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RESEARCH ARTICLE

Hydroperoxide method for the co-production of methyl ethyl ketone and phenol

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Abstract

Objectives. Applying the hydroperoxide method for the co-production of methyl ethyl ketone and phenol, the work studies the kinetic and other characteristics of the individual stages of the developed process to select the optimal conditions for producing the maximum yield of intermediate and target products.

Methods. The research relied on the main theoretical and methodological provisions for the synthesis of intermediate and target products of the cumene technology for the co-production of phenol and acetone. The obtained intermediate and target products were qualitatively and quantitatively analyzed according to modern physicochemical approaches. Gas–liquid chromatography was performed with a Chromatec-Crystal 5000.2 hardware and software complex. The infrared (IR) spectra of the synthesized compounds were recorded with a Spectrum RX-1 IR Fourier spectrometer. ^{1}H nuclear magnetic resonance (NMR) spectroscopy of substances was conducted using a Bruker DRX 400 NMR spectrometer. A quantitative determination of the content of *sec*-butylbenzene hydroperoxide was carried out using iodometric titration.

Results. The main stages of the developed method for the co-production of methyl ethyl ketone and phenol based on the hydroperoxide oxidation of *sec*-butylbenzene were investigated. *sec*-Butylbenzene was synthesized by alkylation of benzene with 1-butanol in the presence of concentrated sulfuric acid at a yield of about 82%. The hydrocarbon compound was subjected to aerobic liquid-phase oxidation catalyzed by *N*-hydroxyphthalimide to the corresponding hydroperoxide with a main substance content of 30–35 wt %, feedstock conversion of 34–37%, and selectivity of hydroperoxide formation above 95%. The kinetic and other characteristics were studied for the final stage of the developed method, comprising the acid decomposition of hydroperoxide to methyl ethyl ketone and phenol. Suitable conditions for obtaining target products with high yields were identified.

Conclusions. Methyl ethyl ketone and phenol of high purity with yields of 72 and 74%, respectively, were obtained by the hydroperoxide method. The structures of the synthesized substances were confirmed by IR and ^{1}H NMR spectroscopy.

Keywords

methyl ethyl ketone, phenol, *sec*-butylbenzene, hydroperoxide, alkylation, aerobic liquid-phase oxidation, *N*-hydroxyphthalimide, acid decomposition

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НАУЧНАЯ СТАТЬЯ

Гидропероксидный способ совместного получения метилэтилкетона и фенола

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Аннотация

Цели. Разработка научных и прикладных основ химии и технологии гидропероксидного способа совместного получения метилэтилкетона и фенола. Исследование закономерностей протекания отдельных стадий разрабатываемого процесса и подбор условий, обеспечивающих максимальный выход промежуточных и целевых продуктов.

Методы. Методологию исследования составили основные положения о способах синтеза промежуточных и целевых продуктов кумольной технологии получения фенола совместно с ацетоном. Качественный и количественный анализ полученных промежуточных и целевых продуктов осуществлялся с применением современных физико-химических методов анализа. Газожидкостная хроматография проводилась на аппаратно-программном комплексе Хроматэк-Кристалл 5000.2. Инфракрасные (ИК) спектры синтезируемых соединений были записаны на приборе ИК Фурье Spectrum RX-1, анализ веществ методом спектроскопии ядерного магнитного резонанса (ЯМР) ^{1}H был проведен с помощью ЯМР-спектрометра Bruker DRX 400. Количественное определение содержания гидропероксида *втор*-бутилбензола проводилось с использованием йодометрического титрования.

Результаты. Исследованы основные стадии разрабатываемого способа совместного получения метилэтилкетона и фенола на основе гидропероксидного окисления *втор*-бутилбензола. Алкилированием бензола бутанолом-1 в присутствии концентрированной серной кислоты синтезирован *втор*-бутилбензол с выходом около 82%. Данный углеводород подвергнут аэробному жидкофазному окислению, катализируемому *N*-гидроксифталимидом, до соответствующего гидропероксида с содержанием основного вещества 30–35 мас. % при конверсии исходного сырья 34–37% и селективности образования гидропероксида выше 95%. Исследованы закономерности протекания заключительной стадии разрабатываемого метода — кислотного разложения гидропероксида до метилэтилкетона и фенола. Определены условия, позволяющие получать целевые продукты с высокими выходами.

Выводы. Гидропероксидным способом получены метилэтилкетон и фенол высокой степени чистоты с выходами 72 и 74% соответственно. Структуры синтезированных веществ подтверждены методами ИК- и ^{1}H ЯМР-спектроскопии.

Ключевые слова

метилэтилкетон, фенол, *втор*-бутилбензол, гидропероксид, алкилирование, аэробное жидкофазное окисление, *N*-гидроксифталимид, кислотное разложение

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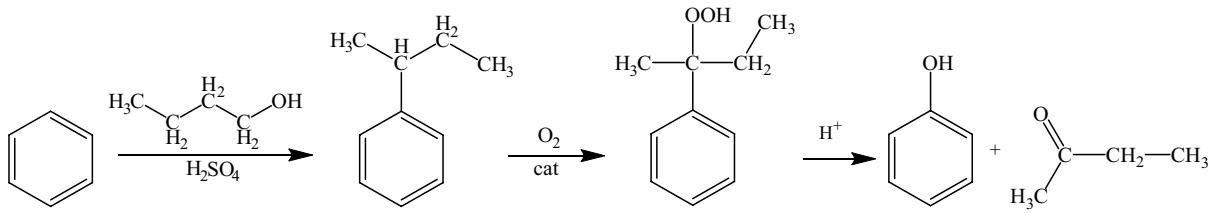
INTRODUCTION

Methyl ethyl ketone (MEK) is a basic large-tonnage organic synthesis product widely used in the production of polymers and paints and varnishes [1]. In industry, MEK is widely known as an effective solvent for many substances and materials, such as printing inks and epoxy resins [2]. MEK is also used in the production of glue, magnetic tapes, artificial leather, smokeless powders, and rubber antioxidants [3–5]. In fine organic synthesis, MEK is used as a feedstock for the production of a number of monomers for acrylic glass [4].

In industry, MEK is obtained by several methods, including catalytic oxidation of 2-butanol by silver on a zeolite support [6, 7] and dehydrogenation of butyl alcohol in the presence of zinc copper catalysts [8, 9]. These MEK production processes are characterized by temperatures of about 500°C and the presence of expensive and low-stable catalysts. There are also methods for producing MEK from butylene fractions, e.g., involving the direct oxidation of *n*-butylenes [4, 10], where the catalyst is an aqueous solution of a complex of palladium(II) and Mo-V-phosphoric heteropoly acid (HPA) of the general composition $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA–x, $2 \le x \le 6$).

In the present work, an alternative hydroperoxide method is proposed for the co-production of MEK and phenol, an important petrochemical monomer used



Scheme. Hydroperoxide method for the synthesis of methyl ethyl ketone and phenol

in the production of plastics, fibers, dyes, cosmetics, and medicines [11, 12]. The proposed method is based on the cumene technology for the production of phenol and acetone. Although highly efficient, this technology has the main disadvantage that it produces excess amounts of acetone, which is not a highly demanded product in the chemical market [13].

The developed method includes the stages of synthesis of the initial *sec*-butylbenzene (*sec*-BB) by alkylation of benzene with 1-butanol in the presence of concentrated sulfuric acid, aerobic liquid-phase oxidation of this hydrocarbon to its hydroperoxide (HP) using an effective organic catalyst—*N*-hydroxyphthalimide (*N*-HPI), and acidic decomposition of *sec*-BB HP into target products according to the following scheme:

In this paper, the kinetic and other characteristics of these stages were studied.

MATERIALS AND METHODS

The following reagents were used in the study: benzene (chemical purity grade, GOST 5955-75[1], *EKOS-1*, Russia), 1-butanol (chemical purity grade, GOST 6006-78[2], *EKOS-1*, Russia), sulfuric acid (chemical purity grade, GOST 4204-771[3], *Sigma-Tek*, Russia), sodium hydroxide (analytical purity grade, GOST 4328-77[4], *Komponent-Reaktiv*, Russia), calcium chloride (analytical purity grade, GOST 450-77[5], *Mosreaktiv*, Russia), compressed oxygen (chemical purity grade, GOST 5583-78[6]), *N*-hydroxyphthalimide (*Sisco Research Laboratories*, India), acetic acid (chemical purity grade, GOST 61-75[7], *Spektr Khim*, Russia), potassium iodide (chemical purity grade, GOST 4232-74[8], *Spektr Khim*, Russia), and sodium thiosulfate (analytical purity grade, GOST 27068-86[9], *Uralkhiminvest*, Russia).

Qualitative and quantitative analysis of the synthesized intermediate and target products was carried out using contemporary physicochemical analysis methods. The contents of the synthesized compounds were determined by gas–liquid chromatography with a Chromatec-Crystall 5000.2 hardware and software complex (*Chromatec*, Russia). The obtained compounds were identified by infrared (IR) spectroscopy and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. IR spectra were recorded with a Spectrum RX-1 Fourier-transform IR spectrometer (*PerkinElmer*, USA, 4000–400 cm^{-1}, KBr glass). The IR spectra were mathematically processed using the Spektrum v.5.0.1 software. ^{1}H NMR spectroscopy was performed using a Bruker DRX 400 NMR spectrometer (400.4 MHz). The solvent was a dimethyl sulfoxide d_6–CCl_4 mixture, while the internal standard was tetramethylsilane.

The content of *sec*-BB HP in the oxidation products of *sec*-BB, as well as during the process of acid decomposition of HP, was determined by iodometric titration [14].

EXPERIMENTAL

Sulfuric acid alkylation of benzene with 1-butanol was carried out in a round-bottomed three-necked flask equipped with a thermometer and immersed in a water

1 GOST 5955-75. State Standard of the USSR. Reagents. Benzene. Specifications. Moscow: Izdatelstvo standartov; 1994 (in Russ.).

2 GOST 6006-78. State Standard of the USSR. Reagents. 1-Butanol. Specifications. Moscow: IPK Izdatelstvo standartov; 1998 (in Russ.).

3 GOST 4204-77. State Standard of the USSR. Reagents. Sulphuric acid. Specifications. Moscow: Standartinform; 2006 (in Russ.).

4 GOST 4328-77. Interstate Standard. Reagents. Sodium hydroxide. Specifications. Moscow: IPK Izdatelstvo standartov; 1978 (in Russ.).

5 GOST 450-77. State Standard of the USSR. Reagents. Calcium chloride. Specifications. Moscow: IPK Izdatelstvo standartov; 1997 (in Russ.).

6 GOST 5583-78. Interstate Standard. Technical and medical oxygen gas Specifications. Moscow: Standartinform; 2005 (in Russ.).

7 GOST 61-75. Interstate Standard. Reagents. Acetic acid. Specifications. Moscow: Standartinform; 2006 (in Russ.).

8 GOST 4232-74. Interstate Standard.Reagents. Potassium iodide. Specifications. Moscow: Standartinform; 2006 (in Russ.).

9 GOST 27068-86. Interstate Standard. Reagents. Sodium thiosulphate, 5-aqueous. Specifications. Moscow: IPK Izdatelstvo standartov; 1998 (in Russ.).

bath at a given molar ratio of reagents, temperature, and reaction time with continuous stirring of the reaction mass according to the procedure described in [15]. The target product was isolated from the reaction mass by vacuum distillation at a temperature of 85–87°C and a residual pressure of 15–30 mm Hg.

Aerobic liquid-phase oxidation of *sec*-BB was performed in a glass continuous stirred tank reactor at atmospheric pressure with continuous oxygen supply according to a published procedure [16]. Upon completion of the reaction, the oxidized reaction mixture was cooled to room temperature, separated by filtration from the precipitated catalyst (*N*-HPI), and analyzed for *sec*-BB HP content by iodometric titration.

The obtained *sec*-BB HP was concentrated by extraction with a 75% ethyl alcohol solution in a flask with a reflux condenser with continuous vigorous stirring at a temperature of 20–23°C for 1 h until complete phase separation of the reaction mass. Water and alcohol were separated from the extract by vacuum distillation at a temperature of 20–23°C and a residual pressure of 15–30 mm Hg, thereby obtaining the concentrated HP.

Acid decomposition of *sec*-BB HP was performed in a thermostated glass reactor according to a published procedure [17]. The process was conducted at a given temperature with continuous stirring. The progress of the reaction was monitored by the consumption of *sec*-BB HP by taking samples for analysis every 10 min from the start of the reaction. MEK was isolated from the reaction mass by vacuum distillation at a temperature of 36–40°C and residual pressure of 15–20 mm Hg; phenol was isolated by extraction with a 10% aqueous solution of ethanol, followed by evaporation of water and alcohol from the so-called alcohol–phenol layer formed during separation of the mixture.

The characteristics of the synthesized intermediate and target products are presented below.

***sec*-BB.** Yield on the basis of loaded alcohol is 82%. Content of the main substance is 99.3%. IR spectrum, cm^{-1}: 3083, 3063, 3028 (ν C–H_{arom}); 2961, 2875 (ν CH_3); 2929, 2859 (ν CH_2); 1603, 1493 (ν C=C_{arom}); 1451 (δ CH_2); 1378 (δ CH_3); 758, 697 (monosubstitution in aromatic ring). ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.75 t (3H, CH_3), 1.17 d (3H, CH_3), 1.57 m (2H, CH_2), 2.55 m (1H, CH), 7.16 m (3H, CH_{arom}), 7.27 m (2H, CH_{arom}).

***sec*-BB HP.** The content of the main substance is 95%. IR spectrum, cm^{-1}: 3401 (ν O–OH); 2973 (ν CH_3); 2939 (ν CH_2); 1601, 1496 (aromatic ring); 1447 (δ CH_2), 1372 (δ CH_3), 758 and 698 (monosubstitution in the benzene ring).

MEK. Yield on the basis of loaded *sec*-BB HP is 72%. IR spectrum, cm^{-1}: 2980 (ν CH_2); 2941 (ν CH_3); 1709 (ν C=O); 1365 (δ CH_2). ^{1}H NMR (400 MHz), δ, ppm: 2.43 (q, 2H), 2.06 (s, 3H), 0.90 (t, 3H).

Phenol. Yield on the basis of loaded *sec*-BB HP is 74%. IR spectrum, cm^{-1}: 3221 (ν O–H); 3050–3020 (ν C–H_{arom}); 1594, 1473 (ν C–C_{arom}). ^{1}H NMR (400 MHz), δ, ppm: 9.33 (s, 1H), 7.15 (t, 2H), 6.80–6.72 (m, 3H).

RESULTS AND DISCUSSION

Several methods for obtaining *sec*-BB using unsaturated hydrocarbons are described in the scientific and technical literature [18, 19]. However, their main disadvantage is a relatively low yield of the target product (40–60%). An alternative method for synthesizing *sec*-BB is alkylation of benzene with 1-butanol. This method is attractive due to the possibility of performing it under laboratory conditions. Since we found almost no information on this reaction in the literature, we conducted a series of studies aimed at exploring the effect of some parameters on the formation of *sec*-BB by alkylation of benzene with 1-butanol. In terms of the initial conditions, a molar reagent ratio of benzene : 1-butanol : sulfuric acid = 3 : 1 : 3 was selected. The process temperature

Table 1. Effect of temperature and reaction duration on the formation of *sec*-butylbenzene (*sec*-BB) by alkylation of benzene with 1-butanol. The benzene : 1-butanol : sulfuric acid molar ratio is 3 : 1 : 3

Temperature, °C	Reaction duration, h	Yield of *sec*-BB on the basis of loaded alcohol, %	Conversion of benzene, %
50	2	21.6	7.4
	4	30.7	11.1
60	2	48.9	16.5
	4	54.7	18.4
70	2	75.1	25.2
	4	81.7	28.8

Table 2. Material balance of alkylation of benzene with 1-butanol. The molar ratio of benzene : 1-butanol : sulfuric acid is 3 : 1 : 3. The temperature is 70°C. The reaction duration is 4 h

Substance	Molar mass, g/mol	Loaded		Obtained	
		g	wt %	g	wt %
Benzene	78.1	175.8	38.9	125.1	27.7
1-Butanol	74.1	55.6	12.3	5.0	1.1
H_2SO_4*	98.1	220.7	48.8	230.8	51.1
sec-BB	134.2	0.0	0.0	82.3	18.2
Byproducts	–	0.0	0.0	6.4	1.4
Losses	–	0.0	0.0	2.5	0.5
Total	–	452.1	100.0	452.1	100.0

* Mass of the acid layer containing the water formed during the reaction.

was varied from 50 to 70°C, and the reaction duration was 2–4 h. Table 1 presents the results of studying the effect of these parameters on the formation of *sec*-BB.

Table 1 shows that an increase in temperature and reaction duration promotes an increase in the conversion of benzene and the yield of the target *sec*-BB. It was found that the benzene alkylation with butyl alcohol at 50°C gives an extremely low yield of the target product (no more than 30% on the basis of loaded alcohol). A higher yield of *sec*-BB can be achieved by performing the reaction at 70°C for 4 h. These optimal conditions provide a high yield of *sec*-BB of about 82%. Carrying out the reaction at higher temperatures or for a longer time leads to the formation of an increased content of disubstituted *sec*-BB in the reaction mass, which is a byproduct in the developed technology.

Based on the results of the scaled-up synthesis of *sec*-BB under the selected conditions, the material balance was calculated (Table 2).

The target product was isolated by vacuum distillation at a yield of around 82% on the basis of loaded 1-butanol at a conversion of benzene of about 29%. The characteristics of the compound are presented in the experimental part of this work.

The key stage of the developed method for the co-production of MEK and phenol is the oxidation of the obtained *sec*-BB to its tertiary HP: it is the efficiency of this stage that determines the economy of the entire process. Initially, aerobic oxidation of *v*-BB was studied in the absence of any additives (the so-called autoxidation process). As the results showed, even at a high temperature of 140°C, only 2 wt % HP can be accumulated in 60 min of the reaction (Fig. 2, curve *1*), making this method unacceptable for further studies.

A method for the joint aerobic oxidation of *sec*-BB and isopropylbenzene was proposed [20], where the resulting isopropylbenzene hydroperoxide acts as an oxidation initiator. It was found that the rate of *sec*-BB oxidation in such a process is about 1.7 wt %/h with a conversion of *sec*-BB of about 15% and a selectivity for the formation of *sec*-BB HP of no more than 70%. In technological terms, such results are considered inefficient.

Therefore, an attempt was made to intensify the process under study. To achieve this goal, *N*-HPI was used as a catalyst. The advantages of using this compound include its nontoxicity, a relatively simple synthesis method based on available phthalic anhydride, and a high efficiency of *N*-HPI for various types of substrates [21, 22]. In addition, it was found that the use of *N*-HPI can significantly increase the conversion of the hydrocarbon being oxidized, as well as achieve high selectivity for the formation of the corresponding HP (over 90%) [21].

The work studied the effect of temperature and catalyst content on the oxidation of *sec*-BB to its HP. The process was carried out according to the method described in the experimental section at temperatures of 120–150°C and a catalyst content of 1–4 wt % of loaded *sec*-BB. The HP content in the oxidation products was determined by iodometric titration. The results obtained are presented in Figs. 1 and 2.

According to the obtained results, an increase in temperature favors the accumulation of HP in the reaction products. For example, in 40 min at a temperature

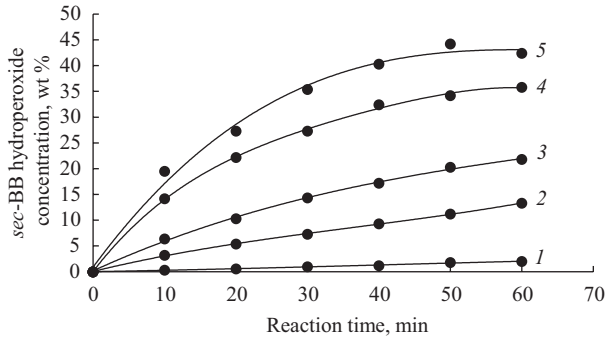


Fig. 1. Kinetics of aerobic liquid-phase oxidation of *sec*-BB to hydroperoxide at *N*-HPI concentrations of (*1*) 0.0 and (*2*)–(*5*) 2.0 wt % and temperatures of (*1*) 140, (*2*) 120, (*3*) 130, (*4*) 140, and (*5*) 150°C

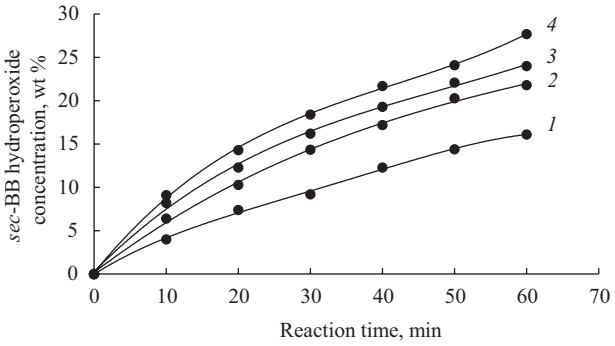


Fig. 2. Effect of the catalyst concentration on aerobic liquid-phase oxidation of *sec*-BB to hydroperoxide at a temperature of 130°C and catalyst concentrations of (*1*) 1.0, (*2*) 2.0, (*3*) 3.0, and (*4*) 4.0 wt %

of 130°C, it is possible to obtain *sec*-BB HP with a main substance content of about 17 wt %, a conversion of *sec*-BB of 18%, and a selectivity for the formation of HP of 97.2%. With an increase in temperature by only 10°C for the same 40 min, the content of *sec*-BB HP is increased to 32 wt % while maintaining the selectivity for its formation at a sufficiently high level (95.5%). A further increase in temperature leads to a sharp decrease in the selectivity for the formation of *sec*-BB HP, which can also reach 90%. This is caused by the predominance of the thermal decomposition of HP formed during the reaction, which leads to the formation of oxidation byproducts.

A study of the effect of the catalyst content on the oxidation of *sec*-BB showed that an increase in the catalyst concentration leads to an increase in the content of *sec*-BB HP. This can be clearly seen when increasing the concentration of *N*-HPI from 1.0 to 2.0 wt % (Fig. 2). Thus, at 130°C in 40 min of reaction in the presence of 1.0% *N*-HPI, it is possible to accumulate HP up to 17 wt %. Increasing the catalyst content by one percent leads to an increase in the oxidation rate of *v*-BB by a factor of 1.3. The use of the *N*-HPI catalyst in an amount of 3 wt % or more is not economically feasible, since an insignificant increase in the HP content is observed in the reaction products.

Thus, oxidation of *sec*-BB at a temperature of 130–140°C and a concentration of *N*-HPI catalyst of 2 wt % in 1 h of reaction can yield *sec*-BB HP with a content of 22 to 35 wt % and a selectivity of about 94–97%.

To ensure that it is the tertiary HP that is actually formed in the course of oxidative transformations of *sec*-BB, the obtained oxidized reaction mixture with a *sec*-BB HP content of 24 wt % was subjected to five-stage extraction. The 75% ethanol solution chosen as an extractant has a proven efficiency when used in processes of extraction and concentration of HP [12]. Table 3 presents the material balance of this process.

Vacuum distillation of the combined extract yielded 95% *sec*-BB *tert*-HP, whose structure was confirmed by IR spectroscopy. The main advantage of this process is the possibility to use isolated concentrated HP as an initiator of polymerization and aerobic oxidation.

The final stage of our work consisted in studying the characteristics of the acid decomposition of *sec*-BB HP to MEK and phenol. A series of experiments were carried out at temperatures of 40–70°C, an initial concentration

Table 3. Material balance of five-stage extraction of *sec*-BB HP from *sec*-BB oxidation products with 75% ethanol solution

Component	Molar mass, g/mol	Loaded		Obtained			
		g	wt %	Raffinate		Combined extract	
				g	wt %	g	wt %
sec-BB	134.1	78.9	18.7	78.0	99.7	0.0	0.0
sec-BB HP	166.1	13.9	3.3	0.2	0.3	13.5	4.0
Ethanol	46.1	260.0	61.5	0.0	0.0	259.0	75.8
Water	18.0	70.0	16.5	0.0	0.0	69.2	20.2
Losses	–	0.0	0.0	2.9			
Total	–	422.8	100.0	78.2	100.0	341.7	100.0

Table 4. Effect of temperature and concentrations of HP and catalyst on the acid-catalytic decomposition of *sec*-BB HP

Initial concentration of *sec*-BB HP, wt %	Concentration of H_2SO_4 catalyst, wt %	Temperature, °C	Initial reaction rate, mol/(L·min)	Conversion of HP, %	Yield on basis of reacted HP, %	
					Phenol	MEK
20	0.8	40	0.024	98.0	73	71
		50	0.054	98.5	74	72
		60	0.133	98.3	75	68
		70	0.239	99.5	73	66
10	0.8	50	0.034	99.0	36	29
15			0.038	98.7	70	69
20	1.0	50	0.067	99.5	78	70
	1.2		0.080	98.5	76	68
	1.4		0.110	97.5	75	64

of *sec*-BB HP of 10–20 wt %, and a content of sulfuric acid used as a catalyst of 0.8–1.4 wt % of the amount of loaded HP. The reaction progress was monitored by the consumption of *sec*-BB HP using iodometric titration. The initial reaction rates were determined from the slope of the kinetic curve at the initial point of time [17], since it is at this point of time that the low concentrations of the reaction products have little effect on the process. Table 4 presents the studied characteristics of the process.

The initial reaction rate was shown to increase significantly with increasing temperature. Moreover, with a change in temperature from 40 to 70°C, the content of byproducts in the reaction mass increases. This fact also explains the sharp decrease in the yield of the target MEK down to 66%. For this reason, it was decided to conduct further studies at a temperature of 50°C. Along with increased temperature, an increase in the initial concentration of HP also leads to a more rapid process rate. For example, with a change in the concentration of *sec*-BB HP from 10 to 20 wt %, the reaction rate increases by a factor of 1.6. Meanwhile, it is the decomposition of 20% HP that is characterized by the highest yield of target products. Increasing the initial concentration of HP above 20 wt % is impractical due to the release of a large amount of heat during the decomposition of HP, which can be hazardous. As for increasing the concentration of the catalyst, even a small change in it (from 0.8 to 1.4 wt %) significantly reduces the selectivity of the formation of target products.

The data obtained in the series of experiments on the effect of various parameters on the process under discussion made it possible to determine the conditions for conducting it with a high yield of products. At a temperature of 50°C, a concentration of HP of 20 wt %, and a catalyst content in the reaction mass of 0.8 wt %, a scaled-up process of acid decomposition of *sec*-BB HP was carried out, the results of which are presented in Table 5.

The yields of MEK and phenol were 72 and 74%, respectively, with a conversion of HP of 99.5%.

Table 5. Material balance of sulfuric acid catalytic decomposition of *sec*-BB HP at a temperature of 50°C, an initial concentration of HP of 20 wt %, and a catalyst concentration of 0.8 wt %

Substance	Molar mass, g/mol	Loaded		Obtained	
		g	wt %	g	wt %
sec-BB	134.2	66.4	79.9	66.4	79.9
sec-BB HP	166.1	16.6	20.0	0.1	0.1
H_2SO_4	98.1	0.1	0.1	0.1	0.1
Phenol	94.1	0.0	0.0	7.0	8.4
MEK	72.1	0.0	0.0	5.2	6.3
Byproducts	–	0.0	0.0	1.2	1.4
Losses	–	0.0	0.0	3.1	3.8
Total	–	83.1	100.0	83.1	100.0

CONCLUSIONS

In the present work, the scientific and applied chemical and technological fundamentals of the hydroperoxide method used for the co-production of MEK and phenol are described and developed. The effects of some parameters on the main stages of the developed method was studied. Alkylation of benzene with 1-butanol at a benzene : 1-butanol : H_2SO_4 molar ratio of 3 : 1 : 3, a temperature of 70°C, and a reaction duration of 4 h, produced *sec*-BB at a yield of about 82% and a conversion of the initial hydrocarbon of about 30%.

The effect of such parameters as temperature, reaction duration, and catalyst concentration on the liquid-phase oxidation of *sec*-BB to its tertiary HP was investigated. Aerobic oxidation of *sec*-BB in the presence of *N*-HPI gave *sec*-BB HP with a selectivity of about 95% at a conversion of *sec*-BB of 35–40%.

Extraction of *sec*-BB HP from the *sec*-BB oxidation products by extraction with a 75% ethanol solution was tested. The obtained concentrated (up to 95%) HP can further be used in polymerization or initiated oxidation of alkyl aromatic hydrocarbons.

Sulfuric acid catalytic decomposition of *sec*-BB HP with a content of the main substance of 20 wt % at 50°C and a catalyst concentration of 0.8 wt % gave MEK and phenol with yields of 72 and 74%, respectively.

The results of the studies confirmed the technological efficiency of this method in comparison with the separate production of MEK and phenol, demonstrating its potential as an alternative to existing technologies for producing these compounds. The proposed hydroperoxide method for the synthesis of MEK and phenol can be used as part of an adapted cumene technology to obtain a wide range of alkylphenols and ketones.

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Authors' contributions

V.S. Kabanova—research concept, conducting experiments, data processing, analysis of the results, writing the text of the manuscript.

E.A. Kurganova—research concept, design of the experiments, analysis of the results, writing the text of the manuscript.

A.S. Frolov—research concept, data processing, writing the text of the manuscript.

G.N. Koshel—research concept, analysis of the results, writing the text of the manuscript.

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The authors declare no conflicts of interest.

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