

ОСОБЕННОСТИ АЛКОГОЛИЗА МЕТИЛОВЫХ ЭФИРОВ ЖИРНЫХ КИСЛОТ ТРИМЕТИЛОЛПРОПАНОМ

И.С. Козеева, М.С. Воронов, В.Н. Сапунов, Р.А. Козловский, К.Ш. Якубов, В.Э. Петрова

Илона Сергеевна Козеева (ORCID 0000-0001-8302-6748)*, Михаил Сергеевич Воронов (ORCID 0000-0001-8000-9328), Валентин Николаевич Сапунов (ORCID 0000-0002-1006-5436), Роман Анатольевич Козловский, Камиль Шухратович Якубов (ORCID 0009-0003-2283-3804), Влада Эдуардовна Петрова (ORCID 0009-0004-0958-7546)

Кафедра технологии основного органического и нефтехимического синтеза, Российский химико-технологический университет им. Д.М. Менделеева, пл. Миусская, 9/1, Москва, Российская Федерация, 125047
E-mail: iolanta2006@list.ru*, voronov.m.s@muctr.ru, sapunovvals@gmail.com, rakozlovskiy@mail.ru, komil405@gmail.com, nogovitsina.vlada@yandex.ru

На основе научной литературы в этом исследовании анализируются кинетические взаимосвязи, участвующие в перегетерификации триметилпропана (ТМП) и метиловых эфиров жирных кислот (МЭЖК), полученных из растительного масла, с целью получения биоразлагаемых смазочных масел. В работе приведены наиболее благоприятные условия проведения процесса. На основе теоретических представлений выявлены ряд неточностей в классическом видении процесса трансэтерификации между многоатомным спиртом и метиловыми эфирами жирных кислот. Утверждается, что имеются особенности, дополняющие механизм классических последовательно-параллельных обратимых процессов при синтезе моно-, ди- и тризамещенных производных триметилпропана и метиловых эфиров жирных кислот. Считается, что моноэфир триметилпропана может выступать в качестве носителя ацильной группы с образованием соответствующих ди- и триэфиров триметилпропана. При этом межмолекулярные взаимодействия позволяют расширить классический механизм последовательно-параллельных реакций. Утверждается, что возможны межмолекулярные взаимодействия метаболитов "классических" реакций. При этом не происходит образования дополнительных продуктов, что затрудняет идентификацию данных реакций в общем процессе. Участие моноэфира триметилпропана в схеме механизма реакции показало, что реакция является эндергонической и неспонтанной, то есть весь процесс перегетерификации является эндергоническим. Помимо этого, в работе показана взаимосвязь между вероятным пространственным строением триметилпропана, его внутри- и межмолекулярными водородными связями и данными об энергиях Гиббса, полученными в литературных источниках. Представлены общие реакционные схемы процесса и строение анионов триметилпропана. Показан вероятный сценарий взаимодействия промежуточных продуктов. Обозначены потенциальные интермедиаты во всех реакциях.

Ключевые слова: метиловые эфиры жирных кислот, триметилпропан, механизм, алкоголиз, эндергоническая реакция

Для цитирования:

Козеева И.С., Воронов М.С., Сапунов В.Н., Козловский Р.А., Якубов К.Ш., Петрова В.Э. Особенности алкоголиза метиловых эфиров жирных кислот триметилпропаном. *Изв. вузов. Химия и хим. технология*. 2025. Т. 68. Вып. 1. С. 31–38. DOI: 10.6060/ivkkt.20256801.7095.

For citation:

Kozeeva I.S., Voronov M.S., Sapunov V.N., Kozlovskiy R.A., Yakubov K.S., Petrova V.E. Features of alcoholysis of fatty acid methyl esters by trimethylolpropane. *ChemChemTech [Изв. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2025. V. 68. N 1. P. 31–38. DOI: 10.6060/ivkkt.20256801.7095.

FEATURES OF ALCOHOLYSIS OF FATTY ACID METHYL ESTERS BY TRIMETHYLOLPROPANE

I.S. Kozeeva, M.S. Voronov, V.N. Sapunov, R.A. Kozlovskiy, K.S. Yakubov, V.E. Petrova

Iiona S. Kozeeva (ORCID 0000-0001-8302-6748)*, Mikhail S. Voronov (ORCID 0000-0001-8000-9328), Valentin N. Sapunov (ORCID 0000-0002-1006-5436), Roman A. Kozlovskiy, Kamil S. Yakubov (ORCID 0009-0003-2283-3804), Vlada E. Petrova (ORCID 0009-0004-0958-7546)

Department of Chemical Technology of Basic Organic and Petrochemical Synthesis, Mendeleev University of Chemical Technology of Russia, Miusskaya sqr., 9, Moscow, 125047, Russia

E-mail: iolanta2006@list.ru*, voronov.m.s@muctr.ru, sapunovvals@gmail.com, rakozevskiy@mail.ru, komil405@gmail.com, nogovitsina.vlada@yandex.ru

This study analyses the kinetic relationships involved in the transesterification of trimethylolpropane (TMP) and fatty acid methyl esters (FAMEs) derived from vegetable oil to produce biodegradable lubricating oils, based on scientific literature. The work presents the most favourable conditions for the process. In the classical vision of the transesterification process between polyhydric alcohol and methyl esters of fatty acids, a number of inaccuracies have been identified based on theoretical concepts. It is argued that the mechanism of classical sequential parallel reversible processes in the synthesis of mono-, di-, and tri-substituted derivatives of trimethylolpropane and methyl esters of fatty acids can be complemented by certain features. Trimethylolpropane monoester is believed to act as an acyl group carrier, forming the corresponding trimethylolpropane di- and triesters. Additionally, intermolecular interactions expand the classical mechanism of series-parallel reactions. It is suggested that intermolecular interactions between metabolites of 'classical' reactions are possible. In this case, it is difficult to identify these reactions in the overall process as no additional products are formed. The reaction mechanism scheme involving trimethylolpropane monoester showed that the reaction is endergonic and non-spontaneous, indicating that the entire transesterification process is endergonic. Additionally, the work demonstrates the correlation between the likely spatial configuration of trimethylolpropane, its intra- and intermolecular hydrogen bonds, and the Gibbs energies data obtained from literature. The paper presents the overall reaction schemes of the process and the structure of trimethylolpropane anions. It also illustrates a plausible scenario for the interaction of intermediate products, while indicating potential intermediates in all reactions.

Keywords: fatty acid methyl ester, trimethylolpropane, mechanism, alcoholysis, endergonic reaction

INTRODUCTION

According to a report by [1], the annual demand for lubricants is approximately 39 million tonnes. Furthermore, there is an increasing requirement for safer and eco-friendly materials, particularly polyol-based synthetic base oils. These oils have high frost resistance, resistance to friction and wear, and are often used as biodegradable hydraulic fluids [2-5]. TMP esters are commonly used as high-performance insulating oils in small and safe electrical insulation equipment [6, 7]. Since vegetable oils have a known affinity for metal surfaces, chemically modified vegetable oils have excellent viscosity and good anti-corrosion properties [8, 9].

Polyol esters are typically formed by combining neopolyols and monocarboxylic acids with acid

catalysts. The scientific basis for the non-catalytic esterification of polyols and carboxylic acids is currently under investigation [10]. However, alcoholysis (or transesterification) with basic catalysts is the optimal technique for manufacturing polyol esters. The process minimises the amount of by-products, is user-friendly and facilitates the production of fundamental lubricants with optimised physical and chemical characteristics.

CURRENT STATE

However, there is insufficient literature data to support a preference for one synthesis method over another. After reviewing the available sources, it has been concluded that the alcoholysis of fatty acid methyl esters sourced from vegetable oils using trimethylolpropane is the most promising method for producing syn-

thetic oil. We examine the available data on the kinetics of the transesterification reaction of TMP with fatty acid esters to assess the current comprehension of the FAME-based process in terms of its relative simplicity and its agreement with experimental results.

The mechanism of transesterification of FAMES with trimethylolpropane, catalyzed by sodium methoxide with the continuous separation of released methanol, is generally accepted [11]. The reaction mechanism includes three stepwise reversible sequential-parallel elementary reactions. At a molar excess of FAME in comparison to TMP in a ratio of 10:1, the rate constants for the subsequent stages of transesterification decreased as follows (wt./min): 1.0: 0.70-0.80 and 0.21-0.25, respectively. However, the models are only suitable for the initial stages of reactions in a limited temperature range, including at room temperature. The assumption of the irreversibility of reactions, which is utilized in the models, no longer holds beyond these boundaries.

The kinetics of transesterification of palm oil FAMES with TMP were modelled using MATLAB software, based on the irreversibility of the reaction [12]. It is challenging to anticipate how the trimethylolpropane fatty acid diester (DETMP) intermediate will be dispersed at its end-point equilibrium, as indicated by the research. Similarly, Egyptian researchers reached the identical conclusion while evaluating the distribution curves of transesterification compounds of oleic acid methyl ester (OME) with trimethylolpropane at 120 °C, with a molar ratio of OME/TMP = 10:1 and catalyzed by sodium methoxide [13]. At the same time, only the simulated concentration curve of trimethylolpropane fatty acid monoester (METMP) changes agrees relatively well with the experimental data, without any subjective evaluation.

The disagreement regarding the concentrations of trimethylolpropane fatty acid triester (TETMP) between experimental and simulated studies is a topic of discussion. This is despite extensive research on the kinetics of a seemingly uncomplicated process, which comprises of three series-parallel reactions at equilibrium.

THEORETICAL PROBLEMS

We suggest to use the processed data of the following researchers as a starting point for our future work [11, 13, 14]. First, let us examine scientist's observations on transesterification patterns of TMP with FAMES from vegetable oils, focusing on the physico-chemical aspects. Some of these points have already been made above.

As per [14] the maximum yield of TMP triester could not be determined due to the unreliable approximation of the calculated curves, particularly when

scrutinizing the process at high temperature. Consequently, the hypothesis that the said process is a second-order reaction can be dismissed. It should be noted that most authors considering the kinetic laws of the process, which involve three reversible serial-parallel reactions, encounter difficulties when determining the formation of TMP triester. The authors [13] utilized the LINGO software to conduct "classical" processing of experimental data for modelling. The correspondence between the experimental data and the theoretically estimated values of the parameters of the mathematical model was achieved within the experimental error. Under optimal conditions (temperature of 120 °C, a molar ratio of methyl oleic acid to trimethylolpropane of 4:1, a catalyst amount of 0.9% w/w, a pressure of 20 mbar, and a reaction time of 2 h), TETMP was produced at a maximum yield of 85.47%. However, when the reagent ratio was increased to 7:1, the final product yield decreased to 68.83%, contradicting the provided process scheme. Research described in [15-17] confirms the detrimental impacts of excessive FAME.

The effect of microwave radiation on the transesterification process of FAMES and TMP derived from palm oil was investigated in a study conducted by [18, 19], following the same procedural conditions as [13]. The experiment revealed that the activation energy for the reaction under microwave radiation was 17.0 kcal/mol, presenting a 49% reduction in comparison to the convective heat transfer method. The researchers have deduced that the process is endothermic. The positive Gibbs free energy calculated with the Eyring-Polanyi equation ($\Delta G^0 = 24.6-26.5 \text{ kcal/mol} > 0$) suggests that the reaction is endergonic and non-spontaneous. Therefore, we can infer that the entire transesterification process is thermodynamically unfavorable. In other words, external energy is essential to perform such reactions. Consequently, the Gibbs energy rises, and the system performs work.

The ultimate concept could be critical in determining the progression of the investigated reaction. Let us examine the potential transfer of different forms of free energy between the reactants.

Typically, in biochemical processes, reactions exhibit an endergonic nature whereby the entropy components of free energy play a significant role. It is the change in these components that determines the Gibbs free energy. The energy for such processes is stored in high-energy intermediate metabolites, which then transfer the energy to other reagents through vibrations or the formation of an atypical structure. Structural and geometric alterations, as well as modifications in the entropy component of the Gibbs free energy, boost the reactivity of the pseudo-artificial structure of this inter-

mediate. Said structure usually contains strained chemical bonds.

Let us consider a typical TMP possessing the structural and reactive properties of the reaction system concerned in the studied process. It is a widely accepted fact that diols, beginning with ethylene glycol, exhibit intramolecular hydrogen bonding [20]. The strength of these bonds increases as we progress towards propylene glycol and butylene glycol [21]. The "classical" TMP alkoxide (Fig. a) can be stabilized by two hydrogen bonds. Additionally, it can increase the interaction energy by 5.8 kcal/mol of hydrogen bond between uncharged OH-groups (Fig. b). This may lead to pKa values that differ significantly from those in water and can, therefore, aid in enhancing the fundamentals of catalytic reactions [22, 23].

The presence of a pair of free electrons in anion «b» in the sp³-orbital within the condensed ion facilitates the nucleophile's attack on the primary carbonyl carbon of the FAME. One of the features of ion «b» is its enormous intramolecular hydrogen bond energy reserve. The spatial interaction between multiple TMP molecules and an ionized TMP molecule, as well as the formation of intermolecular hydrogen bonds, should be considered ineffective and energy-intensive.

Let us comprehend the intricacies of the mechanism of TMP and FAME transesterification base-catalytic process, which leads to the development of two initial intermediate products in reversible series-parallel reactions. Literature analysis of the kinetics of this process, as shown in Scheme 1, suggests that such reactions are generally problem-free.

This section does not delve into the interactions between TMP or METMP anions. However, during the second stage of DETMP formation, the steric

obstacles are overcome with ease, despite initial expectations (see Scheme 2).

Thus, any doubts concerning steric hindrances to the formation of the intermediate product in the second stage of transesterification are rejected by depicting the METMP molecule as a compact anion with a free electron pair on the hydroxyl oxygen atom, stabilized by the intramolecular hydrogen bond of the remaining OH-group, which can effortlessly engage with the new FAME molecule (Fig. c).

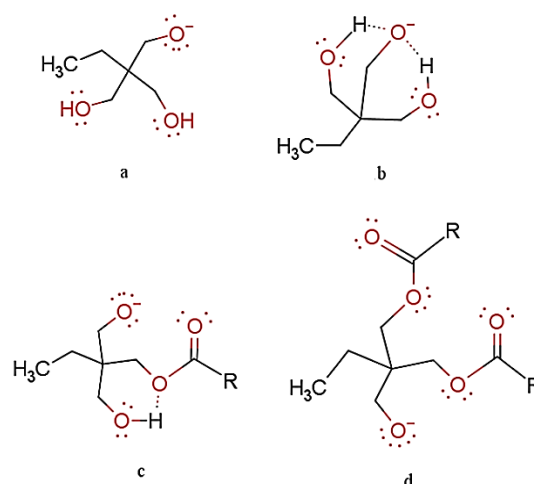
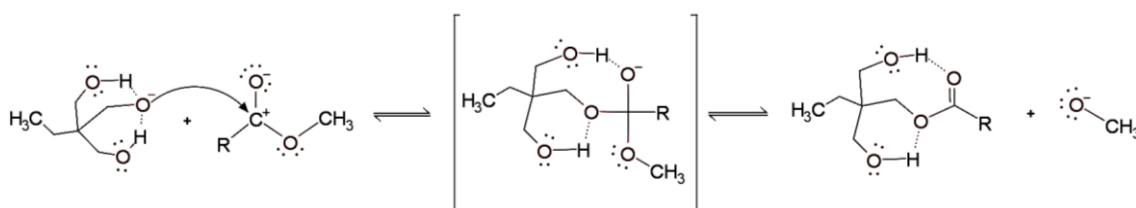
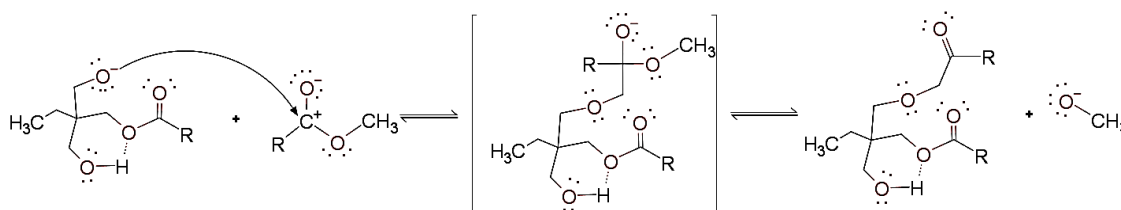


Fig. The structure of a single charged TMP molecule is illustrated variably, with options that exclude hydrogen bonds (a), with two intramolecular hydrogen bonds (b), one intramolecular hydrogen bond located in the METMP-ion (c), and DETMP-ion without intramolecular hydrogen bonds (d)

Рис. Структура однозарядной молекулы ТМП проиллюстрирована по-разному: без водородных связей (а), с двумя внутримолекулярными водородными связями (б), одной внутримолекулярной водородной связью, расположенной в МЭТМП-ионе (с), и ДЭТМП-ионе без внутримолекулярных водородных связей (д)



Scheme 1. First stage of reaction
Схема 1. Первая стадия реакции



Scheme 2. Second stage of reaction
Схема 2. Вторая стадия реакции

The formation of TMP mono- and diesters in these transformation schemes seems to be greatly facilitated by intramolecular hydrogen bonding. They significantly increased the nucleophilicity of the hydroxyl anion of TMP upon interaction with the carboxyl center of the FAME molecule (during the formation of METMP).

The changed nucleophilicity of the oxygen atom in TMP or METMP is merely one facet of the entire process. A considerable amount of energy is expended on altering the entropy of the reaction system during the restructuring of the molecule, such as in creating a compact structure of type «b», by ordering the methylol branches of TMP [21, 22]. In other words, part of the entropy of the initial reactants' free energy was transformed into the free energy of the products.

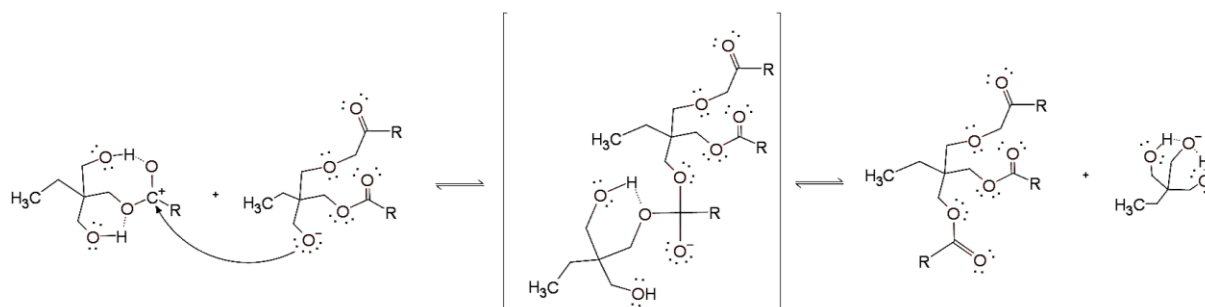
What occurs during the third stage of transesterification? The DETMP anion (shown in Fig. d) lacks an intramolecular hydrogen bond in this scenario. Is this a result of the final stage of producing the TMP

triester being the only challenging aspect of the "classical" mathematical depiction of the three-step transesterification process?

HYPOTHESES

The TMP diester anion does not possess intramolecular hydrogen bonds that can effectively activate the oxygen anion, yet it operates as a nucleophile. Tri-substituted TMP is produced during the third stage of transesterification, with the reaction proceeding differently from the usual sequential three-step reactions traditional order.

Let us visualize a situation where the carbonyl carbon atom in the ester fragment of METMP interacts with the DETMP anion (Scheme 3). This allows us to replicate the standard process of catalytic transesterification of esters with alcohols, where the anion approaches the same carboxyl carbon atom in the METMP and FAME molecule.



Scheme 3. Third stage of reaction
Схема 3. Третья стадия реакции

In addition, it is widely acknowledged that the negative charge of the transition state or intermediate oxygen must be delocalized over all three oxygen atoms. Consequently, the resulting intermediate now bears a partial negative charge on all three of its oxygen atoms. It is not difficult to predict the upcoming events. The TMP ion forms intramolecular hydrogen bonds and takes on the structure of anion «b», which excludes a fragment with the structure of a trisubstituted product. The energy gain resulting from the two intramolecular hydrogen bonds formed by TMP contributes to the complete transfer of charge from the METMP hydroxyl ion to the formed TMP. Without the formation of ion «b» featuring a compact structure, rejection of the anion is unfeasible. It is sufficient to recall that each intramolecular hydrogen bond in a polyol anion generates an energy reserve of 5.8 kcal/mol (refer to above). Since the formation of intramolecular hydrogen bonds is, first of all, a change in entropy that occurs during charge transfer from the DETMP anion to the resulting

TMP, we can generally speak of the occurrence of an endergonic reaction. Part of the free energy from the interplay between the DETMP anion and the electrophilic centre of METMP was utilized in forming the TMP anion with intramolecular hydrogen bonds (Fig. b).

Therefore, a remarkable effect has been observed in the formation mechanism of trisubstituted TMP esters. Specifically, mono-substituted TMP functions as an acyl group carrier from FAME to substituted TMP.

CONCLUSION AND OUTLOOK

The article outlines the different formations of mono-, di-, and triesters of trimethylolpropane when alcoholysis of FAME and TMP occurs. The monoester-diester reaction advances the synthesis of free TMP and the triester, leading to non-congruent experimental kinetic data and the series-parallel process scheme.

High-energy intramolecular bonds within the TMP anion or its anionic fragment of a monosubstituted derivative are significant in the first two stages of

sequential reactions in this scheme. This is a characteristic of the involvement of polyols in transesterification processes when alkali metal bases or alcoholates are used as catalysts. The energy of each intramolecular hydrogen bond is 5.8 kcal/mol. This energy is not lost when the TMP anion (or its fragment in METMP) interacts with the electrophilic center of FAME. Instead, it is transferred to the rearrangement of the ester moiety of the FAME as part of the free energy of rearrangement of the methoxyl groups of the anion. Thus, an endergonic reaction occurs.

There are two reactions occurring in this process. Firstly, the destruction of the intramolecular hydrogen bonds of the reacting TMP ion, and secondly, the electronic rearrangement of the ether center of FAME. A portion of the free energy released during the second reaction is transferred to the first reaction.

In the instance of the reaction involving mono-substituted and disubstituted TMP esters, the reverse reaction takes place. The DETMP anion interacts with the carbonyl atom of the ester group of METMP, transferring electrons to the transition state TMP oxygen atom. Intramolecular hydrogen bonds are formed, and the newly formed type «b» ion is separated from the reaction complex. Two reactions also occur here: the reorganization of the ester group in the newly formed TETMP and the formation of anionic complex 1b. In this instance, stabilization of the anionic TMP complex

arises from the formation of two hydrogen bonds, which leads to the discharge of free energy.

The endergonic nature of the TMP alkylation reaction, as the authors suggest, is confirmed by the formation of a high-energy TMP ion during the reaction and the release of energy during its protonation, i.e., changing the Gibbs free energy (ΔG°) of the transition to stabilize the resulting final product (METMP or DETMP) [18].

It is important to note that processes involving polyglycol ions and reactions that include the formation and breaking of intramolecular hydrogen bonds could result in either endergonic or exergonic reactions.

COMPLIANCE WITH ETHICAL STANDARDS

The search was performed in the framework of the development program "Priority-2030" of the Mendeleev University of Chemical Technology of Russia.

The authors declare the absence of a conflict of interest warranting disclosure in this article.

Исследование проводилось в рамках программы развития «Приоритет-2030» Российского химико-технологического университета им. Д.И. Менделеева.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

ЛИТЕРАТУРА

1. Reportlinker. Global Lubricants Market - SIZE, SHARE, COVID-19 IMPACT & FORECASTS UP TO 2026 [Electronic resource]. URL: https://www.reportlinker.com/p06321706/Global-Lubricants-Market-SIZE-SHARE-COVID-19-IMPACT-FORECASTS-UP-TO.html?utm_source=GNW (accessed: 22.05.2023).
2. Uosukainen E., Linko Y., Lämsä M., Tervakangas T., Linko P. Transesterification of Trimethylolpropane and Rapeseed Oil Methyl Ester. *JAOCs*. 1998. V. 75. N 11. P. 1557–1563.
3. Thanigaiselvan R., Sree Renga Raja T., Karthik R. Investigations on eco friendly insulating fluids from rapeseed and pongamia pinnata oils for power transformer applications. *J. Electr. Eng. and Technol.* 2015. V. 10. N 6. P. 2348–2355. DOI: 10.5370/JEET.2015.10.6.2348.
4. Тонконогов Б.П., Сафиева Р.З., Паренаго О.П., Попова О.В., Киякова А.Ю., Шумакаева С.З., Винокуров В.А. Использование сложных эфиров в качестве дисперсионной среды полимочевинных пластичных смазок. *Изв. вузов. Химия и хим. технология*. 2019. Т. 62. Вып. 9. С. 73–78. DOI: 10.6060/ivkkt.20196209.5909.
5. Леванова С.В., Красных Е.Л., Моисеева С.В., Сафронов С.П., Глазко Е.Л. Научные и технологические особенности синтеза новых сложнэфирных пластификаторов на основе возобновляемого сырья. *Изв. вузов. Химия и хим. технология*. 2021. Т. 64. Вып. 6. С. 69–75. DOI: 10.6060/ivkkt.20216406.6369.
6. Wang K., Wang F., Li J., Huang Z., Lou Z., Han Q., Zhao Q., Hu K. Synthesis of trimethylolpropane fatty

REFERENCES

1. Reportlinker. Global Lubricants Market - SIZE, SHARE, COVID-19 IMPACT & FORECASTS UP TO 2026 [Electronic resource]. URL: https://www.reportlinker.com/p06321706/Global-Lubricants-Market-SIZE-SHARE-COVID-19-IMPACT-FORECASTS-UP-TO.html?utm_source=GNW (accessed: 22.05.2023).
2. Uosukainen E., Linko Y., Lämsä M., Tervakangas T., Linko P. Transesterification of Trimethylolpropane and Rapeseed Oil Methyl Ester. *JAOCs*. 1998. V. 75. N 11. P. 1557–1563. DOI: 10.1007/s11746-998-0094-8.
3. Thanigaiselvan R., Sree Renga Raja T., Karthik R. Investigations on eco friendly insulating fluids from rapeseed and pongamia pinnata oils for power transformer applications. *J. Electr. Eng. Technol.* 2015. V. 10. N 6. P. 2348–2355. DOI: 10.5370/JEET.2015.10.6.2348.
4. Tonkonogov B.P., Kilyakova A.Y., Shumakaeva S.Z., Vinokurov V.A., Safieva R.Z., Popova O.V., Parenago O.P. Using of esters as dispersion medium of polyurea plastic greases. *ChemChemTech*. 2019. V. 62. N 9. P. 73–78. DOI: 10.6060/ivkkt.20196209.5909.
5. Levanova S. V., Krasnykh E. L., Moiseeva S. V., Safronov S. P., Glazko I. L. Scientific and technological features of the synthesis of new ester plasticizers based on renewable raw materials. *ChemChemTech*. 2021. V. 64. N 6. P. 69–75. DOI: 10.6060/ivkkt.20216406.6369.
6. Wang K., Wang F., Li J., Huang Z., Lou Z., Han Q., Zhao Q., Hu K. Synthesis of trimethylolpropane fatty

- acid triester as a high performance electrical insulating oil. *J. Ind. Crops Products*. 2019. V. 142. P. 111834. DOI: 10.1016/J.INDCROP.2019.111834.
- Negi P., Singh Y., Tiwari K.** A review on the production and characterization methods of bio-based lubricants. *Mater. Today: Proc.* 2021. V. 46. P. 10503–10506. DOI: 10.1016/J.MATPR.2020.12.1211.
 - Nie J., Shen J., Shim Y.Y., Tse T.J., Reaney M.J.T.** Synthesis of Trimethylolpropane Esters by Base-Catalyzed Transesterification. *Europ. J. Lipid Sci. Technol.* 2020. V. 122. N 3. P. 1–10. DOI: 10.1002/ejlt.201900207.
 - Shrivastava S., Prajapati P., Virendra, Srivastava P., Lodhi A.P.S., Kumar D., Sharma V., Srivastava S.K., Agarwal D.D.** Chemical transesterification of soybean oil as a feedstock for stable biodiesel and biolubricant production by using Zn Al hydrotalcites as a catalyst and perform tribological assessment. *J. Ind. Crops Prod.* 2023. V. 192. P. 116002. DOI: 10.1016/J.INDCROP.2022.116002.
 - 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 хим. технологии*. 2022. Т. 17. Вып. 1. С. 7–17. DOI: 10.32362/2410-6593-2022-17-1-7-17.
 - Yunus R., Fakhru A., Ooi T.L., Biak D.R.A., Iyuke S.E.** Kinetics of Transesterification of Palm-Based Methyl Esters with Trimethylolpropane. *JAOCs*. 2004. V. 81. N 5. P. 497–503. DOI: 10.1007/s11746-004-0930-7.
 - Abd Hamid H., Yunus R., Choong T.S.Y.** Utilization of MATLAB to simulate kinetics of transesterification of palm oil-based methyl esters with trimethylolpropane for biodegradable synthetic lubricant synthesis. *Chem. Prod. Proc. Model.* 2010. V. 5. N 1. DOI: 10.2202/1934-2659.1458.
 - Elmelawy M.S., El-Meligy A., Mawgoud H.A., Morshedy A.S., Hanafy S.A., El-sayed I.E.** Synthesis and kinetics study of trimethylolpropane fatty acid triester from oleic acid methyl ester as potential biolubricant. *Biomass Convers. Biorefin.* 2023. V. 13. P. 1645-1657. DOI: 10.1007/s13399-020-01220-z.
 - Menkiti M., Anaehobi H., Nnaji P.** Process optimization and kinetics of biolubricant synthesis from fluted pumpkin seed. *Europ. Sci. J.* 2015. V. 11. N 27. P. 30-47.
 - Ramadhas A.S., Jayaraj S., Muraleedharan C.** Biodiesel production from high FFA rubber seed oil. *Fuel*. 2005. V. 84. N 4. P. 335–340. DOI: 10.1016/J.FUEL.2004.09.016.
 - Uosukainen E., Linko Y.Y., Lämsä M., Tervakangas T., Linko P.** Transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants. *J. Am. Oil Chem. Soc.* 1998. V. 75. N 11. P. 1557–1563. DOI: 10.1007/S11746-998-0094-8.
 - Амирханов И.Р., Калева Е.С., Санчы Д.М., Гладышева А.А., Кочановская А.А.** Определение состава продуктов перэтерификации метиловых эфиров жирных кислот методом ¹H-ЯМР. *Усп. в химии и хим. технологии*. 2018. Т. 32. Вып. 5. С. 64-66.
 - Aziz N.A.M., Hamid H.A., Yunus R., Abbas Z., Omar R., Rashid U., Syam A.M.** Kinetics and thermodynamics of synthesis of palm oil-based trimethylolpropane triester using microwave irradiation. *J. Saudi Chem. Soc.* 2020. V. 24. N 8. P. 552–566. DOI: 10.1016/J.JSCS.2020.05.006.
 - Lieu T., Yusup S., Moniruzzaman M.** Kinetic study on microwave-assisted esterification of free fatty acids derived acid triester as a high performance electrical insulating oil. *J. Ind. Crops Products*. 2019. V. 142. P. 111834. DOI: 10.1016/J.INDCROP.2019.111834.
 - Negi P., Singh Y., Tiwari K.** A review on the production and characterization methods of bio-based lubricants. *Mater. Today: Proc.* 2021. V. 46. P. 10503–10506. DOI: 10.1016/J.MATPR.2020.12.1211.
 - Nie J., Shen J., Shim Y.Y., Tse T.J., Reaney M.J.T.** Synthesis of Trimethylolpropane Esters by Base-Catalyzed Transesterification. *Europ. J. Lipid Sci. Technol.* 2020. V. 122. N 3. P. 1–10. DOI: 10.1002/ejlt.201900207.
 - Shrivastava S., Prajapati P., Virendra, Srivastava P., Lodhi A.P.S., Kumar D., Sharma V., Srivastava S.K., Agarwal D.D.** Chemical transesterification of soybean oil as a feedstock for stable biodiesel and biolubricant production by using Zn Al hydrotalcites as a catalyst and perform tribological assessment. *J. Ind. Crops Prod.* 2023. V. 192. P. 116002. DOI: 10.1016/J.INDCROP.2022.116002.
 - 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.* 2022. V. 17. N 1. P. 7–17 (in Russian). DOI: 10.32362/2410-6593-2022-17-1-7-17.
 - Yunus R., Fakhru A., Ooi T.L., Biak D.R.A., Iyuke S.E.** Kinetics of Transesterification of Palm-Based Methyl Esters with Trimethylolpropane. *JAOCs*. 2004. V. 81. N 5. P. 497–503. DOI: 10.1007/s11746-004-0930-7.
 - Abd Hamid H., Yunus R., Choong T.S.Y.** Utilization of MATLAB to simulate kinetics of transesterification of palm oil-based methyl esters with trimethylolpropane for biodegradable synthetic lubricant synthesis. *Chem. Prod. Proc. Model.* 2010. V. 5. N 1. DOI: 10.2202/1934-2659.1458.
 - Elmelawy M.S., El-Meligy A., Mawgoud H.A., Morshedy A.S., Hanafy S.A., El-sayed I.E.** Synthesis and kinetics study of trimethylolpropane fatty acid triester from oleic acid methyl ester as potential biolubricant. *Biomass Convers. Biorefin.* 2023. V. 13. P. 1645-1657. DOI: 10.1007/s13399-020-01220-z.
 - Menkiti M., Anaehobi H., Nnaji P.** Process optimization and kinetics of biolubricant synthesis from fluted pumpkin seed. *Europ. Sci. J.* 2015. V. 11. N 27. P. 30-47.
 - Ramadhas A.S., Jayaraj S., Muraleedharan C.** Biodiesel production from high FFA rubber seed oil. *Fuel*. 2005. V. 84. N 4. P. 335–340. DOI: 10.1016/J.FUEL.2004.09.016.
 - Uosukainen E., Linko Y.Y., Lämsä M., Tervakangas T., Linko P.** Transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants. *J. Am. Oil Chem. Soc.* 1998. V. 75. N 11. P. 1557–1563. DOI: 10.1007/S11746-998-0094-8.
 - Amirkhanov I.R., Voronov M.S., Kaleeva E.S., Sanchy D.M., Gladysheva A.A.** Determination of fatty acid methyl esters transesterification products using ¹H-NMR. *Usp. Khim. Khim. Tekhnol.* 2018. V. 32. N 5. P. 64–66 (in Russian).
 - Aziz N.A.M., Hamid H.A., Yunus R., Abbas Z., Omar R., Rashid U., Syam A.M.** Kinetics and thermodynamics of synthesis of palm oil-based trimethylolpropane triester using microwave irradiation. *J. Saudi Chem. Soc.* 2020. V. 24. N 8. P. 552–566. DOI: 10.1016/J.JSCS.2020.05.006.
 - Lieu T., Yusup S., Moniruzzaman M.** Kinetic study on microwave-assisted esterification of free fatty acids derived from Ceiba pentandra Seed Oil. *Bioresour. Technol.* 2016. V. 211. P. 248–256. DOI: 10.1016/J.BIORTECH.2016.03.105.

- from Ceiba pentandra Seed Oil. *Bioresour. Technol.* 2016. V. 211. P. 248–256. DOI: 10.1016/J.BIORTECH.2016.03.105.
20. **Howard D.L., Jørgensen P., Kjaergaard H.G.** Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy. *J. Am. Chem. Soc.* 2005. V. 127. N 48. P. 17096–17103. DOI: 10.1021/ja055827d.
 21. **Takahashi K.** Theoretical study on the effect of intramolecular hydrogen bonding on OH stretching overtone decay lifetime of ethylene glycol, 1,3-propanediol, and 1,4-butanediol. *Phys. Chem. Chem. Phys.* 2010. V. 12. N 42. P. 13950–13961. DOI: 10.1039/C0CP00788A.
 22. **Shokri A., Schmidt J., Wang X. Bin, Kass S.R.** Hydrogen bonded arrays: The power of multiple hydrogen bonds. *J. Am. Chem. Soc.* 2012. V. 134. N 4. P. 2094–2099. DOI: 10.1021/JA2081907.
 23. **Кольцов Н.И.** Описание критических форм множественности стационарных состояний в кинетике каталитических реакций. *Изв. вузов. Химия и хим. технология.* 2023. Т. 66. Вып. 8. С. 6–21. DOI: 10.6060/ivkkt.20236608.6793.
 20. **Howard D.L., Jørgensen P., Kjaergaard H.G.** Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy. *J. Am. Chem. Soc.* 2005. V. 127. N 48. P. 17096–17103. DOI: 10.1021/ja055827d.
 21. **Takahashi K.** Theoretical study on the effect of intramolecular hydrogen bonding on OH stretching overtone decay lifetime of ethylene glycol, 1,3-propanediol, and 1,4-butanediol. *Phys. Chem. Chem. Phys.* 2010. V. 12. N 42. P. 13950–13961. DOI: 10.1039/C0CP00788A.
 22. **Shokri A., Schmidt J., Wang X. Bin, Kass S.R.** Hydrogen bonded arrays: The power of multiple hydrogen bonds. *J. Am. Chem. Soc.* 2012. V. 134. N 4. P. 2094–2099. DOI: 10.1021/JA2081907.
 23. **Kol'tsov N.I.** Description of Critical Forms of Multiple Station States in the Kinetics of Catalytic Reactions. *ChemChemTech. [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2023. V. 66. N 8. P. 6–21. DOI: 10.6060/ivkkt.20236608.6793.

Поступила в редакцию 16.04.2024

Принята к опубликованию 27.06.2024

Received 16.04.2024

Accepted 27.06.2024