CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES

ХИМИЯ И ТЕХНОЛОГИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ

ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2022-17-1-7-17

UDC 661.11+547.427.1

RESEARCH ARTICLE

Features of the synthesis of pentaerythritol esters and carboxylic acids of aliphatic isomeric structure

Vladimir V. Emelyanov, Eugen L. Krasnykh✉, Dmitriy A. Fetisov, Svetlana V. Levanova, Vladimir A. Shakun

Samara State Technical University, Samara, 443100 Russia
✉Corrresponding author, e-mail: ekras73@mail.ru

Abstract

Objectives. *Due to their structures, pentaerythritol esters have a number of appealing properties such as high viscosity index when used as oils and excellent compatibility with polyvinyl chloride when used as plasticizers. For the production of pentaerythritol and carboxylic acids, natural gas can be used as a feedstock, which implies a strategic development of the petrochemical industry, a decrease in the amount of gas used for combustion, and its applications for the production of chemical products.*
Methods. *The synthesis process was conducted in a self-catalysis mode with excess acids in a molar ratio of 8:1 and in the presence of a solvent (toluene) of ~30% per reaction mass. This ensures a uniform distillation of the reaction water at a constant temperature of 100–110°C, a decrease in the side reaction products, and an increase in process selectivity. The products from the reaction mass were isolated by vacuum distillation, and identification of all the synthesized tetraesters was performed by chromatography–mass spectrometry analysis.*
Results. *This work proposes options for optimizing the conditions of the thermal esterification of pentaerythritol with isomeric monocarboxylic acids (isobutyric, isovaleric, pivalic, and 2-ethylhexanoic acids) that have different reactivities due to their structures. Methods for isolating tetraesters of pentaerythritol and corresponding acids have been developed. The characteristics of the main series of ions of tetraesters of pentaerythritol and aliphatic isomeric acids C_4–C_8 in the mass spectra were obtained.*

Conclusions. *The yields of tetraesters were at 95%–96% of the theoretical value, and product purity was >99.6%. The resulting target products (tetraesters) were characterized by relative color stability, where the maximum degree of color after cleaning was less than 20 units according to Hazen (180 units for tetra-2-ethylhexnoate), which corresponds to the standards in GOST 29131-91 (ISO 2211-73). The esterification rates were compared, and it was shown that the quantitative yields of isomeric tetraesters at 100–110°C were achieved in 12–15 h for isobutyric and isovaleric acids, 25–27 h for 2-ethyl-hexanoic acid, and ~40 h for pivalic acid.*

Keywords: *pentaerythritol, carboxylic acids, esters, esterification, gas chromatography–mass spectrometry*

For citation: Emelyanov V.V., Krasnykh E.L., Fetisov D.A., Levanova S.V., Shakun V.A. Features of the synthesis of pentaerythritol esters and carboxylic acids of aliphatic isomeric structure. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(1):7–17 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2022-17-1-7-17

НАУЧНАЯ СТАТЬЯ

Особенности синтеза сложных эфиров пентаэритрита и алифатических карбоновых кислот изомерного строения

В.В. Емельянов, Е.Л. Красных✉, Д.А. Фетисов, С.В. Леванова, В.А. Шакун

Самарский государственный технический университет, Самара, 443100 Россия
✉Автор для переписки, e-mail: ekras73@mail.ru

Аннотация

Цели. *Сложные эфиры пентаэритрита за счет своей структуры обладают рядом привлекательных свойств: высоким индексом вязкости при их использовании в качестве масел и отличной совместимостью с поливинилхлоридными (ПВХ) полимерами при их использовании в качестве пластификаторов. При этом исходным сырьем для производства как пентаэритрита, так и карбоновых кислот может служить природный газ, что актуально с точки зрения снижения объемов газа, направляемого на сжигание, и его использование в производстве химической продукции. Цель работы – разработка новых методов синтеза тетраэфиров пентаэритрита и алифатических изомерных кислот* C_4*–*C_8.

Методы. *Процесс проводили в режиме самокатализа при избытке кислоты в мольном соотношении 8:1, а также в присутствии растворителя (толуола) ~30% на реакционную массу, обеспечивающего равномерный отгон реакционной воды при постоянной температуре 100–110 °С, уменьшение продуктов побочных реакций и повышение селективности процесса. Продукты из реакционной массы выделяли методом вакуумной ректификации. Идентификация всех синтезированных тетраэфиров проведилась с использованием хроматомасс-спектрометрического анализа.*

Результаты. *В работе предложены варианты оптимизации условий термической этерификации пентаэритрита изомерными монокарбоновыми кислотами (изомасляной, изовалериновой, пивалевой, 2-этилгексановой), обладающими за счет своей структуры различной реакционной способностью. Разработаны методики выделения тетраэфиров пентаэритрита и соответствующих кислот. Получены характеристики основных серий ионов тетраэфиров пентаэритрита и алифатических изомерных кислот* C_4*–*C_8 *в масс-спектрах.*

Выводы. *В предложенных условиях проведения процесса выход тетраэфиров составил 95–96% от теоретического с чистотой не менее 99.6%. Полученные целевые продукты (тетраэфиры) характеризуются относительной цветостабильностью: максимальная степень окрашенности после очистки составляет не более 20 ед. по Хазену (для тетра-2-этилгексаноата – 180), что соответствует ГОСТ 29131-91 (ИСО 2211-73). Количественные выходы изомерных тетраэфиров при 100–110 °С достигаются: за 12–15 ч для изомасляной и изовалериановой кислоты, 25–27 ч для 2-этил-гексановой и ~40 ч для пивалевой кислоты.*

Ключевые слова: *пентаэритрит, карбоновые кислоты, сложные эфиры, этерификация, хромато-масс спектрометрия*

Для цитирования: Емельянов В.В., Красных Е.Л., Фетисов Д.А., Леванова С.В., Шакун В.А. Особенности синтеза сложных эфиров пентаэритрита и алифатических карбоновых кислот изомерного строения. *Тонкие химические технологии.* 2022;17(1):7–17. https://doi.org/10.32362/2410-6593-2022-17-1-7-17

INTRODUCTION

Pentaerythritol (PE) esters and carboxylic acids of aliphatic structure have a high flash point (>200°C) and attractive values of viscosity index (≥135) and flow temperature [1, 2]. An important feature of these compounds is their performance at low temperatures, including in Arctic conditions [3, 4]. The properties of tetraesters depend on the chemical nature of the acid residue and the possibility of combining various acid residues. It is known that solid PE esters of linear fatty acids C_{16}–C_{18} are recommended as components of technical lubricants, cosmetics, and pharmaceutical preparations [2]. PE tetraesters and aliphatic linear acids with an average chain length of the alkyl group (C_5–C_9) correspond to the scarce lubricating oils of the 5th group and have plasticizing properties [3, 5, 6].

Of particular interest are products obtained using isomeric acids for the esterification of PE. Isostructured tetraesters with a molecular weight from 300 to 900 g/mol have high thermal stability, and their plasticizing effect exceeds the effect of the most common industrial phthalate plasticizers by 1.5–2.0 times [2]. Unfortunately, information on the esterification of PE with isomeric carboxylic acids, which could be used to develop effective methods for obtaining esters with desired properties, is rather scarce.

Analysis of the raw material market showed that the existing natural gas-based oxosynthesis technologies in Russia are at the level of foreign analogs and are able to provide the production of esters with polyatomic alcohols and carboxylic acids as raw materials. The global production of PE in 2018–2021 amounted to ~500000 t/year, and 5% of which is produced in Russia. Unfortunately, the current main consumers of PE in Russia are the manufacturers of inexpensive paint and varnish products, whereas ~60% of Russia's PE is exported to Europe and Asia.[1]

It is important to note here that the process of oxosynthesis for the production of oxygen-containing compounds from natural gas is mainly focused on maximum regioselectivity for products with linear structure, which account for 70%–75% and the rest is isostructured aldehydes that can be used to produce isomeric carboxylic acids [7]. Thus, there is a need to develop new more technologically advanced options for the synthesis of PE tetraesters and aliphatic isomeric acids C_4–C_8.

---

[1] *Godovoi otchet kompanii "Metafraks" (Annual report of the Metafrax company).* 2018. 124 p. (in Russ.). URL: https://metafrax.ru/files/disclosure_documents/10_RU_1597244243.pdf. Accessed December 10, 2022.

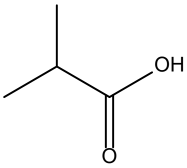
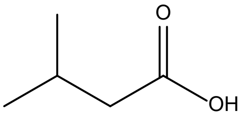
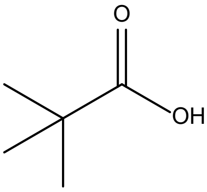
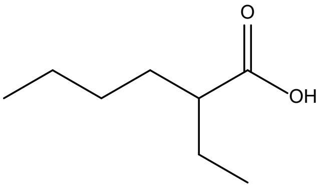
EXPERIMENTAL

Commercial samples of PE and isomeric aliphatic acids with a purity of at least 97 wt % (*Sigma-Aldrich*, USA and *Vekton*, Russia) were used as initial reagents (Table 1).

The design of the reaction units of the process depends on the type of the catalyst used. Three variants of the industrial esterification process are known: self-catalysis, homogeneous catalysis in the presence of mineral acids, and heterogeneous catalysis using ion-exchange resins [8]. The possibility of using any of the listed catalysis options is ambiguous, especially in the presence of fragments in the molecules of the initial compounds responsible for the appearance of steric and/or induction effects that affect the speed of the process [9].

In the conditions of self-catalysis, we are dealing with a slow reversible reaction proceeding by a carbonium-ion mechanism. The use of mineral acids can increase the reaction rate tenfold [9]. However, there are risks of adverse reactions such as dehydration and tarring, which lead to the formation of colored samples (Hazen color reaches 500 units at the maximum permissible according to GOST 29131-91[2] from 20 to 80–100 units for esters) [10, 11]. In this regard, it is necessary to conduct a set of measures for the purification of target products, which is characterized by the complexity of the technology and the use of expensive reagents [10, 11]. Heterogeneous catalysis using cation exchange resins has undeniable technological advantages of less corrosion, ease of separation from the reaction mass, and organization of continuous processes over homogeneous acid catalysis especially for low-molecular reagents [12, 13]. However, the disadvantage of this approach is the more stringent process conditions, where higher reaction temperature and amount of catalyst are required. This leads to tarring of the reaction mass and a decrease in the color stability

Table 1. Characteristics of the acids used

No.	Acid name	Formula	T_{bp}, °C	Dissociation constants pK
1	Isobutyric acid / 2-methylpropanoic		155.0	4.86
2	Isovaleric / 3-methylpropanoic		176.5	4.78
3	Pivalic / 2,2-dimethylpropanoic		163.8	5.05
4	2-Ethylhexanoic		227.0	–

---

[2] GOST 29131-91 (ISO 2211-73) Liquid chemical products. Measurement of color in Hazen units (platinum-cobalt scale). Moscow: IPK Izd. standartov; 2004 (in Russ.).

of the target products, which sharply limit the possible areas of their applications.

Analysis of the available information and results of preliminary studies (conversion, reaction time, quality of the samples obtained, and stability of the reaction mass) resulted to the use of the self-catalysis mode for the esterification process. Table 1 shows that the acid strength values of isomeric acids are similar. Their pK values are comparable and are between the first and second stage of the dissociation of orthophosphoric acid ($pK_1 = 2.12$, $pK_2 = 7.2$), which is widely used in industrial homogeneous catalysis.

In the synthesis of isomeric PE tetraesters, the method of thermal esterification under self-catalytic conditions for linear carboxylic acids C4–C7 [5] served as the basis. To overcome thermodynamic limitations, the process was carried out in the presence of excess acids at a molar ration of 8:1 to achieve pseudo-zero order reaction and in the presence of a solvent (toluene) of ~30% of the reaction mass for uniform distillation of reaction water at a boiling point of azeotrope 100–110°C. The reaction proceeds without abrupt temperature increase and with high selectivity. The maximum degree of color of the reaction mass is 300–350 units according to Hazen [12].

The target products—tetraisobutyrate and tetrapivalate—are solid crystalline substances. After distillation of azeotrope (toluene + water) and excess acids (vacuum distillation), solid esters were isolated by recrystallization using methanol (for tetraisobutyrate) and acetonitrile (for tetrapivalate). The masterbatch solutions were partially distilled after filtration (fractional recrystallization method), which made it possible to reduce the loss of target products by up to 5%. The reaction mass was analyzed by standard chemical and physicochemical methods [5].

Purification of liquid tetraisovalerate was conducted by vacuum distillation (fraction selection at 290–298°C (26 mmHg)). Due to the high boiling point of tetra-2-ethylhexanoate, the methanol extraction method was used after distillation of unreacted carboxylic acids in vacuum. After the addition of methanol, the resulting mixture was stirred at elevated temperatures, while no side reaction of transesterification was observed. Then, the mixture was kept at negative temperatures for 12 h. After delamination, the product was separated by decantation followed by evaporation of the solvent residues. The last stage of purification of the target product, if necessary, was clarification on bentonite clay, according to the method we used by in our previous work [5]. The return of solvent and excess acids to the cycle helps to minimize losses during synthesis. The purity of the obtained tetraesters was >99%.

Identification of the obtained mixtures and purity of the products were determined by gas chromatography–mass spectrometry (GC–MS) using an Agilent 6850 gas chromatograph (*Agilent Technologies*, USA) that was equipped with an Agilent HP-5MS capillary column (30 m × 250 µm × 0.25 µm), an Agilent 5975C VL MSD mass selective detector, an ionizing voltage of 70 eV, and a NIST 2017 v. 2.3 spectra database.

The melting point was measured in accordance with GOST 33454-2015[3]. The crushed solid samples were driven into a capillary sealed on one side, which has an internal diameter of ~1 mm and a wall thickness of about 0.2–0.3 mm. The level of filling with the test substance was at the 3 mm. Temperature was fixed and monitored using a mercury thermometer (error ± 0.1°C). Temperature measurement was carried out in a container with a circulating coolant (polymethylsiloxane PMS-200), in which the tip of the thermometer containing a mercury ball was immersed. The heating rate was about 3°C/min until a temperature less than 10°C of the estimated melting point of the compound under study was reached. Afterwards, the heating rate was reduced to 1°C/min, while the capillary was immersed in the container so that it came in contact with the middle of the mercury bulb of the thermometer.

Liquid samples were loaded into a test tube and placed in a container with a refrigerant (methanol), and the mixture was subjected to constant stirring. An immersion Huber cryostat equipped with a cooling rate regulator was used to maintain the the tank temperature. The substance was constantly mixed. After crystallization, the compounds were slowly heated at a rate of 1°C/min.

The normal boiling point was determined by the Sivolobov method. The measured sample was loaded into a glass tube with a diameter of 0.5 cm and a capacity of 0.3–0.5 mL. A capillary sealed at one end with an internal diameter of 1 mm was immersed in the liquid. The installation was immersed in a container with a stirred coolant (PMS-200). Heating speed was 1°C/min, and temperature was measured using a mercury thermometer. Boiling point was measured upon the intense release of vapor bubbles from the capillary. Then, the installation was cooled, the test liquid was drawn into the capillary, and the temperature was recorded during this phenomenon. The adjusted boiling point was calculated as the average between the two values.

---

[3] GOST 33454-2015. Interstate Standard. Testing of chemicals of environmental hazard. Determination of the melting point/melting range. Moscow: Standartinform; 2019 (in Russ.).

RESULTS AND DISCUSSION

Table 2 indicates the characteristics of all the synthesized PE tetraesters. Of all the compounds in the NIST 2017 database, only the mass spectrum for pentaerythritol tetrapivalate is available. Figure 1 shows the mass spectrum of the electron impact of the PE tetrapivalate obtained in this study. The mass spectrum available in the database is shown in Fig. 2.

As can be seen from the mass spectra in Figs. 1 and 2, the mass characteristic ions and radical ions are identical with a difference only in intensity, which is explained by the difference in the energy of ionizing electrons and the temperature regime of ionization.

The characteristics of the mass spectra of the tetraesters of PE and C_4–C_8 carboxylic acids synthesized in this study are given in Table 3. From the data presented, it can be seen that the mass spectra of the branched C_4–C_8 PE tetraesters and the previously studied mass spectra of linear C_4–C_7 carboxylic acid tetraesters [5] have the following characteristics:

- Absence of a molecular ion associated with rapid cleavage of fragments ($C_nH_{2n-1}O_2^{\bullet}$ and $C_nH_{2n-1}O^+$) and water molecules.
- An increase in ion intensity $\left[M^{+\bullet} - C_2H_{2n-1}O_2^{\bullet}\right]^+$ and $\left[M^{+\bullet} - C_nH_{2n-1}O_2^{\bullet}; -C_nH_{2n-2}O\right]^+$ with an increase in the number of carbon atoms in the carboxylic acid from C_4 to C_8.
- A relative intensity of 100% for $C_nH_{2n-1}O^+$ ion for all the considered compounds with the exception of tetrapivalate and tetra-2-ethylhexanoate in the mass spectra, where the intensity is weakened due to branching in the structure of the remainder of the carboxylic acid, in which there is a rupture of the C–C bonds with intense emission alkyl carbocations ($C_4H_9^+$ for tetrapivalate, $C_4H_9^+$ and $C_7H_{15}^+$ for tetra-2-ethylhexanoate).
- An increase in the intensity of $C_{n-1}H_{2n-1}^+$ in the spectrum due to the presence of branching in the carboxylic acid residue.
- Presence of the $\left[M^{+\bullet} - CH_3^{\bullet}\right]^+$ ion and the maximum intensity of the $C_4H_9^+$ ion in the tetrapivalate mass spectrum, which is explained by the energetically advantageous decay paths of a tertiary butyl substituent.

The data obtained in this work were used to estimate the rate of formation of esters in the presence of excess isomeric acids in the kinetic regime, which was provided by effective mixing of the reaction mass at a speed of ~1000 rpm and azeotropic removal of reaction water at a temperature of 100–110°C.

Figure 3 shows the experimental results illustrating the successive transformations of PE into mono-, di-, tri-, and tetraesters.

It is known that in the case of comparable acidity values, as in our case, the rate of esterification depends on the volume of alkyl residues associated with the carboxyl group and on the branching at the α-carbon atom of carboxylic acids [14, 15]. Figure 4 shows a comparison of the dependence of the change in the conversion of PE (the total share of unreacted OH groups) as a function time for isomeric acids.

Quantitative yields of isomeric tetraesters (96%) at 100–110°C are achieved in 12–15 h for isobutyric and isovaleric acids, 25–27 h for 2-ethyl-hexanoic acid, and ~40 h for pivalic acid. The esterification rates of normal valeric and isovaleric acids are comparable.

Table 2. Properties of the resulting products

PE tetraester	T_{bp}, °C	T_{cr}, °C	APHA color	Purity
Tetraisobutyrate	317 ± 2	56	20 ± 2	99.6
Tetraisovalerate	367	−7	18 ± 1	99.5
Tetrapivalate	265	129	19 ± 2	99.8
Tetra-2-ethylhexanoate	493*	−9	180 ± 10	99.6

Note: T_{bp} is the boiling point, T_{cr} is the crystallization temperature, * the temperature predicted is based on the logarithmic Kovacs retention indices obtained in [15].

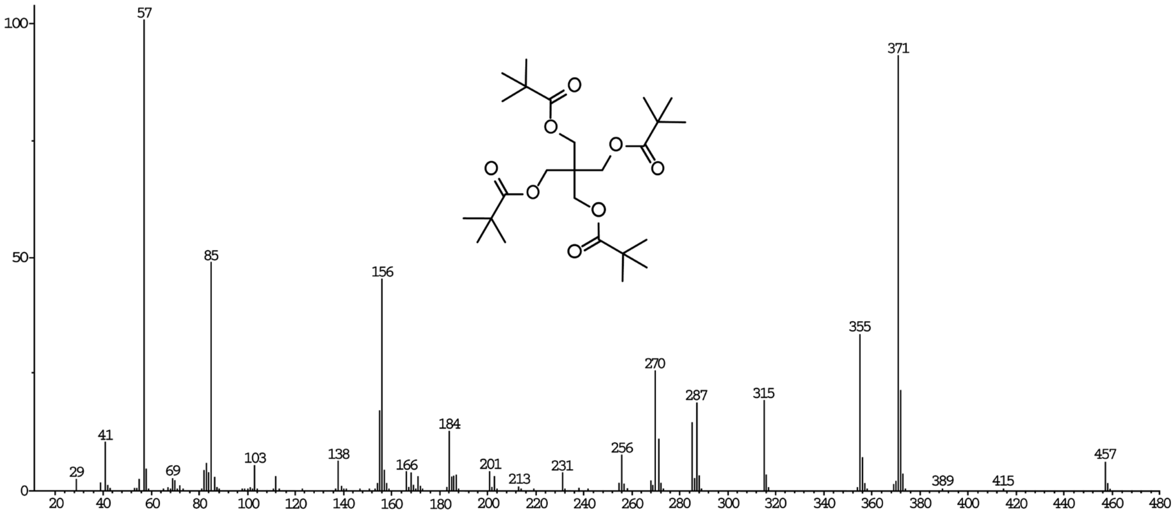


Fig. 1. GC–MS spectrum of the obtained pentaerythritol tetrapivalate.

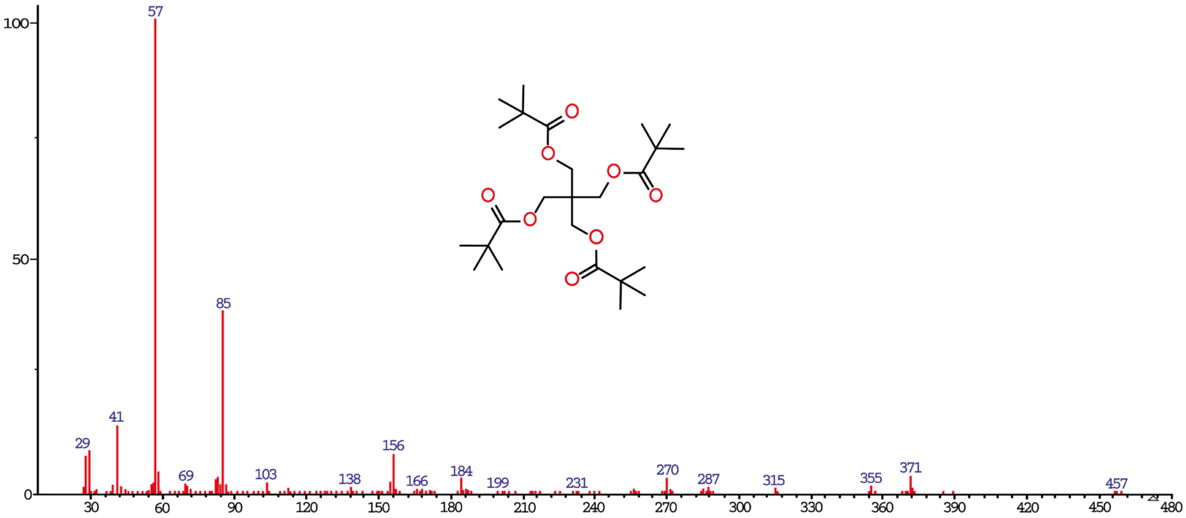


Fig. 2. GC–MS spectrum of pentaerythritol tetrapivalate according to the database.

Table 3. Characterization of the main series of ions in the mass spectra of tetraesters of PE and C_4–C_8 carboxylic acids

Compound	Main series of ions in the mass spectra, 70 eV, *m/z*, (structure, % rel.)
Tetraisobutyrate	**416** ($M^{+\bullet}$, 0); **398** ($[M^{+\bullet}–H_2O]^+$, 1); **329** ($[M^{+\bullet}–C_4H_7O_2^{\bullet}]^+$, 30); **313** ($[M^{+\bullet}–C_4H_7O_2^{\bullet};–CH_4]^+$, 3); **300** ($[M^{+\bullet}–C_4H_7O_2^{\bullet};–CHO^{\bullet}]^{+\bullet}$, 1); **259** ($[M^{+\bullet}–C_4H_7O_2^{\bullet};–C_4H_6O]^+$, 5); **257** ($[M^{+\bullet}–C_4H_7O_2^{\bullet};–C_4H_8O]^+$, 20); **228** ($[M^{+\bullet}–C_4H_7O_2^{\bullet};–C_4H_8O;–CHO^{\bullet}]^{+\bullet}$, 10); **142** ($[M^{+\bullet}–C_4H_7O_2^{\bullet};–C_4H_8O;–CHO^{\bullet};–C_4H_6O_2]^{+\bullet}$, 44); **71** ($C_4H_7O^+$, 100); **43** ($C_3H_7^+$, 41)
Tetraisovalerate	**472**($M^{+\bullet}$, 0); 454 ($[M^{+\bullet}–H_2O]^+$, 1); **371** ($[M^{+\bullet}–C_5H_9O_2^{\bullet}]^+$, 73); **355** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–CH_4]^+$, 47); **341** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–CH_2O]^+$, 1); **287** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_8O]^+$, 63); **285** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_{10}O]^+$, 18); **256** ($M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_{10}O;–CHO^{\bullet}]^{+\bullet}$, 16); **156** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_{10}O;–CHO^{\bullet};–C_5H_8O_2]^{+\bullet}$, 27); **85** ($C_5H_9O^+$, 100); **57** ($C_4H_9^+$, 41)

Table 3. Continued

Compound	Main series of ions in the mass spectra, 70 eV, *m*/*z*, (structure, % rel.)
Tetrapivalate	**472** ($M^{+\bullet}$, 0); 457 ($[M^{+\bullet}–CH_3^{\bullet}]^+$, 13); **371** ($[M^{+\bullet}–C_5H_9O_2^{\bullet}]^+$, 92); **355** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–CH_4]^+$, 37); **341** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–CH_2O]^+$, 0); **287** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_8O]^+$, 18); **285** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_{10}O]^+$, 14); **256** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_{10}O;–CHO^{\bullet}]^{+\bullet}$, 8); **156** ($[M^{+\bullet}–C_5H_9O_2^{\bullet};–C_5H_{10}O;–CHO^{\bullet};–C_5H_8O_2]^{+\bullet}$, 48); **85** ($C_5H_9O^+$, 51); **57** ($C_4H_9^+$, 100)
Tetra-2-ethylhexanoate	**640** ($M^{+\bullet}$, 0); **497** ($[M^{+\bullet}–C_8H_{15}O_2^{\bullet}]^+$, 100); **481** ($[M^{+\bullet}–C_8H_{15}O_2^{\bullet};–CH_4]^+$, 2); **468** ($M^{+\bullet}–C_8H_{15}O_2^{\bullet};–CH_2O]^+$, 16); **371** ($[M^{+\bullet}–C_8H_{15}O_2^{\bullet};–C_8H_{14}O]^+$, 74); **369** ($[M^{+\bullet}–C_8H_{15}O_2^{\bullet};–C_8H_{16}O]^+$, 12); **340** ($[M^{+\bullet}–C_8H_{15}O_2^{\bullet};–C_8H_{16}O;–CHO^{\bullet}]^{+\bullet}$, 8); **198** ($[M^{+\bullet}–C_8H_{15}O_2^{\bullet};–C_8H_{16}O;–CHO^{\bullet};–C_8H_{14}O_2]^{+\bullet}$, 22); **127** ($C_8H_{15}O^+$, 34); **99** ($C_7H_{15}^+$, 26); **57** ($C_4H_9^+$, 50)

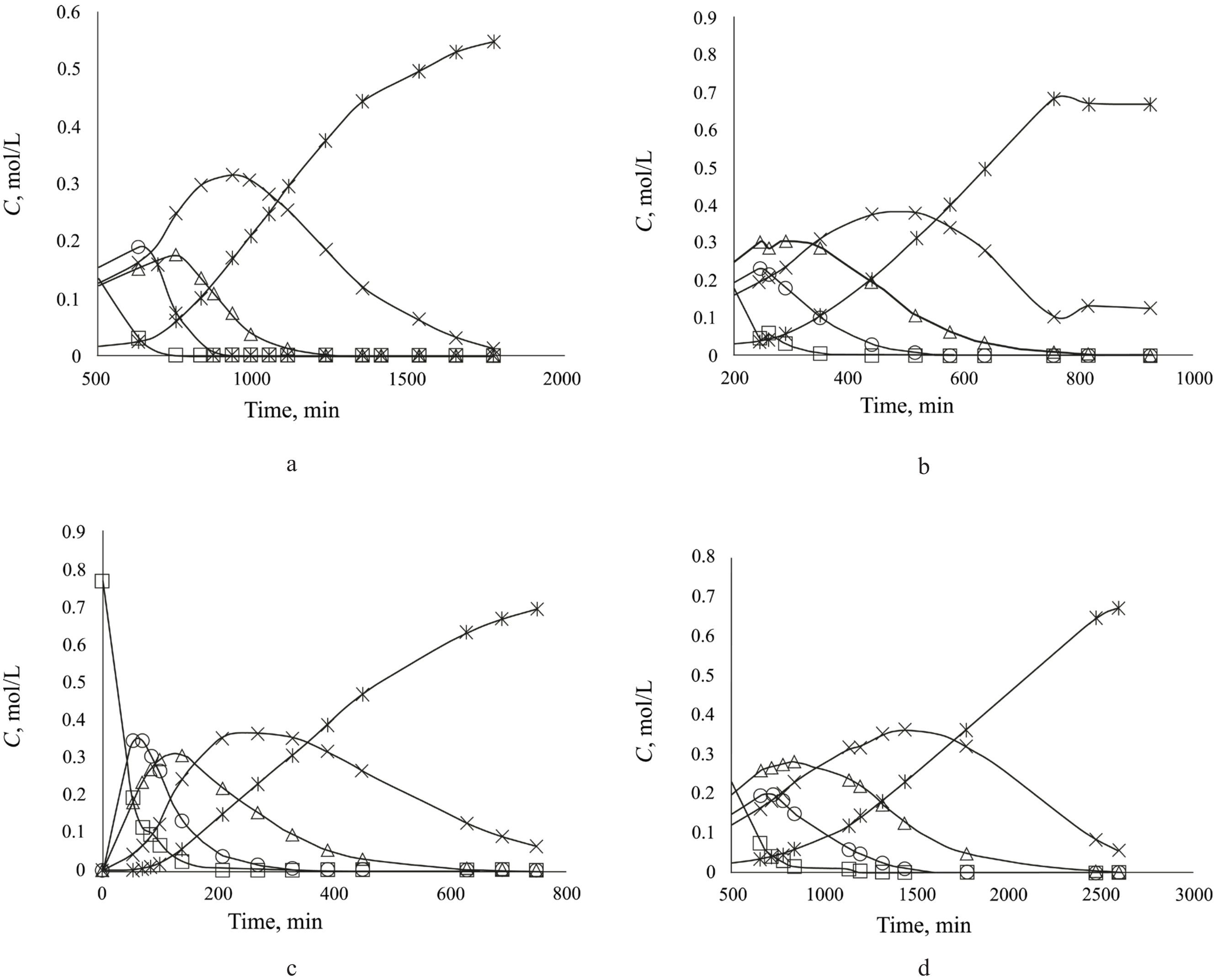
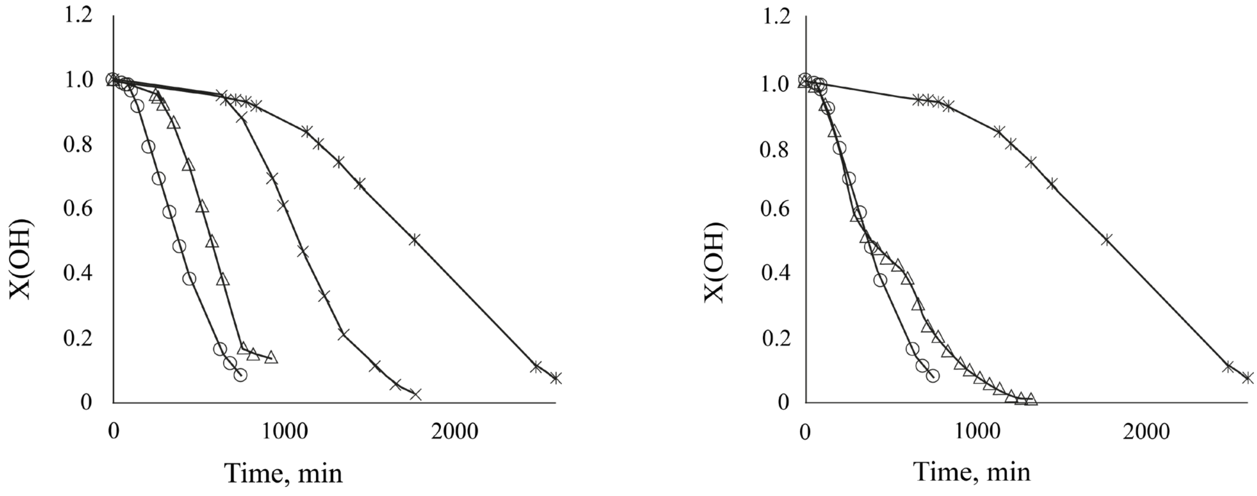


Fig. 3. Conversion of PE into monoesters (○), diesters (△), triesters (×), and tetraesters (⁎): (a) reaction of 2-ethylhexanoic acid and PE, (b) isobutyric acid and PE, (c) isovaleric acid and PE, and (d) pivalic acid and PE. *C* is the concentration.



a

b

Fig. 4. Dependence of the change in the share of unreacted OH groups as a function of time.
(a) Comparison of the data from this study (for reactions of PE with isovaleric acid (○), pivalic acid (⋇), isobutyric acid (△), and 2-ethylhexanoic acid (×)); (b) comparison of the changes in the share of OH groups for the reactions of PE with valeric acid (△), isovaleric acid (○), and pivalic acid (⋇).

CONCLUSIONS

Methods of synthesis and isolation of complex tetraesters of pentaerythritol and isobutyric, isovaleric, pivalic, and 2-ethylhexanoic acids were developed. The purity of the obtained samples was at least 99.6% with a product yield of 95–96% from the theoretical value. For all the synthesized esters, the characteristics of the main series of PE tetraester ions in the mass spectra were obtained.

Kinetic regularities of the thermal esterification of pentaerythritol by isomeric carboxylic acids were investigated, and it was shown that the quantitative yields of isomeric tetraesters at 100–110°C were achieved in 12–15 h for isobutyric and isovaleric acids, 25–27 h for 2-ethyl-hexanoic acid, and ~40 h for pivalic acid.

The results obtained in this work can be used for predicting the rate of the esterification reaction in the case of using new reagents and as initial information for creating a flexible (complex) technology on a single installation. The transition to a particular product should be performed by replacing raw materials and/or adjusting the operating parameters. This approach makes it possible to diversify the range of products, thus adapting to market conditions.

Acknowledgments

The study was supported by the Russian Foundation for Basic Research, project No. 20-38-90141.

Authors' contribution

V.V. Emelyanov – conducting the experiment, data processing, and analysis of the results;

E.L. Krasnykh – analysis of the experimental data and writing the article;

D.A. Fetisov – conducting the experiment, data processing, and analysis of the results;

S.V. Levanova – analysis of the experimental data and writing the article;

V.A. Shakun – performance of chromato-mass-spectrometry research and analysis of the results.

The authors declare no conflicts of interest.

REFERENCES

1. Gromova V.V., Mamarasulova Z.V. Thermal esterification of penthaerytritol by aliphatic monocarbonic acids. *Izvestiya Sankt-Peterburgskogo gosudarstvennogo tekhnologicheskogo instituta = Bulletin of Saint Petersburg State Institute of Technology.* 2013;20(46):64–67 (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Громова В.В., Мамарасулова З.В. Термическая этерификация пентаэритрита алифатическими монокарбоновыми кислотами. *Известия Санкт-Петербургского государственного технологического института*. 2013;20(46):64–67.

2. Faizullina S.R., Builova E.A., Nedopekin D.V., Aminova G.K. Synthesis and properties of some pentaerythritol esters. *Bashkirskii khimicheskii zhurnal = Bashkir Chemical Journal.* 2016;23(3):41–44 (in Russ.).

3. Kopyshev M.V., Khasin A.V., Minyukova T.P., Khassin A.A., Yurieva T.M. Esterification of pentaerythritol by carboxylic acids. *Reac. Kinet. Mech. Cat.* 2016;117(2):417–427. https://doi.org/10.1007/s11144-015-0964-7

4. Golysheva E.A., Zhdaneev O.V., Korenev V.V., Lyadov A.S., Rubtsov A.S. Petrochemical industry of Russia: state of the art and prospects for development. *Russ. J. Appl. Chem.* 2020;93(10):1596–1603. https://doi.org/10.1134/S107042722010158

5. Emel'yanov V.V., Krasnykh E.L., Fetisov D.A., Levanova S.V., Shakun V.A. Synthesis, identification and isolation of esters of pentaerythritol and linear C_4–C_7 carboxylic acids. *Pet. Chem.*2021;61(5):1027–1032. https://doi.org/10.1134/S0965544121090048

6. Rabinovich V.A., Khavin Z.Ya. *Kratkii khimicheskii spravochnik. Izd. 2-e, ispr. i dop.* (*Short chemical reference book. Ed. 2nd, rev. and add.*). Moscow: Khimiya; 1978.392 p. (in Russ.).

7. Marochkin D.V., Noskov Yu.G., Kron T.E., Karchevskaya O.G., Korneeva G.A. Products of oxo-process in the production of ester lubricating oils. *Nauchno-tekhnicheskii vestnik OAO "NK Rosneft'."* 2016;4(45):74–81 (in Russ.).

8. Mancini G., Imparato L., Berti F. *Organic ester for use in lubricant compositions*: Pat. 4317780 USA. Publ. 02.03.1982.

9. Shabarov Yu.S. *Organicheskaya khimiya: ucheb. dlya VUZov (Organic chemistry: textbook for universities*). Moscow: Khimiya; 2000. 846 p. (in Russ.). ISBN 5-7245-1180-0

10. Nosovsky Yu.E., Kutsenko A.I., Kochergina G.K., Belkina F.R., Vorobyov V.A., Zhitkov V.I. *Method of ester purification*: Pat. SU592815A1 USSR. Publ. 15.02.1978.

11. Abdrakhmanova L.K., Rysaev D.U., Aminova G.K., Mazitova A.K. Clarification of di-(2-ethylhexyl)phthalate plasticizer with an aqueous solution of sodium hypochlorite. *Bashkirskii khimicheskii zhurnal = Bashkir Chemical Journal.* 2008;15(4):38–40 (in Russ.).

12. Kolah A.K., Astana N.S., Vu D.T., Lira C.T., Miller D.J. Reaction kinetics for the heterogeneously catalyzed esterification of succinic acid with ethanol. *Ind. Eng. Chem. Res.* 2008;47(15):5313–5317. https://doi.org/10.1021/ie0706616

13. Amirkhanov I.R., Kaleeva E.S., Yazmukhamedova I.M., Dzhabarov G.V., Men'shchikova A.A., Balaeva A.V., Zhila M.Yu., Shpakova P.I. Development of a method for the production of synthetic lube oils. *Uspekhi v khimii i khimicheskoi tekhnologii = Advances in Chemistry and Chemical Technology.* 2017;31(12):36–38 (in Russ.)

14. Ladero M., de Gracia M., Trujillo F., Garcia-Ochoa F. Phenomenological kinetic modelling of the esterification of rosin and polyols. *Chem. Eng. J.* 2012;197:387–397. https://doi.org/10.1016/j.cej.2012.05.053

15. Emel'yanov V.V., Krasnykh E.L., Portnova S.V. Retention Indices and Sorption Enthalpies of Pentaerythritol and C_2–C_8 Acid Esters on Nonpolar Stationary Phases. *Russ. J. Phys. Chem. A.* 2020;94(10):2168–2176. https://doi.org/10.1134/S003602442010009X

2. Файзуллина С.Р., Буйлова Е.А., Недопекин Д.В., Аминова Г.К. Синтез и свойства некоторых эфиров пентаэритрита. *Башкирский химический журнал.* 2016;23(3):41–44.

3. Kopyshev M.V., Khasin A.V., Minyukova T.P., Khassin A.A., Yurieva T.M. Esterification of pentaerythritol by carboxylic acids. *Reac. Kinet. Mech. Cat.* 2016;117(2):417–427. https://doi.org/10.1007/s11144-015-0964-7

4. Голышева Е.А., Жданеев О.В., Коренев В.В., Лядов А.С., Рубцов А.С. Нефтехимическая отрасль России: Анализ текущего состояния и перспектив развития. *ЖПХ.* 2020;93(10):1499–1507. https://doi.org/10.31857/S0044461820100126

5. Емельянов В.В., Красных Е.Л., Фетисов Д.А., Леванова С.В., Шакун В.А. Синтез, идентификация и выделение сложных эфиров пентаэритрита и линейных карбоновых кислот C_4–C_7. *Нефтехимия.* 2021;61(5):652–658. https://doi.org/10.31857/S0028242121050087

6. Рабинович В.А., Хавин З.Я. *Краткий химический справочник. Изд. 2-е, испр. и доп.* Химия; 1978. 392 с.

7. Марочкин Д.В., Носков Ю.Г., Крон Т.Е., Карчевская О.Г., Корнеева Г.А. Продукты оксосинтеза в производстве сложноэфирных смазочных масел. *Научно-технический вестник ОАО «НК Роснефть».* 2016;4(45):74–81.

8. Mancini G., Imparato L., Berti F. *Organic ester for use in lubricant compositions*: Pat. 4317780 USA. Publ. 02.03.1982.

9. Шабаров Ю.С. *Органическая химия: учеб. для ВУЗов*. М.: Химия; 2000. 846 с. ISBN 5-7245-1180-0

10. Патент СССР на изобретение № 592915. Опубл. 15.02.78, Бюл. №6. Носовский Ю.Е., Куценко А.И., Кочергина Г.К., Белкина Ф.Р., Воробьев В.А., Житков В.И. *Способ очистки сложных эфиров*.

11. Абдрахманова Л.К., Рысаев Д.У., Аминова Г.К., Мазитова А.К. Осветление ди-(2-этилгексил) фталатного пластификатора водным раствором гипохлорита натрия. *Башкирский химический журнал.* 2008;15(4):38–40.

12. Kolah A.K., Astana N.S., Vu D.T., Lira C.T., Miller D.J. Reaction kinetics for the heterogeneously catalyzed esterification of succinic acid with ethanol. *Ind. Eng. Chem. Res.* 2008;47(15):5313–5317. https://doi.org/10.1021/ie0706616

13. Амирханов И.Р., Калеева Е.С., Язмухамедова И.М., Джабаров Г.В., Меньщикова А.А., Балаева А.В., Жила М.Ю., Шпакова П.И. Разработка способа получения синтетических смазочных масел. *Успехи в химии и химической технологии.* 2017;31(12):36–38.

14. Ladero M., de Gracia M., Trujillo F., Garcia-Ochoa F. Phenomenological kinetic modelling of the esterification of rosin and polyols. *Chem. Eng. J.* 2012;197:387–397. https://doi.org/10.1016/j.cej.2012.05.053

15. Emel'yanov V.V., Krasnykh E.L., Portnova S.V. Retention Indices and Sorption Enthalpies of Pentaerythritol and C_2–C_8 Acid Esters on Nonpolar Stationary Phases. *Russ. J. Phys. Chem. A.* 2020;94(10):2168–2176. https://doi.org/10.1134/S003602442010009X

About the authors:

Vladimir V. Emelyanov, Postgraduate Student, Technology of Organic and Petrochemical Synthesis Department, Samara State Technical University (244, Molodogvardeyskaya ul., Samara, 443100, Russia). E-mail: dragonage2rus@mail.ru. http://orcid.org/0000-0002-6228-5713

Eugen L. Krasnykh, Dr. Sci. (Chem.), Associate Professor, Head of the Technology of Organic and Petrochemical Synthesis Department, Samara State Technical University (244, Molodogvardeyskaya ul., Samara, 443100, Russia). E-mail: ekras73@mail.ru. http://orcid.org/0000-0002-3886-1450

Dmitriy A. Fetisov, Master Student, Technology of Organic and Petrochemical Synthesis Department, Samara State Technical University (244, Molodogvardeyskaya ul., Samara, 443100, Russia). E-mail: fetis.dim@gmail.com. http://orcid.org/0000-0002-5438-2919

Svetlana V. Levanova, Dr. Sci. (Chem.), Professor, Technology of Organic and Petrochemical Synthesis Department, Samara State Technical University (244, Molodogvardeyskaya ul., Samara, 443100, Russia). E-mail: kinterm@mail.ru. http://orcid.org/0000-0003-2539-8986

Vladimir A. Shakun, Cand. Sci. (Chem.), Associate Professor, Technology of Organic and Petrochemical Synthesis Department, Samara State Technical University (244, Molodogvardeyskaya ul., Samara, 443100, Russia). E-mail: shakyh@mail.ru. http://orcid.org/0000-0003-2682-3024

Об авторах:

Емельянов Владимир Владимирович, аспирант кафедры «Технология органического и нефтехимического синтеза» ФГБОУ ВО «Самарский государственный технический университет» (443100, Россия, г. Самара, ул. Молодогвардейская, д. 244.). E-mail: dragonage2rus@mail.ru. http://orcid.org/0000-0002-6228-5713

Красных Евгений Леонидович, д.х.н, доцент, заведующий кафедрой «Технология органического и нефтехимического синтеза» ФГБОУ ВО «Самарский государственный технический университет» (443100, Россия, г. Самара, ул. Молодогвардейская, д. 244.). E-mail: ekras73@mail.ru. http://orcid.org/0000-0002-3886-1450

Фетисов Дмитрий Александрович, магистрант кафедры «Технология органического и нефтехимического синтеза» ФГБОУ ВО «Самарский государственный технический университет» (443100, Россия, г. Самара, ул. Молодогвардейская, д. 244.). E-mail: fetis.dim@gmail.com. http://orcid.org/0000-0002-5438-2919

Леванова Светлана Васильевна, д.х.н., профессор кафедры «Технология органического и нефтехимического синтеза» ФГБОУ ВО «Самарский государственный технический университет» (443100, Россия, г. Самара, ул. Молодогвардейская, д. 244.). E-mail: kinterm@mail.ru. http://orcid.org/0000-0003-2539-8986

Шакун Владимир Андреевич, к.х.н., доцент кафедры «Технология органического и нефтехимического синтеза» ФГБОУ ВО «Самарский государственный технический университет» (443100, Россия, г. Самара, ул. Молодогвардейская, д. 244.). E-mail: shakyh@mail.ru. http://orcid.org/0000-0003-2682-3024

The article was submitted: August 18, 2021; approved after reviewing: October 27, 2021; accepted for publication: February 07, 2022.

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Enago, an editing brand of Crimson Interactive Inc.