *GosNIIOKhT*; technologies, as well as possible directions for their modernization.

METHODS

The calculation of the main and additional indicators [4] for comparing the developed technologies (Table 1) was carried out using data from technological production regulations.

The final assessment of the developed technology was carried out by comparing the relevant indicators with those of the alternative (implemented or known) technology, while the consumption coefficients for raw materials and auxiliary materials, production waste generation rates, as well as basic and additional technological indicators, were determined on the basis of the material balances of these technologies.

Further, comprehensive indicators of comparison of the developed and alternative production technologies were calculated along with the final indicator of the assessment of the developed technology for compliance with BAT principles (Table 2).

Indicator K_1 characterizes the degree of reduction of waste of the new technology in comparison with the existing alternative. Here, since the target

---

[2] Decree of the Government of the Russian Federation dated December 24, 2014 (as amended on May 24, 2018) No. 2674-r. "On Approval of the List of Areas of Application of the Best Available Technologies." URL: http://www.consultant.ru/. Accessed February 17, 2020 (in Russ.).

[3] Decree of the Government of the Russian Federation "On approval of the criteria for classifying objects that have a negative impact on the environment as objects of categories I, II, III and IV" dated September 28, 2015, No. 1029. URL: http://www.consultant.ru/. Accessed February 17, 2020 (in Russ.).

[4] Decree of the Government of the Russian Federation of December 23, 2014, No. 1458 "On approval of the rules for determining technology as the best available technology, as well as the development, updating and publication of information and technical reference books on the best available technologies." URL: http://www.consultant.ru/. Accessed September 09, 2022 (in Russ.).

Table 1. Main and additional technological indicators for comparing production technologies

Indicator	Indicator characteristics and calculation method
Main technological indicators of production	
A_T	Generation rate of solid and liquid waste, t/t, according to the regulations
B_T	Specific emissions into the atmosphere, t/t, according to the regulations
C_T	Wastewater generation rate, t/t, according to the regulations
Additional technological indicators of production	
J_K	The degree of complexity and completeness of the extraction of useful components from a feedstock is calculated as the sum of the recovery factors of the feedstock components, taking into account the yield and excluding technological losses of the product, t/t $$J_K = \sum_{i=1}^{K} J_i = \sum_{i=1}^{K} \frac{\sum_{Rec=1}^{N} P_i^{Rec}}{\sum_{Raw=1}^{M} P_i^{Raw}}$$ where K is the quantity of valuable components in the raw material; N is the number of product flows; M is the number of raw material flows; P_i^{Rec} is the amount of i useful substance, passed into finished products, t; P_i^{Raw} is the amount of i useful substance contained in raw materials, t
J_O	The degree of utilization of generated waste is calculated as the share of the regenerated component in the total mass of waste, t/t, and calculated according to the material balance of the regeneration operation per single operation. $$J_O = \frac{\sum Q^{Pr} + \sum Q^{P}}{\sum Q^{O}},$$ where $\sum Q^{Pr}$ is the amount of waste used in the production of other products, t/year, $\sum Q^{P}$ is the amount of waste sold, t/year; $\sum Q^{O}$ is the amount of generated waste, t/year.
J_A	The degree of purification of emissions of harmful substances into the atmosphere, which is calculated as the share of captured gases and vapors in the total mass of production off-gases, t/t, can be calculated from material balance data per operation. $$J_A = \frac{\sum_i V_i}{\sum_j V_j},$$ where $\sum_i V_i$ is the total mass of captured emission components, t/year; $\sum_k W_k$ is the total mass of substances contained in gas emissions formed during the production process, t/year
J_B	The degree of purification of discharges into water bodies is calculated by dividing the mass of discharges cleaned from harmful impurities to the total mass of their formation, t/t, using the material balance data per operation. $$J_B = \frac{\sum_l W_l}{\sum_k W_k},$$ where $\sum_l W_l$ is the total mass of discharges, t/year; $\sum_k W_k$ is the total mass of wastewater generated, t/year

is to minimize waste, the values related to the developed technology are given in the numerator to ensure the ratio $K_1 < 1$.

The K_2 indicator characterizes the increased complexity and completeness of the extraction of useful components using the new technology as compared to the existing alternative. Since the aim is to increase the level of raw material utilization, the values related to the developed technology are given in the denominator to ensure the ratio $K_2 < 1$.

The value of the final indicator for assessing the new (developed) technology $I < 2$ supports the conclusion that the developed technology conforms with BAT principles and is more environmentally friendly than the existing alternative [4].

RESULTS

Assessment of the compliance of the tetramethylthiuram disulfide production technology with the BAT principles

The technology for the production of tetramethylthiuram disulfide is based on the one-stage method for its preparation published in our previous work [6], which includes the condensation of dimethylamine with carbon disulfide followed by peroxidation of the formed dimethyldithiocarbamic acid without its isolation.

The formation reaction of tetramethylthiuram disulfide is described by Scheme (1).

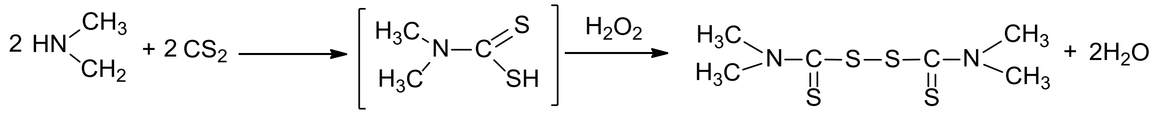
Condensation of dimethylamine with carbon disulfide is carried out at an equimolar ratio of components; peroxidation of the resulting dimethyldithiocarbamic acid is carried out at a molar ratio of dimethylamine : carbon disulfide : hydrogen peroxide equal to 1 : 1 : 0.55–0.57. The process is carried out in a methanol medium.

The calculation of the main and additional technological indicators of the production of tetramethylthiuram disulfide was carried out using the data of the "Temporary technological regulations for the pilot low-tonnage production of tetramethylthiuram disulfide based on domestic raw materials, No. TTR-3-350" on consumption coefficients for raw materials (Table 3) and waste generation rates (Table 4). The calculation data of the main and additional technological indicators of the production of tetramethylthiuram disulfide are presented in Table 5.

We carried out a final assessment of the developed technology for the production of tetramethylthiuram

Table 2. Comprehensive comparison indicators and the final indicator of the assessment of the developed technology for compliance with BAT principles

Indicator	Formula for calculating the indicator
Comprehensive indicator of comparison of the main technological indicators of the developed and alternative technologies K_1	$K_1 = \frac{1}{3}\left(\frac{A_{T,P}}{A_{T,A}} + \frac{B_{T,P}}{B_{T,A}} + \frac{C_{T,P}}{C_{T,A}}\right)$, where $A_{T,P}$, $B_{T,P}$, $C_{T,P}$ and $A_{T,A}$, $B_{T,A}$, $C_{T,A}$ are specific indicators of waste, atmospheric emissions and discharges into natural waters for the developed and alternative technologies, respectively
Comprehensive indicator of comparison of additional technological indicators of the developed and alternative technologies K_2	$K_2 = \frac{1}{4}\left(\frac{J_{K,A}}{J_{K,P}} + \frac{J_{O,A}}{J_{O,P}} + \frac{J_{A,A}}{J_{A,P}} + \frac{J_{B,A}}{J_{B,P}}\right)$, where $J_{K,P}$, $J_{O,P}$, $J_{A,P}$, $J_{B,P}$ and $J_{K,A}$, $J_{O,A}$, $J_{A,A}$, $J_{B,A}$ are additional technological indicators for the developed and alternative technologies, respectively
Final indicator for evaluating the developed technology I	$I = K_1 + K_2$



(1)

disulfide by comparing it with an existing method for obtaining the product by oxidation with hydrogen peroxide in the presence of sulfuric acid of the sodium salt of dimethyldithiocarbamic acid, which is synthesized by the reaction of dimethylamine with carbon disulfide in the presence of alkali at a molar ratio of carbon disulfide : dimethylamine : sodium hydroxide, equal to 1 : 1 : 1.03 [7]. The precipitate of tetramethylthiuram disulfide was filtered off, washed, granulated, and dried [8]. This process was already implemented in the USSR at the Khimprom Volgograd production association [9].

Based on the calculated material balances, the consumption coefficients for raw materials and auxiliary materials (Table 6) were determined along with the waste generation rates for the production of tetramethylthiuram disulfide using an alternative technology (Table 7).

Table 3. Consumption coefficients for raw materials and auxiliary materials in the tetramethylthiuram disulfide production

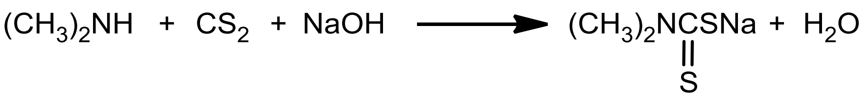
Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Dimethylamine (33%)	72.2	1.29	–
Carbon disulfide	40.2	0.73	–
Hydrogen peroxide (37%)	27.8	0.50	–
Methanol	4.5	0.08	With regeneration
	565.4	10.10	Without regeneration

Table 4. Waste generation standards, emissions, and discharges in the tetramethylthiuram disulfide production

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
VAT residue of methanol regeneration	Liquid	VAT residue, including	100.00	83.9	1.50
		Water	91.18	76.5	1.37
		Organic impurity	4.17	3.5	0.06
		Tetramethylthiuram disulfide	4.65	3.9	0.07
Air emissions		None			
Wastewater discharge		None			

Table 5. Basic and additional technological indicators calculated for the developed and existing alternative technologies used in the tetramethylthiuram disulfide production

Indicator	Calculation method and indicator value	
	Developed technology	**Alternative technology**
Main technological indicators of production		
Generation rate of solid and liquid waste	$A_{T,P}$ = 1.5 t/t (Table 4)	$A_{T,A}$ = 4.58 t/t (Table 7)
Specific emissions into the atmosphere	Off-gases are locally cleaned in contact devices. Since the cleaning efficiency is 100%, there are no emissions into the atmosphere (Tables 4 and 7)	
	$B_{T,P}$ = 0 t/t	$B_{T,A}$ = 0 t/t
Wastewater generation rate	There is no wastewater discharge (Tables 4 and 7)	
	$C_{T,P}$ = 0 t/t	$C_{T,A}$ = 0 t/t
Additional technological indicators		
Degree of complexity and completeness of the extraction of useful components from the feedstock	It is calculated as the sum of the extraction coefficients of dimethylamine P_{DMA} and carbon disulfide P_{CS_2} taking into account the yield of tetramethylthiuram disulfide (56.1 kg per operation, 95%) without taking into account technological losses of the product in the filtrate and washing solution. P_{DMA} = 0.41/0.43 = 0.95 t/t P_{CS_2} = 0.69/0.73 = 0.95 t/t $J_{K,P}$ = 0.95 + 0.95 = 1.90 t/t $J_{K,P}$ = 1.90 t/t	$J_{K,A}$ = 1.90 t/t
Degree of generated waste utilization	It is calculated as the share of regenerated methanol in the total mass of waste according to the material balance of the methanol regeneration stage per one operation $J_{O,P}$ = 558.2/644.9 = 0.87 t/t	$J_{O,A}$ = 0.69 t/t
Degree of purification of emissions of harmful substances into the atmosphere	It is calculated as the share of captured methanol vapors in the trap and in the process of local purification in contact devices in the total mass of off-gases, taking into account 100% efficiency of their purification (Tables 4 and 7)	
	$J_{A,P}$ = 1.00 t/t	$J_{A,A}$ = 1.00 t/t
Degree of purification of discharges into water bodies	There is no wastewater discharge (Tables 4 and 7)	
	$J_{B,P}$ = 0 t/t	$J_{B,A}$ = 0 t/t


(2)

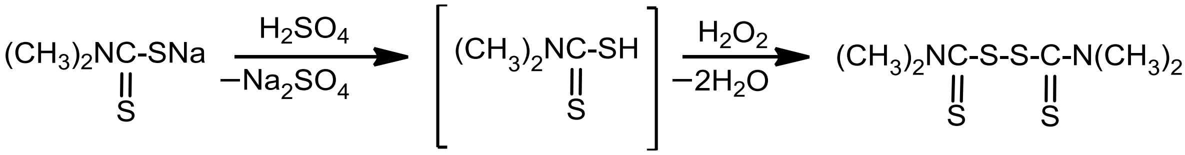

(3)

Table 6. Consumption coefficients for raw materials and auxiliary materials in the tetramethylthiuram disulfide production using an alternative technology

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Dimethylamine (33%)	72.20	1.29	–
Carbon disulfide	40.20	0.73	–
Hydrogen peroxide (37%)	27.80	0.50	–
Sodium hydroxide (44%)	50.92	0.91	–
Sulfuric acid (60%)	45.75	0.82	–
Methanol (99.47%)	1.81	0.03	With regeneration
	240.00	4.28	Without regeneration
Water	76.97	1.37	With regeneration
	412.00	7.34	Without regeneration

Table 7. Waste generation standards, emissions, and discharges in the alternative tetramethylthiuram disulfide production technology (with methanol and water regeneration)

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
VAT residue (methanol regeneration operation)	Liquid	VAT residue, including:	100.00	7.57	0.13
		Water	91.17	2.71	0.05
		Organic impurities	8.83	4.86	0.09

Table 7. Continued

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
VAT residue (water regeneration operation)	Liquid	VAT residue, including:	100.00	249.46	4.45
		Sodium sulfate	15.95	39.78	0.71
		Water	83.06	207.19	3.69
		Organic impurities	1.00	2.49	0.04
Air emissions		None			
Wastewater discharge		None			

Further, we calculated comprehensive indicators for comparing the developed and alternative technologies used in the production of tetramethylthiuram disulfide along with the final indicator for evaluating the developed technology for compliance with BAT principles (Table 8).

The value of the final indicator I of the assessment of the new technology 1.04 < 2 supports the conclusion that the technology developed by us for the production of tetramethylthiuram disulfide meets BAT principles and is more environmentally friendly compared to the alternative one originally implemented in the USSR [4]. The technology developed by us was introduced in the branch of *GosNIIOKhT—Separate Plant No. 4* (Novocheboksarsk, Chuvash Republic), whose experimental low-tonnage tetramethylthiuram disulfide production capacity is 5000 kg/year.

The high efficiency (K_1 = 0.11) of the developed technology for the production of tetramethyl thiuram disulfide (Table 8) was determined by the low waste rate of the technological process. The achieved level of environmental friendliness of production (K_2 = 0.93) was ensured by the regeneration of raw materials (methanol).

Table 8. Comprehensive indicators and the final evaluation indicator of the developed tetramethylthiuram disulfide production technology

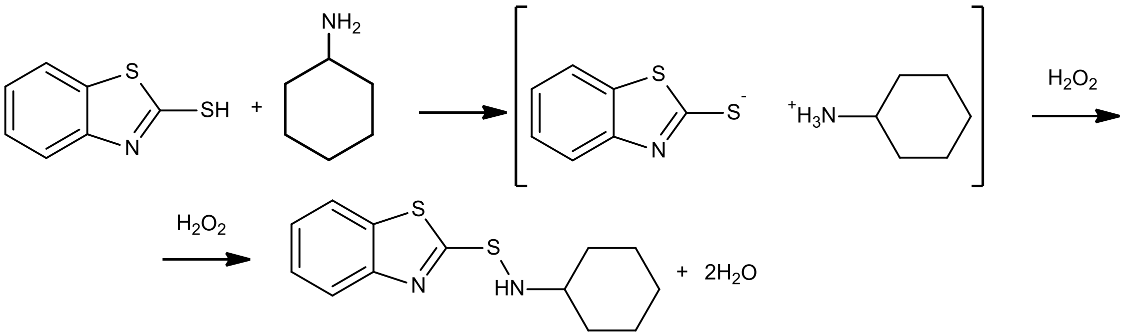
Indicator	Calculation method and indicator value
Comprehensive indicator of comparison of the main technological indicators of the developed and alternative technology K_1	Due to the absence of emissions of harmful substances into the atmosphere or discharges into water bodies for the developed and alternative technologies, no comparison of specific indicators of such emissions and discharges is carried out. $K_1 = (A_{T,P}/A_{T,A})/3$ $K_1 = (1.50/4.58)/3 = 0.11$
Comprehensive indicator of comparison of additional technological indicators of the developed and alternative technology K_2	Due to the absence of discharges of harmful substances into water bodies for the developed and alternative technologies, no calculation or comparison of the degree of purification of discharges into water bodies is carried out. $K_2 = (J_{K,A}/J_{K,P} + J_{O,A}/J_{O,P} + J_{A,A}/J_{A,P})/3$ $K_2 = (1.9/1.9 + 0.69/0.87 + 1.00/1.00)/3$ $K_2 = 0.93$
Technology assessment outcome I	$I = 0.11 + 0.93 = 1.04$

Assessment of the compliance of the *N*-cyclohexyl-2-benzothiazolylsulfenamide production technology with the BAT principles

The technology for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide is based on the one-stage method for its preparation published in [9], which includes the condensation of 2-mercaptobenzothiazole and cyclohexylamine, followed by peroxidation of the resulting intermediate compound, cyclohexylammonium 1,3-benzothiazole-2-thiolate, without its selection. The process is carried out in an aqueous medium at a molar ratio of 2-mercaptobenzothiazole : cyclohexylamine : hydrogen peroxide equal to 1 : 3 : 1.1 and is described by Scheme (4).

The calculation of the main and additional technological indicators of the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide was carried out using the data of "Temporary technological regulations for pilot low-tonnage production of *N*-cyclohexyl-2-benzothiazolylsulfenamide, No. TTR-5-350" on consumption coefficients for raw materials (Table 9) and the generation rate of production waste (Table 10). The results of the calculation of the main and additional technological indicators are presented in Table 11.

The final assessment of the developed technology for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide was carried out by comparing this technology with an alternative one based on the method of its production by the interaction of the sodium salt of 2-mercaptobenzothiazole (captax) with cyclohexylamine in the presence of sodium hypochlorite. The sodium salt of Captax was mixed with cyclohexylamine, the reaction mass was acidified with 37% hydrochloric acid. This gave the cyclohexylamine salt of Captax, which was oxidized with sodium hypochlorite in the presence of alkali. Unreacted cyclohexylamine was isolated from wastewater by nitrogen purge at a temperature of 120–130°C. The described method for the preparation of *N*-cyclohexyl-2-benzothiazolylsulfenamide was implemented in the USSR at *Novokemerovo Chemical Plant* [11].



(4)

Table 9. Consumption coefficients for raw materials and auxiliary materials in the *N*-cyclohexyl-2-benzothiazolylsulfenamide production

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
2-Mercaptobenzothiazole (97%)	68.80	0.872	–
Cyclohexylamine (99%)	33.31	0.422	With regeneration
	119.99	1.521	Without regeneration
Hydrogen peroxide (37%)	39.60	0.502	–
Water	0.00	0.000	With regeneration
	800.00	10.139	Without regeneration

Table 10. Waste generation standards, emissions, and discharges in the *N*-cyclohexyl-2-benzothiazolylsulfenamide production (with regeneration of water and cyclohexylamine)

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
VAT residue (water regeneration operation)	Liquid	VAT residue, including:	100.00	64.76	0.821
		Water	62.25	40.31	0.511
		Organic impurities	37.75	24.45	0.310
Air emissions		None			
Wastewater discharge		None			

Table 11. Basic and additional technological indicators calculated for the developed and existing alternative technologies used in the *N*-cyclohexyl-2-benzothiazolylsulfenamide production

Indicator	Calculation method and indicator value	
	Developed technology	Alternative technology
Main technological indicators		
Generation rate of solid and liquid waste	$A_{T,P} = 0.821$ t/t (Table 10)	$A_{T,A} = 4.45$ t/t (Table 13)
Specific emissions into the atmosphere	Abgases are absent, emissions into the atmosphere are absent (Tables 10 and 13)	
	$B_{T,P} = 0$	$B_{T,A} = 0$
Wastewater generation rate	There is no wastewater discharge (Tables 10 and 13)	
	$C_{T,P} = 0$	$C_{T,P} = 0$
Additional technological indicators		
Degree of complexity and completeness of the extraction of useful components from the feedstock	It is calculated as the sum of the recovery factors of 2-mercaptobenzothiazole P_{MBT} and cyclohexylamine P_{CHA} taking into account the yield of *N*-cyclohexyl-2-benzothiazolylsulfenamide (78.9 kg per operation, 75%) and the regeneration of cyclohexylamine $P_{MBT} = 0.632/0.846 = 0.75$ t/t $P_{CHA} = 1.447/1.506 = 0.96$ t/t $J_{K,P} = 0.75 + 0.96 = 1.71$ t/t	$J_{K,A} = 1.64$ t/t

Table 11. Continued

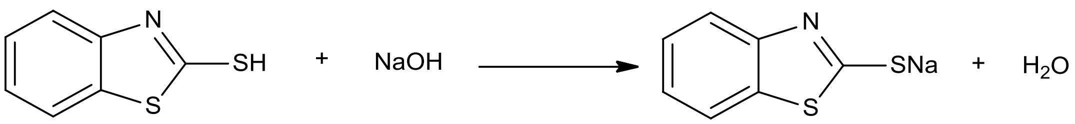
Indicator	Calculation method and indicator value	
	Developed technology	Alternative technology
Degree of utilization of generated waste	It is calculated as the share of regenerated cyclohexylamine and water in the total mass of waste (mother liquor) per one operation: $J_{O,P}$ = (84.64 + 800)/949.40 = 0.93 t/t	$J_{O,A}$ = 0.55 t/t
Degree of purification of emissions of harmful substances into the atmosphere	Abgases are absent, emissions into the atmosphere are absent (Tables 10 and 13)	
	$J_{A,P}$ = 0 t/t	$J_{A,A}$ = 0 t/t
Degree of purification of discharges into water bodies	Wastewater is absent (Tables 10 and 13)	
	$J_{B,P}$ = 0 t/t	$J_{B,A}$ = 0 t/t

The reaction to obtain the sodium salt of 2-mercaptobenzothiazole is described by Scheme (5).

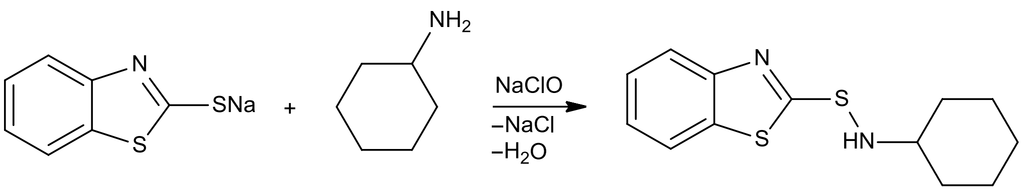
The formation of *N*-cyclohexyl-2-benzothiazolylsulfenamide can be described by Scheme (6).

Based on the material balances calculated by us, we determined the consumption coefficients for raw materials and auxiliary materials (Table 12) and the waste generation rates for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide using an alternative technology (Table 13).

Next, we calculated comprehensive indicators for comparing the developed and alternative technologies used in the production of this product along with the final indicator for evaluating the developed technology for compliance with BAT principles (Table 14).



(5)



(6)

Table 12. Consumption coefficients for raw materials and auxiliary materials in the *N*-cyclohexyl-2-benzothiazolylsulfenamide production using an alternative technology

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
2-Mercaptobenzothiazole, 97%	68.80	0.73	–
Sodium hydroxide, 44% solution	44.46	0.47	–
Water	581.04	6.16	Without regeneration
	52.24	0.55	With regeneration

Table 12. Continued

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Cyclohexylamine, 99%	47.98	0.51	Without regeneration
	40.12	0.42	With regeneration
Hydrochloric acid, 37% solution	51.30	0.54	–
Sodium hypochlorite, 15% solution	253.96	2.69	–
Sodium sulfite	14.69	0.16	–

Table 13. Waste generation standards, emissions, and discharges in the *N*-cyclohexyl-2-benzothiazolylsulfenamide production using an alternative technology (with water and cyclohexylamine regeneration)

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
Wastewater	Liquid	VAT residue, including:	100.00	420.38	4.45
		Total organic impurities	3.19	13.41	0.14
		Sodium chloride	14.47	60.84	0.64
		Sodium sulfate	3.94	16.56	0.18
		Water	78.40	329.57	3.49
Air emissions		None			
Wastewater discharge		None			

Table 14. Comprehensive indicators and the final evaluation of the developed technology for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide

Indicator	Calculation method and indicator value
Comprehensive indicator of comparison of the main technological indicators of the developed and alternative technologies K_1	Due to the absence of emissions of harmful substances into the atmosphere or discharges of effluents into water bodies for the developed and alternative technologies, no comparison of specific indicators of such emissions into the atmosphere and discharges into water bodies is carried out. $K_1 = (A_{T,P}/A_{T,A})/3$ $K_1 = (0.82/4.45)/3 = 0.06$
Comprehensive indicator of comparison of additional technological indicators of the developed and alternative technologies K_2	Due to the absence of discharges into water bodies and emissions of harmful substances into the atmosphere for the developed and alternative technologies, no calculation or comparison of the degree of purification of discharges into water bodies and emissions of harmful substances into the atmosphere is carried out. $K_2 = (J_{K,A}/J_{K,P} + J_{O,A}/J_{O,P})/4$ $K_2 = (1.64/1.71 + 0.55/0.93)/4 = 0.39$
Technology assessment outcome I	$I = 0.06 + 0.39 = 0.45$

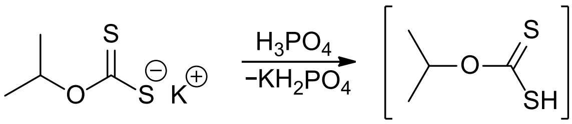
The value of the final indicator of technology assessment $I = 0.45 \ll 2$ supports the conclusion that the technology developed by us for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide meets BAT principles and is much more environmentally friendly compared to the alternative [11] implemented in the USSR. This process has been introduced in aforementioned *Separate Plant No. 4*; the capacity of the pilot low-tonnage production is 5000 kg/year.

A distinctive feature of the technology developed by us for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide compared to that implemented earlier in the USSR is a significant reduction in the level of waste generation and a high degree of raw material recovery, which makes it possible to characterize the new technology as much more efficient ($K_1 = 0.06$). The high level of environmental friendliness of the developed technology ($K_2 = 0.39$) is ensured by minimizing losses due to high rates of resource saving (raw material conversion) and recovery of the solvent (water) and excess raw material component (cyclohexylamine).

Assessment of the compliance of the diisopropyl xanthogen disulfide production technology with the BAT principles

The technology for the production of diisopropyl xanthogen disulfide is based on the method published in [12], which includes the oxidation of potassium isopropyl xanthate (PIX) [13] with hydrogen peroxide in the presence of phosphoric acid in water [14]. The interaction of PIX with phosphoric acid with the formation of the corresponding xanthogenic acid is described by Scheme (7).

The oxidation of the obtained xanthogenic acid with hydrogen peroxide to form diisopropyl xanthogen disulfide is represented by Scheme (8).



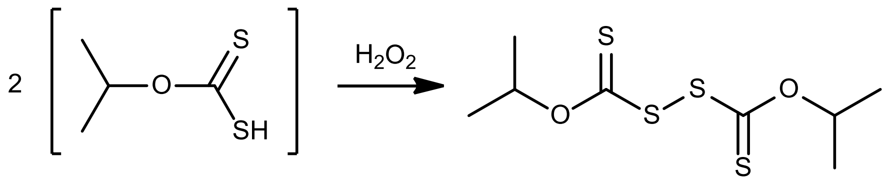
(7)

The resulting suspension was filtered, washed with water and dried. Wash water was reused in the next synthesis as a solvent. PIX was obtained by the interaction of isopropanol, potassium hydroxide, and carbon disulfide according to Scheme (9).

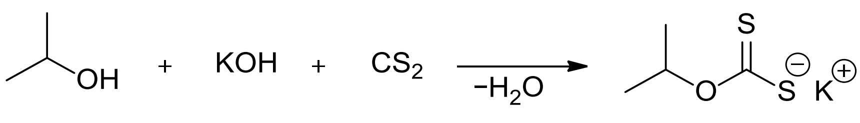
The process was carried out in isopropanol at a molar ratio of isopropanol : carbon disulfide : potassium hydroxide equal to 7 : 1 : 1 and a temperature of 25–35°C. To restore the quality of alcohol, the method of two-stage distillation of the filtrate was used.

The calculation of the main and additional technological indicators of the production of diisopropyl xanthogen disulfide to assess the compliance of the technology with the principles of BAT was carried out using the data of the "Temporary process regulations for pilot low-tonnage production of potassium isopropyl xanthate, No. TTR-12-350" and "Temporary process regulations for pilot low-tonnage production of diisopropylxanthogendisulfide, No. TTR-13-350" on consumption coefficients for raw materials (Table 15) and the generation rate of production waste (Table 16). The results of calculating the main and additional technological indicators for the production of diisopropyl xanthogen disulfide using an alternative technology are presented in Table 17.

The final assessment of the developed technology for the production of diisopropyl xanthogen disulfide was carried out by comparing the developed technology with an alternative one based on the known method of its production by oxidation of alkali metal xanthate with sodium nitrite in the presence of mineral acids (HCl, H_2SO_4) [15]: one mole of acid is used to decompose sodium nitrite to nitrogen oxides, and the second mol—on the formation of xanthogenic acid from the corresponding salt. The liberated nitric oxide (IV) acts as an oxidizing agent in this process, which can be generally described by reaction Schemes (10)–(13):



(8)



(9)

Table 15. Consumption coefficients for raw materials and auxiliary materials in the production of diisopropyl xanthogen disulfide

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Obtaining PIX (98.88%)			
Isopropyl alcohol (99.59%)	416.16	2.593	–
	145.89	0.909	With regeneration
Carbon disulfide (100%)	72.68	0.453	–
Potassium hydroxide (86.11%)	61.70	0.384	–
Isopropanol recovery			
Toluene (99.5%)	98.63	0.616	–
Obtaining diisopropyl xanthogen disulfide			
PIX (98.88%)	150.00	1.42	–
Hydrogen peroxide (37%)	43.56	0.41	–
Orthophosphoric acid (85%)	99.39	0.94	–
Water	850.00	8.03	–
	440.00	4.16	Taking into account the return of wash water

Table 16. Waste generation standards, emissions, and discharges in the diisopropyl xanthogen disulfide production (with isopropanol regeneration and return of washing water)

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
VAT residue after rectification of the filtrate (stage of obtaining PIX)	Liquid	VAT residue, including:	100.00	12.89	0.086
		Isopropanol	51.32	5.42	0.039
		Impurity	48.68	7.47	0.047

Table 16. Continued

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
Azeotrope isolated at the stage of rectified absolutization (stage of obtaining PIX)	Liquid	Azeotrope, including:	100.00	201.53	1.260
		Isopropanol	38.20	76.98	0.481
		Water	13.10	26.40	0.165
		Toluene	48.70	98.14	0.613
Distillation residue after absolute rectification (stage of obtaining PIX)	Liquid	VAT residue, including:	100.00	9.29	0.021
		Isopropanol	85.71	8.80	0.018
		Impurity	14.29	0.49	0.003
Wastewater (diisopropyl xanthogen disulfide production stage)	Liquid	Filtrate, including:	100.00	620.63	5.862
		Water	79.03	490.47	4.632
		Impurity	20.97	130.16	1.229
Air emissions	None				
Wastewater discharges	None				

Table 17. Basic and additional technological indicators calculated for the developed and alternative technologies used in the diisopropyl xanthogen disulfide production

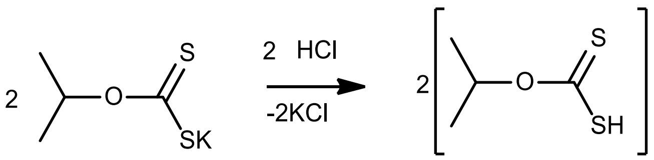
Indicator	Calculation method and indicator value	
	Developed technology	Alternative technology
Main technological indicators		
Generation rate of solid and liquid waste	$A_{T,P}$ = 7.228 t/t (Table 16)	$A_{T,A}$ = 7.337 t/t (Tables 20 and 21)
Specific emissions into the atmosphere	Process off-gases are water vapor. There are no emissions of harmful substances into the atmosphere (Table 16) $B_{T,P}$ = 0 t/t	Off-gases are a mixture of nitrogen and carbon dioxide. There are no emissions of harmful substances into the atmosphere (Tables 20 and 21) $B_{T,A}$ = 0 t/t

Table 17. Continued

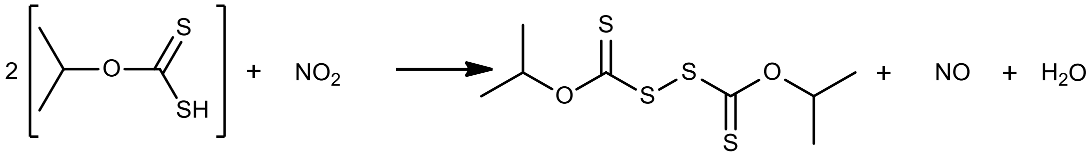
Indicator	Calculation method and indicator value	
	Developed technology	Alternative technology
Wastewater generation rate	There is no wastewater discharge due to the high hazard class for fishery water bodies (hazard class 2*). $C_{T,P} = 0$ t/t	There is no wastewater discharge due to the high hazard class of the leachate for water bodies of fishery significance (hazard class 1*). $C_{T,A} = 0$ t/t
Additional technological indicators		
The degree of complexity and completeness of the extraction of useful components from the feedstock	It is calculated as the sum of the recovery factors for isopropanol P_{IP}, potassium hydroxide P_{KOH}, carbon disulfide P_{CS_2}, PIX P_{PIX}, hydrogen peroxide $P_{H_2O_2}$, and phosphoric acid $P_{H_3PO_4}$ taking into account the yield of diisopropylxanthogendisulfide (105.88 kg per operation, 90%). $P_{IP} = 0.341/0,358 = 0.95$ t/t $P_{KOH} = 0.319/0.334 = 0.95$ t/t $P_{CS_2} = 0.433/0.453 = 0.95$ t/t $P_{PIX} = 1.261/1.401 = 0.90$ t/t Taking into account the degree of extraction of the components of the PIX production process: $P_{PIX} = 0.95 \times 0.90 = 0.86$ t/t $P_{H_2O_2} = 0.123/0.152 = 0.81$ t/t $P_{H_3PO_4} = 0.713/0.798 = 0.89$ t/t $J_{K,P} = 0.86 + 0.81 + 0.89 = 2.56$ t/t	Recovery factors for carbon disulfide P_{CS_2}, isopropanol P_{IP}, potassium hydroxide P_{KOH} for the stage of obtaining PIX: $P_{IP} = 0.341/0.358 = 0.95$ t/t $P_{KOH} = 0.319/0.334 = 0.95$ t/t $P_{CS_2} = 0.433/0.453 = 0.95$ t/t Recovery factors of PIX, sodium nitrite P_{NaNO_2}, and phosphoric acid $P_{H_3PO_4}$ taking into account the yield of the product (108.25 kg per operation, 94.1%). $P_{PIX} = 0.95 \times 0.94 = 0.89$ t/t $P_{NaNO_2} = 0.44/0.47 = 0.94$ t/t $P_{H_3PO_4} = 0.611/0.611 = 1.00$ t/t $J_{K,A} = 0.89 + 0.94 + 1.00 = 2.83$ t/t
Degree of utilization of generated waste	It is calculated as the share of regenerated isopropanol in the total mass of waste (filtrate and condensate). According to the material balance of isopropanol regeneration per 1 t of product: $J_{O,P} = (0.984 + 0.700)/3.049 = 0.55$ t/t	It is calculated as the share of returned water in the total mass of waste (filtrate, wash water and waste absorbent). According to the material balance per 1 t of product: $J_{O,A} = 4.610/9.772 = 0.47$ t/t
Degree of purification of emissions of harmful substances into the atmosphere	Process off-gases are water vapor. There are no emissions of harmful substances into the atmosphere. $J_{A,P} = 1.00$ t/t	It is calculated as the share of captured nitrogen oxide in the total mass of off-gases: $J_{A,A} = 0.030/0.030 = 1.00$ t/t
Degree of purification of discharges into water bodies	There is no wastewater discharge (Tables 16, 20, and 21)	
	$J_{B,P} = 0$ t/t	$J_{B,A} = 0$ t/t

* Order of the Ministry of Natural Resources of Russia dated December 4, 2014 No. 536 "On approval of the criteria for classifying wastes as hazard classes I–V according to the degree of negative impact on the environment" (Registered in the Ministry of Justice of Russia on December 29, 2015, No. 40330).

$$2NaNO_2 + 2H^{\oplus} \longrightarrow 2Na^{\oplus} + NO + NO_2 + H_2O \quad (10)$$

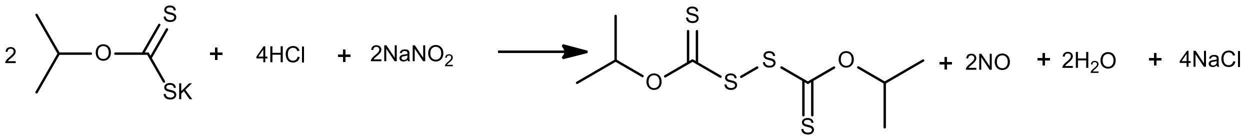


(11)



(12)

In total:



(13)

Purification of gas emissions is carried out by absorption of off-gases with an aqueous solution of urea. The process of absorption of nitrogen oxides can be described by Scheme (14):

$$NO + NO_2 + (NH_2)_2CO = 2H_2O + CO_2 + 2N_2 \qquad (14)$$

Based on the calculated by us material balances, the consumption coefficients for raw materials and auxiliary materials (Tables 18 and 19) and the waste generation rate in the production of diisopropyl xanthogen disulfide using an alternative technology were determined (Tables 20 and 21).

Table 18. Consumption coefficients for raw materials and auxiliary materials in the potassium isopropyl xanthate production

Name of raw materials	**Expense coefficients**		**Note**
	kg/operation	**t/t**	
Obtaining PIX			
Isopropyl alcohol (99.6%)	416.16	2.593	–
	145.89	0.909	With regeneration
Carbon disulfide (100%)	72.68	0.453	–
Potassium hydroxide (86.8%)	61.70	0.384	–
Isopropanol recovery			
Toluene (99.5%)	98.63	0.616	–

Table 19. Consumption coefficients for raw materials and auxiliary materials in the diisopropyl xanthogen disulfide production using an alternative technology

Name of raw materials	**Expense coefficients**		**Note**
	kg/operation	**t/t**	
PIX (98.88%)	150.00	1.355	–
Sodium nitrite (98.50%)	59.60	0.552	–
Orthophosphoric acid (85%)	127.10	1.196	–

Table 19. Continued

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Water	850.00	7.870	–
	433.86	4.017	With the return of wash water and condensate from the sludge drying process
Urea (100%)*	133.02*	0.172	With recycling
	121.63*	0.157	With the regeneration of the absorbent
Water for absorbent preparation*	399.06*	0.515	With recycling

* Based on 7 operations for obtaining diisopropyl xanthogen disulfide.

Table 20. Waste generation standards, emissions, and discharges in the potassium isopropyl xanthate production

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
VAT residue after distillation of the filtrate	Liquid	VAT residue, including:	100.00	12.89	0.086
		Isopropanol	51.32	5.42	0.039
		Impurities	48.68	7.47	0.047
Azeotrope isolated at the stage of absolute rectification	Liquid	Azeotrope, including:	100.00	201.53	1.260
		Isopropanol	38.20	76.98	0.481
		Water	13.10	26.40	0.165
		Toluene	48.70	98.14	0.613
Distillation residue after absolute rectification	Liquid	VAT residue, including:	100.00	9.29	0.021
		Isopropanol	85.71	8.80	0.018
		Impurities	14.29	0.49	0.003
Air emissions		None			
Wastewater discharges		None			

Table 21. Waste generation standards, emissions, and discharges in the diisopropyl xanthogen disulfide production using an alternative technology

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
Wastewater	Liquid	Filtrate, including:	100.00	629.60	5.830
		Water	74.13	466.72	4.321
		Impurities	1.25	7.87	0.073
		Sodium and potassium salts of phosphoric acid	24.62	155.01	1.435
Wastewater	Liquid	Waste absorbent, including:	100.00	15.45	0.140
		Urea	2.78	0.43	0.004
		Water	97.22	15.02	0.136
Abgases	Gas	Abgases, including	100.00	13.82	0.125
		Nitrogen	10.34	1.43	0.013
		Carbon dioxide	89.66	12.39	0.112
Air emissions		None			
Wastewater discharges		None			

Further, we calculated the comprehensive indicators for comparing the developed and alternative technologies used in the production of diisopropyl xanthogen disulfide along with the final indicator for evaluating the developed technology for compliance with BAT principles (Table 22).

The value of the final indicator of the technology assessment $I = 1.97 < 2$ supports the conclusion that the technology developed by us for the production of diisopropyl xanthogen disulfide meets BAT principles and is more environmentally friendly compared to the alternative one [4]. This technology was introduced in *Separate Plant No. 4*; the capacity of the pilot low-scale production is 2000 kg/year for diisopropyl xanthogen disulfide and 3000 kg/year for PIX.

Thus, the developed technology is more environmentally friendly than the alternative one due to the high level of environmental friendliness achieved through the regeneration of isopropanol at the stage of PIX production. However, the specific indicator of waste generation by this technology is quite high (7.23 t/t, Table 17), and the main production waste is the filtrate from the stage of obtaining diisopropyl xanthogen disulfide (5.862 t/t, Table 21), the water content of which is 79.03%. It should be noted that during the development process, we managed to reduce the hazard class of this waste from 1st to 2nd, which, in our opinion, is a significant result in achieving environmental protection goals and increases the level of environmental friendliness of the technology we developed for the production of diisopropyl

[6] Order of the Ministry of Agriculture of Russia dated December 13, 2016, No. 552 (as amended on March 10, 2020) “On approval of water quality standards for fishery water bodies, including standards for maximum permissible concentrations of harmful substances in the waters of fishery water bodies” (Registered with the Ministry of Justice of Russia on January 13, 2017, No. 45203) (in Russ.).

Table 22. Comprehensive indicators and the final evaluation indicator of the developed diisopropyl xanthogen disulfide production technology

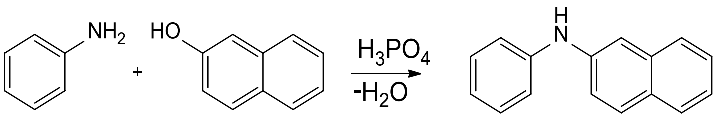
Indicator	Calculation method and indicator value
Comprehensive indicator of comparison of the main technological indicators of the developed and alternative technologies K_1	Due to the absence of emissions of harmful substances into the atmosphere or discharges into water bodies for these technologies, no comparison of specific indicators of emissions into the atmosphere and discharges into water bodies is carried out. $K_1 = A_{T,P}/A_{T,A} = 7.23/7.34 = 0.98$
Comprehensive indicator of comparison of additional technological indicators of the developed and alternative technologies K_2	Due to the absence of discharges of harmful substances into water bodies using these technologies, no calculation or comparison of the degree of purification of discharges into water bodies is carried out. $K_2 = (2.83/2.56 + 0.47/0.55 + 1.00/1.00)/3 = (1.11 + 0.85 + 1.00)/3 = 0.99$
Technology assessment outcome I	$I = 0.98 + 0.99 = 1.97$

xanthogen disulfide. Regeneration of the solvent (water) from the waste (filtrate) can be considered as a possible direction for the modernization of the technology, which will lead to a decrease in the specific indicator of production waste and will increase the degree of use of raw materials and generated waste.

Assessment of the compliance of the developed technology for the *N*-phenyl-2-naphthylamine production with the BAT principles

The technology for the production of *N*-phenyl-2-naphthylamine was based on a one-stage method developed in [16], which includes the aramination of 2-naphthol with aniline in the presence of catalytic amounts of orthophosphoric acid at a molar ratio of 2-naphthol : aniline : orthophosphoric acid equal to 1 : 1.065 : 0.017, within 2.0–2.5 h [17, 18]. The return of the initial aniline to the reaction sphere is ensured by separating the azeotropic aniline/water mixture and separating *N*-phenyl-2-naphthylamine in the form of a powder by crystallization from the reaction mass in an isobutanol/xylene mixture [16, 17]. The process of obtaining *N*-phenyl-2-naphthylamine is described by Scheme (15).

The calculation of the main and additional technological indicators [4] of the production of *N*-phenyl-2-naphthylamine was carried out by us using data of “Temporary process regulations for pilot low-tonnage production of *N*-phenyl-2-naphthylamine, No. TTR-8-350” on consumption coefficients for raw materials (Table 23) and



(15)

Table 23. Consumption coefficients for raw materials and auxiliary materials in the *N*-phenyl-2-naphthylamine production

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Aniline (99.9%)	121.00	0.475	–
2-Naphthol (99.5%)	175.00	0.686	–
Phosphoric acid (85%)	2.40	0.009	–
Isobutanol (99.3%)	433.42	1.700	Without regeneration
	1.90	0.007	With regeneration
Petroleum xylene (99.6%)	82.91	0.325	Without regeneration
	32.27	0.127	With regeneration

production waste generation rates (Table 24). The results of the calculation of the main and additional technological indicators are presented in Table 25.

The final assessment of the developed technology for the *N*-phenyl-2-naphthylamine production was also carried out by comparing this technology with an alternative one, which was implemented in the 1960s at *Novomoskovsk Anilino-Paint Plant* (*Novomoskovsk Organic Synthesis Plant*) [19]. The technology was based on the condensation of 2-naphthol with aniline in the presence of a benzenesulfonic acid catalyst at a molar ratio of 2-naphthol to aniline equal to 1 : 1.5. The process of formation of *N*-phenyl-2-naphthylamine can be described by the Scheme (16).

Table 24. Waste generation standards, emissions, and discharges in the *N*-phenyl-2-naphthylamine production (with regeneration of isobutanol–*o*-xylene mixture)

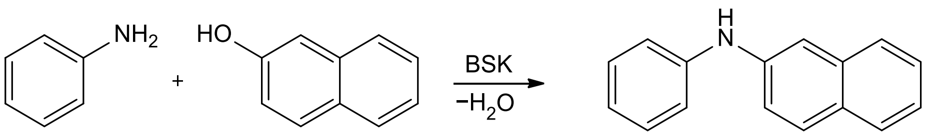
Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
Distillation residue after regeneration of isobutanol-xylene mixture	Liquid	VAT residue, including:	100.00	54.23	0.213
		N-phenyl-2-naphthylamine	8.32	10.03	0.039
		Aniline phosphate	3.30	3.98	0.016
		o-Xylene	81.07	31.90	0.125
		Aniline	5.09	6.14	0.024
		Impurities	1.14	2.18	0.009
Aqueous phase (azeotrope)	Liquid	Water	100.00	22.15	0.087
Organic phase (azeotrope)	Liquid	Organic phase, including:	100.00	2.61	0.010
		Aniline	13.08	0.34	0.001
		Isobutanol	70.11	1.90	0.007
		Xylene	16.81	0.37	0.001
Air emissions	None				
Wastewater discharges	None				

Table 25. Basic and additional technological indicators calculated for the developed and alternative technologies used in the *N*-phenyl-2-naphthylamine production

Indicator	Calculation method and indicator value	
	Developed technology	Alternative technology
Main technological indicators		
Generation rate of solid and liquid waste	$A_{T,P}$ = 0.310 t/t (Table 24)	$A_{T,P}$ = 1.85 t/t (Table 27)
Specific emissions into the atmosphere	There are no emissions into the atmosphere (Tables 24 and 27)	
	$B_{T,P}$ = 0 t/t	$B_{T,A}$ = 0 t/t

Table 25. Continued

Indicator	Calculation method and indicator value	
	Developed technology	Alternative technology
Wastewater generation rate	There is no wastewater discharge (Tables 24 and 27)	
	$C_{T,P} = 0$ t/t	$C_{T,A} = 0$ t/t
Additional technological indicators		
The degree of complexity and completeness of the extraction of useful components from the feedstock	It is calculated as the sum of the recovery factors of 2-naphthol and aniline, taking into account the yield of *N*-phenyl-2-naphthylamine (255.00 kg per operation, 96%) $P_{2\text{-Naphthol}} = 0.659/0.683 = 0.96$ t/t $P_{\text{Aniline}} = 0.424/0.474 = 0.89$ t/t $J_{K,P} = 0.96 + 0.89 = 1.85$ t/t	$J_{K,A} = 1.59$ t/t
Degree of utilization of generated waste	It is calculated as the share of regenerated isobutanol and xylene in the total mass of the waste (filtrate, washing solution, and condensate). It can be calculated from the material balance data for the regeneration of the isobutanol/xylene mixture per operation. $J_{O,P} = (431.47 + 50.60)/538.39 =$ $= 0.90$ t/t	$J_{O,A} = 0.31$ t/t
Degree of purification of emissions of harmful substances into the atmosphere	There are no emissions into the atmosphere (Tables 24 and 27)	
	$J_{A,P} = 0$ t/t	$J_{A,A} = 0$ t/t
Degree of purification of discharges into water bodies	There is no wastewater discharge (Tables 24 and 27)	
	$J_{B,P} = 0$ t/t	$J_{B,A} = 0$ t/t



(16)

The condensation of 2-naphthol and aniline was carried out at a temperature of 240 ± 5°C until the content of 2-naphthol was 0.8%. Aniline vapor was partially returned to the reactor by reflux. The reaction mass was neutralized with solid caustic soda. Unreacted aniline was distilled off with live steam until it was completely absent in the reaction mass. The selection of the target *N*-phenyl-2-naphthylamine was carried out in the form of a melt, followed by distillation and flaking.

Regeneration of excess aniline that did not react with 2-naphthol was carried out using vacuum distillation and rectification methods. The extraction of aniline from aniline water was carried out in the process of rectification by azeotropic distillation, followed by separation of the heteroazeotrope by centrifugation.

Based on the calculated by us material balances, the consumption coefficients for raw materials andauxiliary materials (Table 26) and the generation rate of *N*-phenyl-2-naphthylamine production waste using an alternative technology were determined (Table 27).

Next, we calculated comprehensive indicators for comparing the developed and alternative technologies and the final indicator for evaluating the new technology for compliance with BAT principles (Table 28)

Table 26. Consumption coefficients for raw materials and auxiliary materials in the *N*-phenyl-2-naphthylamine production using an alternative technology

Name of raw materials	Expense coefficients		Note
	kg/operation	t/t	
Technical aniline (99.8%)	1854.55	0.663	Without regeneration
	1185.99	0.424	With regeneration
2-Naphthol (98.5%)	1940.00	0.693	–
Benzenesulfonic acid (95%)	8.90	0.003	–
Technical sodium hydroxide (98.5%)	2.30	0.001	–
Water	3500.00	1.250	Without regeneration
	2659.57	0.950	With regeneration
Water vapor	2238.24	0.800	–

Table 27. Waste generation standards, emissions, and discharges in the *N*-phenyl-2-naphthylamine production using an alternative technology (with water and aniline regeneration)

Type of waste	Aggregate state of waste	Composition	Amount, %	Production waste generation rate	
				kg/operation	t/t
Wastewater	Liquid	Filtrate, including:	100.00	121.099	0.433
		2-Naphthol	0.09	0.114	0.0004
		Sodium salt of benzenesulfonic acid	0.60	0.722	0.0026
		Sodium salt of sulfuric acid	0.02	0.029	0.0001
		Water	95.06	115.117	0.4113
		Impurities	4.23	5.118	0.0183
Wastewater	Liquid	Wash water, including:	100.00	255.532	0.913
		2-Naphthol	0.09	0.222	0.0008
		Sodium salt of benzenesulfonic acid	0.09	0.241	0.0009
		Sodium salt of sulfuric acid	0.004	0.010	0.00004
		Water	99.31	253.779	0.9067
		Impurities	0.50	1.280	0.0046
VAT residue	Liquid	VAT residue, including:	100.00	0.400	0.001
		Resin	100.00	0.400	0.001
Wastewater	Liquid	Water, including:	100.00	141.110	0.504
		Aniline	0.15	0.210	0.0008
		Water	99.85	140.900	0.5034
Air emissions		None			
Wastewater discharges		None			

Table 28. Comprehensive indicators and the final evaluation indicator of the developed *N*-phenyl-2-naphthylamine production technology

Indicator	Calculation method and indicator value
Comprehensive indicator of comparison of the main technological indicators of the developed and alternative technologies K_1	Due to the absence of emissions of harmful substances into the atmosphere or discharges into water bodies for the technologies under consideration, the formula for calculating the indicator is transformed as follows: $K_1 = A_{T,P}/A_{T,A}$ $K_1 = 0.31/1.85 = 0.17$
Comprehensive indicator of comparison of additional technological indicators of the developed and alternative technologies K_2	Due to the absence of emissions of harmful substances into the atmosphere for the technologies under consideration, no calculation or comparison of the degree of purification of emissions of harmful substances into the atmosphere is carried out. $K_2 = (J_{K,A}/J_{K,P} + J_{O,A}/J_{O,P} + J_{B,A}/J_{B,P})/3$ $K_2 = (1.59/1.85 + 0.31/0.90 + 1.00/1.00)/3 = 0.73$
Technology assessment outcome *I*	$I = 0.17 + 0.73 = 0.90$

The value of the final technology assessment indicator $I = 0.90 << 2$ supports the conclusion that the *N*-phenyl-2-naphthylamine production technology developed by us meets BAT principles and is much more environmentally friendly [4] compared to the alternative one implemented in the USSR. The technology developed by us has been implemented in *Separate Plant No. 4*; the capacity of the experimental low-tonnage production is 5000 kg/year.

An analysis of the evaluation of the developed *N*-phenyl-2-naphthylamine production technology determines it as highly efficient ($K_1 = 0.17$) and having a high level of environmental friendliness ($K_2 = 0.73$). The new technology is distinguished by a significantly lower (almost 6 times) level of waste generation compared to the alternative technology implemented in the USSR, and is also characterized by a high degree of resource saving and recuperation of generated waste. The obtained result is ensured by the adopted technological solutions using the return of aniline to the reaction sphere after the separation of the condensed in florentine vapors of the azeotropic aniline–water mixture, as well as the regeneration of the mixture of solvents (isobutanol/xylene).

DISCUSSION

Based on the analysis of new low-tonnage chemical production technologies developed at *GosNIIOKhT* according to the criteria for achieving environmental protection objectives using the methodology [4], the adopted technological solutions for resource saving and environmental protection are concluded to be highly effective.

The quantitative assessment methodology [4] is based on determining achieved levels of manufacturability and environmental friendliness of new technologies along with the calculation of comprehensive indicator for comparison with alternative (BAT) technologies (Table 29). The calculated values of the main technological indicators characterize the achieved level of technology efficiency: the lower the value of the K_1 indicator, the higher the efficiency of the new technology compared to the existing alternative. In turn, the values of additional technological indicators of technologies reflect the achieved level of environmental friendliness of the technology, while the criterion for the effectiveness of the development (compared to the existing technology) also consists in the achievement of the minimum values of the K_2 indicator. The effectiveness of development as a whole characterizes the final indicator of comparison *I*: the lower its value, the higher the achieved degree of compliance of the new technology with BAT principles and the current level of development according to the criteria for achieving the environmental protection objectives.

The current absence of BAT for the production of tetramethylthiuram disulfide (thiuram D), *N*-cyclohexyl-2-benzothiazolylsulfenamide (sulfenamide C), diisopropyl xanthogen disulfide (diproxide and *N*-phenyl-2-naphthylamine (neozone D) is due to these materials having previously been produced in the USSR.

As a result of the calculations, it was found that all the new technologies developed by us in accordance with BAT principles are environmentally more advanced than those implemented earlier during the Soviet period (Table 30). The most

Table 29. Criteria for the development and evaluation indicators of new technologies in accordance with BAT principles

Criteria for development in accordance with BAT principles	**Evaluation indicators for developed and alternative production technologies in accordance with BAT principles**		
	K_1 (achieved level of technology efficiency)	**K_2 (achieved level environmental friendliness of the technology)**	**I (overall development efficiency)**
Development efficiency criterion	$K_1 < 1$ Reaching the minimum values of K_1	$K_2 < 1$ Reaching the minimum values of K_2	$I < 2$ Reaching the minimum values of I
Characteristics of development evaluation indicators	Comprehensive indicator of comparison of the main technological indicators of production technologies	Comprehensive indicator of comparison of additional technological indicators of the developed and alternative production technologies	Final indicator of the comparison of the developed and alternative production technologies
Semantic content of development evaluation indicators	Level of waste generation, air emissions and water discharges.	Degree of complexity and completeness of the extraction of useful components from the feedstock, the use of waste generated, the purification of emissions of harmful substances into the atmosphere and discharges into water bodies.	Degree of compliance of the new technology with BAT principles and the current level of development according to the criteria for achieving the objectives of environmental protection
Conclusion on the results of the development evaluation	$K_1 < 1$. The lower the K_1 indicator, the higher the achieved level of efficiency of the developed technology compared to the alternative.	$K_2 < 1$. The lower the K_2 indicator, the higher the achieved level of environmental friendliness of the developed technology compared to the alternative.	$I < 2$. The lower I, the more the developed technology complies with BAT principles and is more environmentally friendly compared to the alternative.

Table 30. Results of the quantitative assessment of the developed technologies for the production of materials in accordance with BAT principles

Development evaluation indicators in accordance with BAT principles	**Subject of development—production technology**			
	Tetramethylthiuram disulfide	***N*-cyclohexyl-2-benzothiazolylsulfenamide**	**Diisopropyl xanthogen disulfide**	***N*-phenyl-2-naphthylamine**
Development evaluation results				
K_1	0.11	0.06	0.98	0.17
K_2	0.93	0.39	0.99	0.73
I	1.04	0.45	1.97	0.90

Table 30. Continued

Development evaluation indicators in accordance with BAT principles	Subject of development—production technology			
	Tetramethylthiuram disulfide	*N*-cyclohexyl-2-benzothiazolylsulfenamide	Diisopropyl xanthogen disulfide	*N*-phenyl-2-naphthylamine
Conclusion on the results of the development evaluation:				
Achieved level of efficiency	Very high	Very high	Comparable	Very high
Achieved level of environmental friendliness	Comparable	Very high	Comparable	High
Overall development efficiency	Very high	Very high	Comparable	Very high
Compliance with BAT principles	Yes	Yes	Yes	Yes
Identification of possible directions for development modernization				
Possible modernization measures	Regeneration of water from waste (leachate)	–	Solvent (water) recovery from waste (filtrate)	–
Expected result of modernization measures	Reducing the specific indicator of production waste	–	Reducing the specific indicator of production waste	–
	Increasing the utilization of generated waste	–	Increasing the utilization of generated waste	–
	Further improvement of the environmental friendliness of the development	–	Further increase in efficiency and environmental friendliness	–

effective technological solutions have been developed for the production of tetramethylthiuram disulfide (K_1 = 0.11 << 1), *N*-cyclohexyl-2-benzothiazolylsulfenamide (K_1 = 0.06 << 1) and *N*-phenyl-2-naphthylamine (K_1 = 0.17 << 1). The maximally efficient use of raw materials and purification of emissions and discharges is achieved by implementing the technologies for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide (K_2 = 0.39 < 1) and *N*-phenyl-2-naphthylamine (K_1 = 0.73 < 1). The achieved levels of manufacturability (K_1) and environmental friendliness (K_2) provide a high level of efficiency and compliance with BAT principles for the production of tetramethylthiuram disulfide (I = 1.04 << 2), *N*-cyclohexyl-2-benzothiazolylsulfenamide (I = 0.45 << 2) and *N*-phenyl-2-naphthylamine (I = 0.9 << 2).

The developed new technology for the production of diisopropyl xanthogen disulfide is characterized by the levels of manufacturability (K_1 = 0.98 ≈ 1) and environmental friendliness (K_2 = 0.99 ≈ 1) comparable with the alternative option. The efficiency of the developed technological solutions is also comparable with the efficiency of the alternative (I = 1.97). Nevertheless, compliance with the development efficiency criterion (I = 1.97 < 2) supports the conclusion that the new technology offers some advantage in terms of achieved resource saving and environmental protection in accordance with BAT principles.

A possible direction for the modernization of this development consists in the search for new technological solutions for the recovery of a solvent (water) from waste (filtrate), which will increase its efficiency and environmental friendliness by reducing the specific indicator of waste production and enhancing the utility of generated wastes.

CONCLUSIONS

The introduction of modern low-tonnage chemical production technologies on an industrial scale is a complex system task, whose successful solution is ensured by the achievement of high levels of efficiency, safety and quality of development. Decisions on the prospects for industrial implementation of possible new technologies should be made based on the results of their analysis according to criteria for determining the result achieved during implementation, as well as compliance with regulatory and legislative requirements. An objective assessment must have a scientific methodological basis that takes technological, economic and environmental factors into account, as well as an algorithm for evaluating achieved indicators, comparing them with the target ones, and drawing a conclusion about the level of development.

To assess the compliance of new technologies with modern environmental requirements, we have developed a "Methodology for the quantitative assessment of new technologies for the production of organic substances in accordance with BAT principles," which is used in the development process to make decisions on resource saving and waste reduction.

On the example of low-tonnage technologies for the production of tetramethylthiuram disulfide, *N*-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthogen disulfide and *N*-phenyl-2-naphthylamine created at *GosNIIOKhT*, the quantitative assessment of new technologies based on the calculation of comprehensive indicators of comparison with alternative technologies by technological (quantity waste, emissions and discharges) and environmental indicators (the degree of use of raw materials and waste and the effectiveness of measures to clean up gas emissions and discharges into water bodies) is shown to be useful for assessing the compliance of new technologies with BAT principles, as well as determining the directions for modernizing existing industries.

The developed "Methodology for a comprehensive assessment of possible technological solutions according to the criteria of economic and environmental efficiency," along with the "Methodology for the quantitative assessment of new technologies for the production of materials in accordance with BAT principles" allowed us to create a methodological basis for use at the stage of making basic technological decisions on the introduced production method to ensure a high level of economic and environmental efficiency, as well as fulfilling legal requirements for technologies used in the field of environmental safety for achieving environmental protection objectives.

Authors' contributions

N.A. Kostikova – development and industrial implementation of technologies for the production of tetramethylthiuram disulfide, *N*-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthohen disulfide, and *N*-phenyl-2-naphthylamine; development of the "Methodology for the quantitative assessment of new technologies for the production of organic substances in accordance with BAT principles," approbation of this technique, and the comparative evaluation of developed and alternative (previously implemented in the USSR) technologies by the level of environmental impact.

E.N. Glukhan – formation of the scientific concept of quantitative assessment of new technologies in accordance with BAT principles, development of "Methodology for the quantitative assessment of new technologies for the production of organic substances in accordance with BAT principles."

P.V. Kazakov – development of technology for obtaining tetramethylthiuram disulfide, industrial introduction of technologies for obtaining tetramethylthiuram disulfide, *N*-cyclohexyl-2-benzothiazolylsulfenamide, diisopropyl xanthohen disulfide, and *N*-phenyl-2-naphthylamine.

M.M. Antonova – development and industrial implementation of technologies for the production of diisopropyl xanthohen disulfide and *N*-phenyl-2-naphthylamine.

D.I. Klimov – development and industrial implementation of technologies for the production of *N*-cyclohexyl-2-benzothiazolylsulfenamide and *N*-phenyl-2-naphthylamine.

The authors declare no conflicts of interest.

REFERANCES

1. Bondarenko V.I., Eremenko O.V., Tret'yakova Yu.V. Algorithm for choosing the best available technology. *Tonk. Khim. Tekhnol*. = *Fine Chem. Technol*. 2011;6(4):113–115 (in Russ.).

2. Erusheva K.I., Kolybanov K.Yu., Tishaeva I.R. Functional modeling of the process of choosing the best available technique. *Tonk. Khim. Tekhnol*. = *Fine Chem. Technol*. 2017;12(4):98–105 (in Russ.). https://doi.org/10.32362/2410-6593-2017-12-4-98-105

3. Panova S.A., Tishaeva I.R. System model for identification of best available technology (BAT). *Tonk. Khim. Tekhnol*. = *Fine Chem. Technol*. 2014;9(5):83–85 (in Russ.).

4. Glukhan E.N., Kostikova N.A. Methodology for assessment of new technologies for of organic substances production according to the best available technologies principles. *Khimiya i tekhnologiya organicheskikh veshchestv* = *Chemistry and Technology of Organic Substance*. 2018;2(6):36–42 (in Russ.). https://doi.org/10.54468/25876724_2018_2_36

5. Kostikova N.A., Glukhan E.N. Methodology of quantitative assessment of new technologies for the production of organic substances in accordance with the criteria of economic and environmental efficiency. *Khimiya i tekhnologiya organicheskikh veshchestv* = *Chemistry and Technology of Organic Substances*. 2021;4(20):54–63 (in Russ.). https://doi.org/10.54468/25876724_2021_4_54

6. Zinina E.A., Kostikova N.A., Kondratenko S.M., Sazonova Z.G. High-efficient method of tetramethylthiuramdisulfide production. *Khimiya i tekhnologiya organicheskikh veshchestv* = *Chemistry and Technology of Organic Substances*. 2017;3(3):20–29 (in Russ.). https://doi.org/10.54468/25876724_2017_3_20

7. Gorbunov B.N., Gurevich Ya.A., Maslova I.P. *Khimiya i tekhnologiya stabilizatorov polimernykh materialov* = *Chemistry and Technology of Stabilizers of Polymeric Materials*. Moscow: Khimiya; 1981. 368 p. (in Russ.).

8. Blokh G.A. *Organicheskie uskoriteli vulkanizatsii kauchukov.* In: Zakharchenko P.I. (Ed.). *Organic Rubber Vulcanization Accelerators*. Moscow-Leningrad: Khimiya; 1964. P. 43–44 (in Russ.).

9. Gurvich Ya.A. *Spravochnik molodogo apparatchika-khimika* (*Handbook of a Young Apparatchik-Chemist*). Moscow: Khimiya; 1991. 253 p. 197 (in Russ.).

10. Sazonova Z.G., Shchekina M.P., Kostikova N.A., Golikov A.G. Low-waste method of *N*-cyclohexyl-2-benzothiazolesulfenamide obtaining. *Khimiya i tekhnologiya organicheskikh veshchestv* = *Chemistry and Technology of Organic Substances*. 2018;1(5):27–34 (in Russ.). https://doi.org/10.54468/25876724_2018_1_27

11. Rozina E.A., Anokhina D.I., Romanova P.S., Dmitriev K.V., Mukanin V.M., Kuderskii O.V. *Method of Obtaining N-cyclohexyl-2-benzthiazolylsulfenamide*: USSR Inventor's Certificate No. 271524. Publ. 26.05.1970 (in Russ.).

12. Kondrat'ev V.B., Golikov A.G., Kostikova N.A., Antonova M.M., Kondratenko S.M., Korneeva O.I. *The method for obtaining diisopropylxanthogendisulfide*: RF Pat. RU 2713402. Publ. 05.02.2020.

13. Antonova M.M., Kondratenko S.M., Kostikova N.A., Korneeva O.I., Shibkov O.O., Cherenkov M.A., Klimov D.I., Prikhod'ko V.V. Development of a production method isopropyl potassium xanthate, promising for industrial implementation. *Khimiya i tekhnologiya organicheskikh veshchestv* = *Chemistry and Technology of Organic Substances*. 2021;3(19):14–26 (in Russ.). https://doi.org/10.54468/25876724_2021_3_14

СПИСОК ЛИТЕРАТУРЫ

1. Бондаренко В.И., Ерёменко О.В., Третьякова Ю.В. Алгоритм выбора наилучшей доступной технологии. *Тонкие химические технологии*. 2011;6(4):113–115.

2. Ерушева К.И., Колыбанов К.Ю., Тишаева И.Р. Функциональное моделирование процесса выбора наилучшей доступной технологии. *Тонкие химические технологии*. 2017;12(4):98–105. https://doi.org/10.32362/2410-6593-2017-12-4-98-105

3. Панова С.А., Тишаева И.Р. Системная модель наилучшей доступной технологии. *Тонкие химические технологии*. 2014;9(5):83–85.

4. Глухан Е.Н., Костикова Н.А. Методика количественной оценки новых технологий производства органических веществ в соответствии с принципами наилучших доступных технологий. *Химия и технология органических веществ*. 2018;2(6):36–42. https://doi.org/10.54468/25876724_2018_2_36

5. Костикова Н.А., Глухан Е.Н. Методика количественной оценки новых технологий производства органических веществ в соответствии с критериями экономической и экологической эффективности. *Химия и технология органических веществ*. 2021;4(20):54–63. https://doi.org/10.54468/25876724_2021_4_54

6. Зинина Е.А., Костикова Н.А., Кондратенко С.М., Сазонова З.Г. Высокоэффективный способ получения тетраметилтиурамдисульфида. *Химия и технология органических веществ*. 2017;3(3):20–29. https://doi.org/10.54468/25876724_2017_3_20

7. Горбунов Б.Н., Гуревич Я.А., Маслова И.П. *Химия и технология стабилизаторов полимерных материалов*. М.: Химия; 1981. 368 с.

8. Блох Г.А. *Органические ускорители вулканизации каучуков*; под ред. П.И. Захарченко. М.-Л.: Химия; 1964. С. 43–44.

9. Гурвич Я.А. *Справочник молодого аппаратчика-химика*. М.: Химия; 1991: 253 с.

10. Сазонова З.Г., Щекина М.П., Костикова Н.А., Голиков А.Г. Малоотходный способ получения *N*-циклогексил-2-бензотиазолсульфенамида. *Химия и технология органических веществ*. 2018;1(5):27–34. https://doi.org/10.54468/25876724_2018_1_27

11. Розина Е.А., Анохина Д.И., Романова П.С., Дмитриев К.В., Муканин В.М., Кудерский О.В. *Способ получения N-циклогексил-2-бензтиазолилсульфенамида*: А.С. СССР № 271524. заявка № 1297876/23-4; заявл. 14.01.1969; опубл. 26.05.1970.

12. Кондратьев В.Б., Голиков А.Г., Костикова Н.А., Антонова М.М., Кондратенко С.М., Корнеева О.И. *Способ получения диизопропилксантогендисульфида*: Пат. RU 2713402. заявка № 2019135649, заявл. 07.11.2019, опубл. 05.02.2020.

13. Антонова М.М., Кондратенко С.М., Костикова Н.А., Корнеева О.И., Шибков О.О., Черенков М.А., Климов Д.И., Приходько В.В. Разработка способа получения изопропилового ксантогената калия, перспективного для промышленной реализации. *Химия и технология органических веществ*. 2021;3(19):14–26. https://doi.org/10.54468/25876724_2021_3_14

14. Антонова М.М., Кондратенко С.М., Костикова Н.А., Корнеева О.И., Шибков О.О., Черенков М.А., Климов Д.И., Приходько В.В. Новый способ получения диизопропилксантогендисульфида с использованием перекиси водорода в качестве окислителя. *Химическая промышленность сегодня*. 2022;(1):26–35. https://doi.org/10.53884/27132854_2022_1_26

14. Antonova M.M., Kondratenko S.M., Kostikova N.A., Korneeva O.I., Shibkov O.O., Cherenkov M.A., Klimov D.I., Prikhod'ko V.V. A new method for the production of diisopropylxanthogen disulfide using hydrogen peroxide as an oxidant. *Khimicheskaya promyshlennost' segodnya = Chemical Industry Developments*. 2022;(1):26–35 (in Russ.). https://doi.org/10.53884/27132854_2022_1_26

15. Cambron A., Whitby G.S. The oxidation of xanthates and some new dialkyl sulphur- and disulphur-dicarbothionates. *Canadian Journal of Research*. 1930;2(2):144–152. https://doi.org/10.1139/cjr30-011

16. Kondrat'ev V.B., Golikov A.G., Kazakov P.V., Kostikova N.A., Klimov D.I., Antonova M.M. *The method for obtaining N-phenyl-2-naphthylamine*: RF Pat. RU2676692 S1. Publ. 10.01.2019 (in Russ.).

17. Antonova M.M., Kostikova N.A., Golikov A.G., Klimov D.I. Highly efficient method of producing neozone D. *Khimiya i tekhnologiya organicheskikh veshchestv = Chemistry and Technology of Organic Substances.* 2018;1(5):9–18 (in Russ.). https://doi.org/10.54468/25876724_2018_1_9

18. Klimov D.I., Kostikova N.A., Kaabak L.V., Shibkov O.O., Cherenkov M.A., Pyzh'yanov I.V. Research of acid catalysis mechanism of the reaction of obtaining *N*-phenyl-2-naphthylamine from 2-naphthol and aniline. *Khimiya i tekhnologiya organicheskikh veshchestv = Chemistry and Technology of Organic Substances*. 2020;2(14):69–89 (in Russ.). https://doi.org/10.54468/25876724_2020_2_69

19. Magergut V.Z., Maslennikov I.M., Stal'nov P.I., Sanaev V.S., Dorokhin P.N., Korshakov M.K., Druzhbin N.N. *Method for Producing Neozone D*: USSR Inventor's Certificate No. 781201. Publ. 23.11.1980 (in Russ.).

15. Cambron A., Whitby G.S. The oxidation of xanthates and some new dialkyl sulphur- and disulphur-dicarbothionates. *Canadian Journal of Research*. 1930;2(2):144–152. https://doi.org/10.1139/cjr30-011

16. Кондратьев В.Б., Голиков А.Г., Казаков П.В., Костикова Н.А., Климов Д.И., Антонова М.М. *Способ получения N-фенил-2-нафтиламина*: Пат. RU 2676692 C1. заявка № 2018128083; заявл. 01.08.2018, опубл. 10.01.2019.

17. Антонова М.М., Костикова Н.А., Голиков А.Г., Климов Д.И. Высокоэффективный способ получения неозона Д. *Химия и технология органических веществ*. 2018;1(5):9–18.https://doi.org/10.54468/25876724_2018_1_9

18. Климов Д.И., Костикова Н.А., Каабак Л.В., Шибков О.О., Черенков М.А., Пыжьянов И.В. Исследование механизма кислотного катализа реакции получения *N*-фенил-2-нафтиламина из анилина и 2-нафтола. *Химия и технология органических веществ*. 2020;2(14):69–89. https://doi.org/10.54468/25876724_2020_2_69

19. Магергут В.З., Масленников И.М., Стальнов П.И., Санаев В.С., Дорохин П.Н., Коршаков М.К., Дружбин Н.Н. *Способ получения неозона Д*: А.С. СССР № 781201. заявка № 2677374/23-04; заявл. 09.10.78; опубл. 23.11.1980.

About the authors:

Natalya A. Kostikova, Cand. Sci. (Eng.), Associate Professor, Head of Department, State Research Institute of Organic Chemistry and Technology (GosNIIOKhT), State Scientific Center of the Russian Federation (23, sh. Entuziastov, Moscow, 111024, Russia). E-mail: kutkin@gosniiokht.ru. RSCI SPIN-code 1540-8520, https://orcid.org/0000-0001-8796-124X

Elena N. Glukhan, Dr. Sci. (Eng.), Assistant Professor, Adviser to the Director-General, State Research Institute of Organic Chemistry and Technology (GosNIIOKhT), State Scientific Center of the Russian Federation (23, sh. Entuziastov, Moscow, 111024, Russia). E-mail: dir@gosniiokht.ru. Scopus Author ID 8706397600, RSCI SPIN-code 6274-1908, https://orcid.org/0000-0002-2369-5648

Pavel V. Kazakov, Dr. Sci. (Chem.), Assistant Professor, Deputy General Director, State Research Institute of Organic Chemistry and Technology (GosNIIOKhT), State Scientific Center of the Russian Federation (23, sh. Entuziastov, Moscow, 111024, Russia). E-mail: kutkin@gosniiokht.ru. RSCI SPIN-code 1920-2930, https://orcid.org/0000-0001-8164-274X

Mariya M. Antonova, Cand. Sci. (Eng.), Head of the Research Department, State Research Institute of Organic Chemistry and Technology (GosNIIOKhT), State Scientific Center of the Russian Federation (23, sh. Entuziastov, Moscow, 111024, Russia). E-mail: kutkin@gosniiokht.ru. Scopus Author ID 56165662600, RSCI SPIN-code 4136-5290, https://orcid.org/0000-0001-6492-2483

Dmitry I. Klimov, Cand. Sci. (Eng.), Head of Sector, State Research Institute of Organic Chemistry and Technology (GosNIIOKhT), State Scientific Center of the Russian Federation (23, sh. Entuziastov, Moscow, 111024, Russia). E-mail: kutkin@gosniiokht.ru. RSCI SPIN-code 7113-2691, https://orcid.org/0000-0002-0649-1440

Об авторах:

Костикова Наталья Алексеевна, к.х.н., начальник отдела, ФГУП «Государственный научно-исследовательский институт органической химии и технологии» (ФГУП «ГосНИИОХТ»), Государственный научный центр Российской Федерации (111024, Россия, Москва, шоссе Энтузиастов, 23). E-mail: kutkin@gosniiokht.ru. SPIN-код РИНЦ 1540-8520, https://orcid.org/0000-0001-8796-124X

Глухан Елена Николаевна, д.т.н., доцент, советник генерального директора, ФГУП «Государственный научно-исследовательский институт органической химии и технологии» (ФГУП «ГосНИИОХТ»), Государственный научный центр Российской Федерации (111024, Россия, Москва, шоссе Энтузиастов, 23). E-mail: dir@gosniiokht.ru. Scopus Author ID 8706397600, SPIN-код РИНЦ 6274-1908, https://orcid.org/0000-0002-2369-5648

Казаков Павел Васильевич, д.х.н., доцент, заместитель генерального директора, ФГУП «Государственный научно-исследовательский институт органической химии и технологии» (ФГУП «ГосНИИОХТ»), Государственный научный центр Российской Федерации (111024, Россия, Москва, шоссе Энтузиастов, 23). E-mail: kutkin@gosniiokht.ru. SPIN-код РИНЦ 1920-2930, https://orcid.org/0000-0001-8164-274X

Антонова Мария Михайловна, к.х.н., начальник научно-исследовательского отделения, ФГУП «Государственный научно-исследовательский институт органической химии и технологии» (ФГУП «ГосНИИОХТ»), Государственный научный центр Российской Федерации (111024, Россия, Москва, шоссе Энтузиастов, 23). E-mail: kutkin@gosniiokht.ru. Scopus Author ID 56165662600, SPIN-код РИНЦ 4136-5290, https://orcid.org/0000-0001-6492-2483

Климов Дмитрий Игоревич, к.х.н., начальник сектора, ФГУП «Государственный научно-исследовательский институт органической химии и технологии» (ФГУП «ГосНИИОХТ»), Государственный научный центр Российской Федерации (111024, Россия, Москва, шоссе Энтузиастов, 23). E-mail: kutkin@gosniiokht.ru. SPIN-код РИНЦ 7113-2691, https://orcid.org/0000-0002-0649-1440

The article was submitted: November 14, 2022; approved after reviewing: February 20, 2023; accepted for publication: June 20, 2023.

Translated from Russian into English by H. Moshkov
Edited for English language and spelling by Thomas A. Beavitt