Chemical Journal of Kazakhstan
Volume 4, Number 80(2022), 89-99 https://doi.org/10.51580/2022-3/2710-1185.97

УДК 661.74

INVESTIGATING COMPUTATIONALLY THE FORMATION MECHANISM OF METHYLTRIPHENYLPHOSPHONIUM BROMIDE AND ETHYLENE GLYCOL - BASED NATURAL DEEP EUTECTIC SOLVENT AND ITS APPLICATIONS IN THE PURIFICATION OF BIOFUEL

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Abstract. *Introduction.* Biodiesel is a new replacement for various types of traditional fuels. There are many advantages of biofuel, including renewable ones, of less-flammability, and cheaper as compared with the traditional fuel, reducing the greenhouse gas emissions, and others. However, the primary challenge of the biofuel production in the large-scale production is related to the purification of its undesirable impurities such as glycerol, water, methanol, soap/catalyst, free fatty acids, glycerides and others. Herein, glycerol is an undesired impurity of biofuel, which leads to the problems including i) deposition in the bottom of the fuel tank, ii) decantation, iii) engine durability problems, iv) setting problems, v) injector fouling, vi) storage problem, and others. Consequently, there are many ways to remove glycerol, and herein, the one alternative is the extraction of glycerol from biodiesel via the Natural Deep Eutectic Solvents. *The goal of this work.* The mixture of a methyltriphenylphosphonium bromide and ethylene glycol, as a the Natural Deep Eutectic Solvent is effective in removing glycerol from biofuel. *Methodology.* We have investigated the formation mechanism of methyltriphenylphosphonium bromide and ethylene glycol, as the Natural Deep Eutectic Solvents, and the extraction of glycerol from biofuel via the Natural Deep Eutectic Solvents via implementing the Quantum Chemical Calculations, using the HyperChem software. *Results.* The results imply that there are strong ionic and covalent interactions between bromine, methyltriphenylphosphonium and ethylene glycol according to the optimized structures, bond length, energies, and others. *Conclusion.* The extraction of glycerol from biofuel is mainly achieved via bromine ion of the Natural Deep Eutectic Solvent, and the structure of the Natural Deep Eutectic Solvent is remaining unchanged after this process, meaning its stability, and can be reused.

Keywords: methyltriphenylphoshonium bromide, ethylene glycol, glycerol, biofuel, extraction

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Citation: Zh.A. Sailau, N.Zh. Almas, K. Toshtai, A.A. Aldongarov, Y.A. Aubakirov. Investigating computationally the formation mechanism of methyltriphenylphosphonium bromide and ethylene glycol - based natural deep eutectic solvent and its applications in the purification of biofuel. *Chem. J. Kaz.*, **2022**, 4*(80),* 89-99. DOI: https://doi.org/10.51580/2022-3/2710-1185.97

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1. Introduction

There has been a requirement of the new world demand for the replacement of the energy sources, based on the traditional petroleum-based fuel, due to the security issue caused by crude oil, continuously burning of petroleum-based fuels, climate change, and others [1-3]. At this stage, the biofuel is one of the important biodegradable fuels, which can replace traditional petroleum-based fuels, including natural gas, coal, and oil. In this regard, biodiesel is an oil-based fuel, containing alkyl ester long chains, and is mainly produced via the reaction of lipids with an alcohol to obtain fatty acid monoesters. Biodiesel could be easily prepared from animal fats, vegetable oils, oleaginous microbial biomass, pine trees, soybean and others [2-5]. Herein, there are many advantages of biofuel including renewable, less-flammability, and cheaper fuels as compared with the traditional fuel, reducing greenhouse gas emissions, and others. Although, the major challenge of biofuel production in the large scale is connected with the purification of its undesired impurities, including glycerides, glycerol, water, methanol, soap/catalyst, free fatty acids, and others [3-6]. Due to this, it is highly important to remove glycerol from the biofuels content. Glycerol causes many problems in the biofuel content including i) storage problems, ii) setting problems, iii) injector fouling, iv) engine durability, v) deposition in the bottom of the fuel tank, vi) decantation and others [6-10]. At this stage, there are many ways to remove glycerol from biofuel, and one of the important ways is related to the extraction of glycerol from biofuel by the Natural Deep Eutectic Solvents.

In the modern society, the Natural Deep Eutectic Solvents are new types of Deep Eutectic Solvents, Ionic Liquids, and traditional solvents. Hence, the Natural Deep Eutectic Solvents have attracted great attention of the scientists, because of their many advantages, including the formation from the natural compounds, high stabilization and extraction potential, bio-degradable, simple preparation technique, low cost, sustainability, low volatility and others [10-13]. Sequentially, there are many applications of the Natural Deep Eutectic Solvents, including i) stabilization, enzyme reactions, iii) extraction, iv) biotransformation, v) bioactivity enhancement, vi) purification of biofuels and others [13-15]. Interestingly, some Natural Deep Eutectic Solvents have been explored, which can extract glycerol from biofuel [13-17]. For example, 1:1 mixture of glycerol and quaternary ammonium salt has been implemented to remove glycerol from biofuel, and consequently, it has been found that choline chloride and glycerol - based Natural Deep Eutectic Solvent has been effective in removal of glycerol from the biofuel content [18]. For instance, 51 wt% of glycerol has been extracted from biofuel via choline chloride and glycerol - based Natural Deep Eutectic Solvent at the ratio of 1:1 [18]. Moreover, choline chloride/trifluoroacetamide, and choline chloride/ethylene glycol - based Natural Deep Eutectic Solvents have been shown also as an effective for the extraction of glycerol from palm oil derived biofuel [19]. In addition, Shahbaz et al. reveal that the Natural Deep Eutectic Solvents formed from methyltriphenylphosphonium bromide and ethylene glycol are highly effective for the removal of the glycerols, diglycerides, and monoglycerides from the biofuels content [20]. In this line, a comprehensive investigation of the formation mechanism of methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvents and their application in the extraction of glycerol from biofuel via Natural Deep Eutectic Solvents are important at the molecular level [17-25].

Herein, we are going to study the intermolecular formation of the trimethylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvents and their extraction ability of glycerol from biofuel, using the quantum chemical calculation. We had implemented the PM3 method of the HyperChem software for quantum chemical calculations. Basically, we have studied the optimized structures, energies, molecular electrostatic maps, and molecular orbitals for the formation of the Natural Deep Eutectic Solvents and extraction of glycerol from biofuel via the Natural Deep Eutectic Solvents.

2. Methods and materials

The HyperChem with the PM3 method have been implemented for quantum chemical calculations in order to get optimized structures, calculate molecular electrostatic potentials, molecular orbitals, bond distances, and energies[25]. Herein, we have selected methyltriphenylphosphonium bromide (MTPPBr), ethylene glycol as a computational model of the Natural Deep Eutectic Solvents (NADES), and glycerol with methyl linoleate as a model of biofuel.

The designed simulation systems are presented in Table 1. As can be seen in Table 1, initially we have performed quantum chemical calculations for pure methyltriphenylphosphonium bromide (MTPPBr), ethylene glycol, and then the mixture of methyltriphenylphosphonium bromide (MTPPBr) and ethylene glycol as a Natural Deep Eutectic Solvent. After that, we have simulated a pure modeled biofuel, which consists of glycerol and methyl linoleate as a mixture and as a separate form. Finally, we have performed the quantum chemical calculations for the process of extraction of glycerol from biofuel via methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvents.

Table 1 – The designed simulation system for the study of the Natural Deep Eutectic Solvent Its formation and application in the extraction of glycerol from biofuel

MTPPBr	EthyleneGlycol	Glycerol	MethylLinoleate	IntendedPurpose
1	-	-	-	PureMTPPBr
-	1	-	-	PureEthyleneGlycol
1	1	-	-	NADES
-	-	1	-	PureGlycerol
-	-	-	1	PureBiofuel
-	-	1	1	Biofuel
1	1	1	1	Extraction

$$E_{binding} = E_{AB} – (E_A – E_B) \qquad (1)$$

The calculation formula for binding energy is shown in equation 1. By the analytical calculations of the second derivatives of energy, stationary points have been confirmed to be the minima for their potential energy surfaces, respectively.

3. Results

The formation mechanism of methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvents. The 2D structures of methyltriphenylphosphonium bromide, ethylene glycol, glycerol, and methyl linoleate are presented in Figure 1. Firstly, to study the intermolecular interactions for the formation of the Natural Deep Eutectic Solvents, we have studied the methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvents in terms of the optimized structures, molecular electrostatic maps, molecular orbitals and energies. We have begun our quantum chemical calculations analysis on methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solventsas can be seen in Figure 2, 3, 4 and in Table 2.

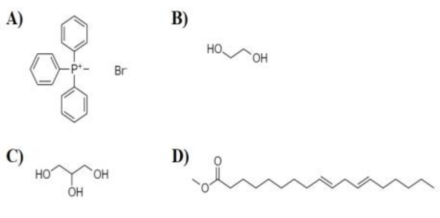

Figure 1 -The 2D chemical structures of A) methyltriphenylphosphonium bromide, B) ethylene glycol, C) glycerol, and D) methyl linoleate.

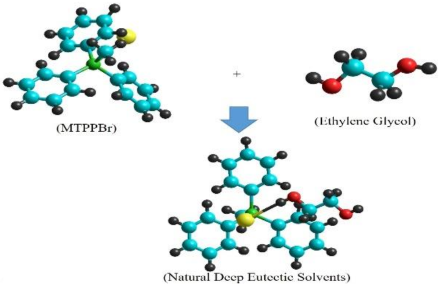

Figure 2 – The quantum chemical calculation - based optimized structures of methyltriphenylphosphonium bromide, ethylene glycol, and the Natural Deep Eutectic Solvents. The key colors: black: hydrogen; grey: carbon; green: phosphorus; red: oxygen; yellow: bromide.

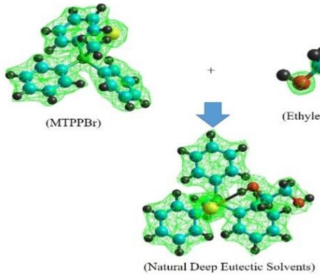

Figure 3 – The quantum chemical calculation - based molecular electrostatic maps of methyltriphenylphosphonium bromide, ethylene glycol, and the Natural Deep Eutectic Solvents.

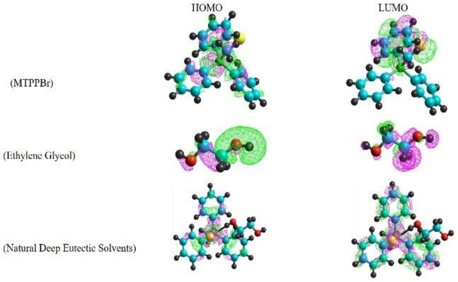

Figure 4 – The quantum chemical calculation - based molecular orbitals of methyltriphenylphosphonium bromide, ethylene glycol, and the Natural Deep Eutectic Solvents.

Table 2 – Energies for the formation of the Natural Deep Eutectic Solvents. Unit: kcal/mol

	MTPPBr	Ethylene Glycol	Natural Deep Eutectic Solvent
Energy (kcal/mol)	-69182.50	-21044.70	-90331.40

Extraction of Glycerol from Biofuel via the Natural Deep Eutectic Solvents. Secondly, we have studied the extraction of glycerol from biofuel via the Natural Deep Eutectic Solvents. Herein, we have analyzed quantum chemically calculated optimized structures, molecular electrostatic maps, molecular orbitals, and energies for extraction process of glycerol from biofuel via the Natural Deep Eutectic Solvents as can be seen in Figure 5-7 and in Table 3.

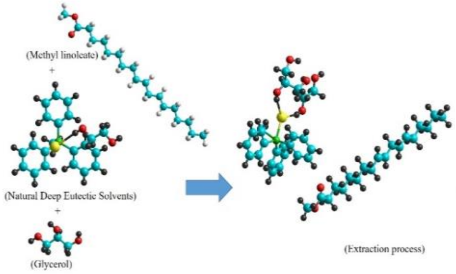

Figure 5 – The quantum chemical calculation - based optimized structures of the Natural Deep Eutectic Solvents, glycerol, and methyl linoleate. The key colors: black: hydrogen; grey: carbon; green: phosphorus; red: oxygen; yellow: bromide.

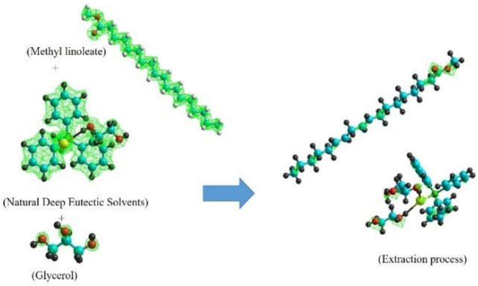

Figure 6 – The quantum chemical calculation - based molecular electrostatic maps of the Natural Deep Eutectic Solvents, glycerol, and methyl linoleate. The key colors: black: hydrogen; grey: carbon; green: phosphorus; red: oxygen; yellow: bromide.

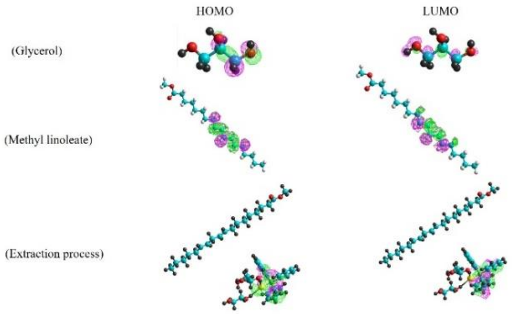

Figure 7 – The quantum chemical calculation - based molecular orbitals of the Natural Deep Eutectic Solvents, glycerol, and methyl linoleate. The key colors: black: hydrogen; grey: carbon; green: phosphorus; red: oxygen; yellow: bromide.

Table 3 – Energies for the formation of the Natural Deep Eutectic Solvents, glycerol, and methyl linoleate. Unit: kcal/mol

	Glycerol	Methyl Linoleate	Natural Deep Eutectic Solvent + Biofuel
Energy (kcal/mol)	-31376.50	-77595.70	-199310.00

4. Discussion

The first part of our work has been devoted to the study the formation of methyltriphenylphosphonium bromide ethylene glycol - based Natural Deep Eutectic Solvents. Initially, we have built and optimized the geometrical structure of a pure methyltriphenylphosphonium bromide, ethylene glycol, and their mixture as a Natural Deep Eutectic Solvent. Figure 2 has illustrated the results of the optimized structures of the methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvent. It can be seen clearly that bromine ion acts as a connecting agent between the methyltriphenylphosphonium and ethylene glycol. Moreover, the shortest distances between bromine and methyltriphenylphosphonium, and between bromine and ethylene glycol have been 4.92 Å and 4.01 Å, respectively.

Secondly, we have studied the molecular electrostatic maps for the geometrical structure of a pure methyltriphenylphosphonium bromide, ethylene glycol, and their mixture as a Natural Deep Eutectic Solvent. Figure 3 has illustrated the results of the molecular electrostatic maps of the methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvent. It can be seen that the charges are localized around the bromine ion which is located between methyltriphenylphosphonium and ethylene glycol.

Thirdly, the HOMO and LUMO molecular orbitals have been represented for the geometrical structure of a pure methyltriphenylphosphonium bromide, ethylene glycol, and their mixture as a Natural Deep Eutectic Solvent. Figure 4 has illustrated the results of HOMO-LUMO of the methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvent. We can note from Figure 4 that the HOMO orbital is mainly located around bromine ion, while LUMO is populated around phenyl group of the formed Natural Deep Eutectic Solvent.

Fourthly, the total energy for MTPPBr has been -69182.50 kcal/mol, and the total energy for ethylene glycol has been -21044.70 kcal/mol, while the total energy for the formation of Natural Deep Eutectic Solvent has been around -90331.40 kcal/mol. Herein, the binding energy for this formation process of the Natural Deep Eutectic Solvent can be calculated as below:

$E_{binding}$= -90331.40 kcal/mol – (-69182.50 kcal/mol - 21044.70 kcal/mol) = -104.2 kcal/mol

Herein, a low value of $E_{binding}$ as observed in the above calculation suggests a low melting point of the methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvent, as compared with the constituent components.

The second part of our work is related to the extraction of glycerol from biofuel via the Natural Deep Eutectic Solvents. Initially, we have been built and optimized the geometrical structure of a pure glycerol, methyl linoleate, and their mixture as a biofuel with the Natural Deep Eutectic Solvent. Figure 5 has illustrated the results of the optimized structures of the glycerol, methyl linoleate-based biofuel in the presence of the Natural Deep Eutectic Solvent. It can be seen clearly that bromine ion acts as a connecting agent between the glycerol, methyltriphenylphosphonium and ethylene glycol. Moreover, the shortest distances between bromine and glycerol, between bromine and methyltriphenylphosphonium, and between bromine and ethylene glycol have been 2.43 Å, 2.62 Å and 2.65 Å, respectively.

Secondly, we have studied the molecular electrostatic maps for the geometrical structure of a pure glycerol, methyl linoleate, and their mixture as a biofuel with the Natural Deep Eutectic Solvent. Figure 6 has illustrated the results of molecular electrostatic maps of the glycerol, methyl linoleate, and their mixture as a biofuel with the Natural Deep Eutectic Solvent. It can be seen that the charges are localized around the bromine ion, which is located via glycerol, methyltriphenylphosphonium and ethylene glycol.

Thirdly, the HOMO and LUMO molecular orbitals have been represented for the geometrical structure of a glycerol, methyl linoleate, and their mixture as a biofuel with the Natural Deep Eutectic Solvent. Figure 7 has illustrated the results of HOMO-LUMO of the glycerol, methyl linoleate, and their mixture as a biofuel with the Natural Deep Eutectic Solvent. We can note from Figure 7 that the HOMO orbital is mainly located around bromine ion, while LUMO is populated around phenyl group of the formed Natural Deep Eutectic Solvent.

Fourthly, the total energy for glycerol has been -31376.50 kcal/mol, and the total energy for methyl linoleate has been -77595.70 kcal/mol, and the formation energy of the Natural Deep Eutectic Solvent has been -90331.40 kcal/mol, while the total energy for the extraction process of glycerol from biofuel by the Natural

Deep Eutectic Solvent has been around -199310.00 kcal/mol. Herein, the binding energy for this formation process of the Natural Deep Eutectic Solvent can be calculated as below:

$E_{binding}$= -199310.00 kcal/mol – (-31376.50 kcal/mol -77595.70 kcal/mol -90331.40 kcal/mol) = -6.40 kcal/mol

Herein, a low value of $E_{binding}$ as observed in the above calculation suggesting a preferred extraction efficiency of the glycerol from methyl linoleate-based biofuel via the Natural Deep Eutectic Solvents.

5. Conclusion

In this work, the formation of methyltriphenylphosphonium bromide and ethylene glycol - based Natural Deep Eutectic Solvents and then the extraction of glycerol from biofuel via Natural Deep Eutectic Solvents have been studied via the quantum chemical calculations.

The first part of our work has demonstrated that bromine ion acts as a connecting agent between the methyltriphenylphosphonium and ethylene glycol according to the optimized structures, molecular electrostatic maps, molecular orbitals, and energies.

In the the second part of our work we have concluded that the bromine ion acts as an extracting and connecting agent within glycerol, the methyltriphenylphosphonium and ethylene glycol.

The current work could help us make the rational design and improve the extraction process of glycerol from biofuel by the Natural Deep Eutectic Solvents.

Funding: This research has been supported by the grant №AP08052504 from the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan.

Conflict of Interests: No conflict of interests.

ТАБИҒИ ТЕРЕҢ ЭВТЕКТИКАЛЫҚ ЕРІТКІШТІҢ МЕТИЛТРИФЕНИЛФОСФОРЛЫ БРОМИДІ ЖӘНЕ ЭТИЛЕНГЛИКОЛ НЕГІЗІНДЕГІ ТҮЗІЛУ МЕЗАНИЗМІН ЖӘНЕ ОНЫҢ БИООТЫНДЫ ТАЗАЛАУДА ҚОЛДАНЫЛУЫН ЕСЕПТІК ЖОЛМЕН ЗЕРТТЕУ

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Түйіндеме. *Кіріспе.* Биодизель–казіргі таңда дәстүрлі отынның әртүрлі түрлерін алмастыра алатын тиімді отынның түрі. Биоотынның басқа отын түрлерінен көптеген артықшылықтары бар, оның ішінде жаңартылатын, аз тұтанғыш және дәстүрлі отынмен салыстырғанда арзанырақ, парниктік газдар шығуының азаюы және тағы басқа. Дегенмен, ауқымды өндірістегі биоотын өндірісінің негізгі міндеті оның глицерин, су, метанол, сабын/катализатор, бос майқышқылдары, глицеридтер және тағы басқа қажетсіз қоспаларын тазартумен байланысты. Бұл жерде глицеринб иоотынның қажетсіз қоспасы болып табылады, ол I) жанармай багының түбінде тұндыру, II) декантация, III) қозғалтқыштың ұзақ жұмыс істеу проблемалары, IV) орнату ақаулары, V) инжектордың ластануы, VI) сақтау мәселесі және басқалар. Демек, глицеринді жоюдың көптеген жолдары бар және мұнда бір балама – табиғи терең эвтектикалық еріткіштер арқылы биодизельден глицеринді алу. Табиғи терең евтектикалық еріткіштер басқа еріткіштерден артықшылығы бағасы арзан, экологияға зиянсыз, денсаулыққа қауіпсіз, қол жетімді және тағы басқа артықшылықтары бар. *Бұл жұмыстың мақсаты* табиғи терең эвтектикалық еріткіш ретінде метилтрифенилфосфоний бромиді мен этиленгликоль қоспасыналып, биоотыннан глицеринді осы қоспамен кетіру. *Әдістемесі.* Біз табиғи терең эвтектикалық еріткіштер ретінде метилтрифенилфосфоний бромидінің және этиленгликольдің түзілу механизмін зерттедік, содан кейін HyperChem бағдарламалық жасақтамасын пайдалана отырып, кванттық химиялық есептеулерді енгізу арқылы табиғи терең эвтектикалық еріткіштер арқылы биоотыннан глицеринді алдық. *Жұмыстың нәтижелері.* Нәтижелер оңтайландырылған құрылымдарға, байланыс ұзындығына, энергияларға және тағы басқаға сәйкес бром, метилтрифенилфосфоний және этиленгликоль арасында күшті иондық және коваленттік өзара әрекеттесулердің бар екенін көрсетеді. *Қорытынды.* Биоотыннан глицеринді алу негізінен табиғи терең эвтектикалық еріткіштің бром ионы арқылы жүзеге асырылады, ал табиғи терең эвтектикалық еріткіштің құрылымы осы процестен кейін өзгеріссіз қалады, бұл оның тұрақтылығын білдіреді және қайта пайдалануға болатын көрсетеді.

Түйінді сөздер: метилтрифенилфосфор бромид,этиленгликоль, глицерин, биоотын,экстракция

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ВЫЧИСЛИТЕЛЬНОЕ ИССЛЕДОВАНИЕ МЕХАНИЗМА ОБРАЗОВАНИЯ ПРИРОДНОГО ГЛУБОКОГО ЭВТЕКТИЧЕСКОГО РАСТВОРИТЕЛЯ НА ОСНОВЕ МЕТИЛТРИФЕНИЛФОСФОНИИ БРОМИДА И ЭТИЛЕНГЛИКОЛЯ И ЕГО ПРИМЕНЕНИЯ В ОЧИСТКЕ БИОТОПЛИВА

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Резюме. *Введение.* Биодизель – эффективное топливо, способное сегодня заменить различные виды традиционного топлива. Биотопливо имеет много преимуществ по сравнению с другими видами топлива, в том числе возобновляемость, менее воспламеняющееся и более дешевое, чем традиционное топливо, более низкие выбросы парниковых газов и многое другое. Однако основная проблема производства биотоплива в крупномасштабном производстве связана с очисткой его нежелательных примесей, таких как глицерин, вода, метанол, мыло/катализатор, свободные жирные кислоты, глицериды и другие. Здесь глицерин является нежелательной примесью биотоплива, которая приводит к проблемам, включая I) отложение на дне топливного бака, II) декантацию, III) проблемы с долговечностью двигателя, IV) проблемы с настройками, V) загрязнение форсунок, VI) проблемы с хранением и другие. Следовательно, существует множество способов удаления глицерина, и в данном случае одной из альтернатив является извлечение глицерина из биодизельного топлива с помощью натуральных растворителей глубокой эвтектики. Преимущества природных глубинных эвтектических растворителей перед другими растворителями заключаются в их дешевизне, экологичности, безопасности для здоровья, доступности и т.д. *Целью данной работы* является удаление глицерина из биотоплива смесью метилтрифенилфосфония бромида и этиленгликоля в качестве природного растворителя глубокой эвтектики. *Методология*. Мы исследовали механизм образования бромистого метилтрифенилфосфония и этиленгликоля в качестве природных растворителей глубокой эвтектики, а затем извлекли глицерин из биотоплива с помощью природных растворителей глубокой эвтектики путем реализации квантово-химических расчетов с использованием программного обеспечения HyperChem. *Результаты*. Результаты показывают сильные ионные и ковалентные взаимодействия между бромом, метилтрифенилфосфонием и этиленгликолем в соответствии с оптимизированными структурами, длинами связей, энергиями и т. д. *Заключение*. Извлечение глицерина из биотоплива в основном осуществляется ионом брома природного растворителя глубокой эвтектики, при этом структура природного растворителя глубокой эвтектики после этого процесса остается неизменной, что свидетельствует о его стабильности и возможности повторного использования.

Ключевые слова: метилтрифенилфосфоний бромид, этиленгликоль, глицерин, биотопливо, экстракция

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