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RESEARCH ARTICLE

Study of calcium-containing compounds as catalysts for the esterification of glycerol with higher carboxylic acids

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Abstract

Objectives. *To investigate the catalytic activity of calcium-containing basic catalysts for the esterification of glycerol with higher carboxylic acids in order to develop a low-waste technology for the production of multifunctional additives, as well as to assess the possibility of using the reaction products for the processing of polyvinyl chloride.*
Methods. *The consumption of oleic acid during synthesis was monitored using a titrimetric method of analysis with visual indication. The structure of the synthesized calcium-containing catalysts was confirmed by infrared spectroscopy; elemental analysis was additionally performed for calcium glyceroxide. Quantitative and qualitative analyses of the resulting mixtures of oleic acid glycerides were carried out using chromato-mass spectrometry. A sample of a multifunctional additive was tested in a model formulation of a medical plastic compound based on polyvinyl chloride.*
Results. *It is shown that the catalytic activity of calcium derivatives in the reaction of esterification of glycerol with higher carboxylic acids increases in the series* $CaO < Ca(OH)_2 < Ca(C_{17}H_{33}COO)_2 < Ca(C_2H_5O)_2 < Ca(C_4H_9O)_2 < Ca(C_3H_7O_3)_2$, *while the use of calcium glyceroxide as a catalyst in an amount from 1 to 6 mol % increases the conversion of carboxylic acid from 58 to 86% in 10 h of synthesis. However, varying the amount of calcium glyceroxide from 1.5 to 6 mol % results in no observed changes in the conversion of carboxylic acid. The multifunctional additive obtained by selecting calcium glyceroxide*

as a catalyst has a thermally stabilizing and plasticizing effect on the polymer composition. The introduction of the developed additive into the formulation of a polyvinyl chloride composition for medical purposes reduces the processing torque and time to reach the dry point. By combining these factors, energy costs during production were reduced by more than 11% compared to the control composition.

Conclusions. *It is established that calcium alcoholates catalyze the reaction of esterification of glycerol with oleic (or higher) acid to increase the conversion of the initial substances and selectivity for the formation of monoglycerides as compared with calcium oxide, hydroxide, and oleate. By optimizing the ratio of glycerol : oleic acid : calcium glyceroxide at 1 : 1 : 0.015, the maximum conversion of oleic acid of up to 86% in 10 h was obtained via synthesis. The proposed method for esterification of glycerol with higher carboxylic acids in the presence of a calcium-containing catalyst avoids the stage of purification from the catalyst to obtain a composition with multifunctional additive properties for the processing of polyvinyl chloride.*

Keywords: *esterification, glycerol, oleic acid, calcium alcoholates, calcium glyceroxide*

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НАУЧНАЯ СТАТЬЯ

Исследование кальцийсодержащих соединений в качестве катализаторов этерификации глицерина высшими карбоновыми кислотами

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Аннотация

Цели. *Исследовать каталитическую активность кальцийсодержащих основных катализаторов для процесса этерификации глицерина высшими карбоновыми кислотами с целью разработки малоотходной технологии получения многофункциональных добавок. Провести оценку возможности применения продуктов реакции для переработки поливинилхлорида.*

Методы. *За расходованием олеиновой кислоты во время синтеза наблюдали с использованием титриметрического метода анализа с визуальной индикацией. Строение синтезированных кальцийсодержащих катализаторов было подтверждено методом инфракрасной спектроскопии. Для глицерата кальция дополнительно был проведен элементный анализ. Количественный и качественный анализ полученных смесей глицеридов олеиновой кислоты проводили с использованием хромато-масс-спектрометрии. Образец многофункциональной добавки прошел испытания в модельной рецептуре пластиката медицинского назначения на основе поливинилхлорида.*

Результаты. *Установлено, что каталитическая активность производных кальция в реакции этерификации глицерина высшими карбоновыми кислотами возрастает в ряду* $CaO < Ca(OH)_2 < Ca(C_{17}H_{33}COO)_2 < Ca(C_2H_5O)_2 < Ca(C_4H_9O)_2 < Ca(C_3H_7O_3)_2$, *при этом использование глицерата кальция в качестве катализатора в количестве от 1 до 6 мол. % повышает конверсию карбоновой кислоты с 58 до 86% за 10 ч проведения синтеза. Обнаружено, что при изменении количества глицерата кальция от 1.5 до 6 мол. % конверсия карбоновой кислоты практически не меняется. Выбранный в ходе исследований глицерат кальция в качестве катализатора позволяет получить многофункциональную добавку, обладающую термостабилизирующим и пластифицирующим действием на полимерную композицию. Введение разработанной добавки в рецептуру поливинилхлоридной композиции медицинского назначения снижает при переработке крутящий момент и сокращает время достижения «сухой» точки. Оба этих фактора позволили снизить затраты энергии при выпуске продукции более чем на 11% по сравнению с контрольной композицией.*

Выводы. *Установлено, что алкоголяты кальция катализируют реакцию этерификации глицерина олеиновой (или высшими) кислотой, повышают конверсию исходных веществ и селективность образования моноглицеридов по сравнению с оксидом, гидроксидом и олеатом кальция. Найдено, что оптимальное соотношение компонентов глицерин : олеиновая кислота : глицерат кальция составляет 1 : 1 : 0.015 и позволяет достичь максимальной конверсии олеиновой кислоты (до 86%) за 10 ч синтеза. Предложен способ этерификации глицерина высшими карбоновыми кислотами в присутствии кальцийсодержащего катализатора. Данный способ позволяет исключить стадию очистки от катализатора и получить композицию, обладающую свойствами многофункциональной добавки для переработки поливинилхлорида.*

Ключевые слова: *этерификация, глицерин, олеиновая кислота, алкоголяты кальция, глицерат кальция*

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INTRODUCTION

Global production of biodiesel, representing an alternative fuel derived from renewable natural resources, is currently about 40 mln tons/year [1]. As compared with traditional diesel, biodiesel offers a combination of valuable properties that significantly extend the life of engines running on it [2]. One of the by-products in the production of biodiesel is the formation of approximately 10 wt % glycerol. Thus, according to the latest report from *Global Industry Analysts* (USA)[1], the development of biodiesel fuel production technologies has led to an increase in the amount of glycerol on the world market. In this regard, the development of new approaches for using glycerol to obtain products with high added value represents an urgent task, which solution will expand medium- and long-term prospects for industrial uses of glycerol.

Glycerol can serve as a raw material for the production of acrolein, 1,3-propanediol, glyceric acid, and a number of other valuable products [3]. Representing surfactants having amphiphilic, non-ionic and excellent emulsifying properties, mono- and diglycerides of higher carboxylic acids are widely used in the food, cosmetic and pharmaceutical industries [4], as well as non-toxic plasticizers for the polymer industry [5].

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[1] https://strategyr.blogspot.com/2016/10/the-global-market-for-private-tutoring.html. Accessed September 22, 2022.

In earlier works, we proposed to use the products of glycerol esterification with higher carboxylic acids in the presence of calcium compounds as a multifunctional additive for the processing of polyvinyl chloride (PVC) [6], including mono- and diglycerides of higher carboxylic acids [7]. In this case, the spent calcium-containing catalyst remaining in the reaction mass as part of the multifunctional additive acts as a heat stabilizer. Implementation of such approach to the use of the obtained products significantly simplifies the technological process, as well as reduces the stage of isolation and purification.

The synthesis of glycerol esters with carboxylic acids on an industrial scale is generally carried out by esterification of glycerol with a fatty acid, which is catalyzed by strong acids such as sulfuric (H_2SO_4), orthophosphoric (H_3PO_4) acids, etc. [8]. However, the classical methods of esterification have a number of disadvantages: the occurrence of side processes, such as the dehydration of alcohols to olefins and sulfonation of unsaturated compounds; the formation of a large amount of acidic waste water with a high chemical oxygen demand; corrosion of equipment; low selectivity for the formation of monoglycerides (40–50%).

Currently, research and development of new catalysts for the esterification of glycerol is underway. For example, mesoporous silicon dioxide, metal oxides, modified zeolites, catalysts based on heteropoly acids [9], ion exchange resins (Amberlyst 15, Amberlyst 16, Amberlyst 31) [10], complexes of double metal cyanides Fe–Zn [11], and layered double hydroxides of the $MgAlCO_3$ complex [12], as well as processes based on sulfated metal oxides [13] are being used. Such catalysts are used to increase the conversion of raw materials and reuse processed alcohols while obviating the laborious stage of neutralization of the reaction mass. However, their disadvantages include the higher cost compared to acid catalysts, the need to use high temperatures (180–200°C), and chemical contamination of the product by the catalyst.

In recent decades, studies have been carried out on the effectiveness of calcium oxide, calcium hydroxide, and calcium alcoholates when used in processes of transesterification of vegetable oils with alcohols. The results presented in [14] demonstrate that the most effective method for increasing the catalytic activity of CaO is its activation with glycerol to form calcium glyceroxide. The studied calcium alkoxide has several advantages compared to calcium oxide, including higher catalytic activity during the transesterification reaction [15, 16] and greater resistance to air [17].

While the literature describes the use of calcium-containing compounds (CaO, $CaFe_2O_4$, and $Ca(OOCR)_2$) as catalysts for the esterification, we did not find studies on the catalytic activity of calcium alcoholate derivatives in the esterification of glycerol with higher carboxylic acids.

The aim of the present work is to study the use of calcium-containing basic catalysts for the esterification of glycerol with higher carboxylic acids, to carry out the process selectively for the formation of monoglycerides and with a high conversion of the starting materials, and to evaluate the possibility of using the reaction products for the processing of polyvinyl chloride.

MATERIALS AND METHODS

This work includes the use of reagents manufactured by *CHIMMED*, Russia: glycerol (chemically pure, 98.5%, GOST 6259-75[2]), oleic acid grade B-115 (tech., 97.4%, TU 9145-172-4731297-94), calcium hydroxide (analytical grade, 97%, GOST 9262-77[3]), calcium oxide (pure, 97%, GOST 22688-77[4]) was used after calcination at 900°C for 2 h, metallic calcium (pure, 98.6%, TU 083.5.314-94), ethyl alcohol (pure, 96%, GOST R 55878-2013[5]) was used after dehydration with calcium oxide, butyl alcohol (analytical grade, 99.7%, GOST 6006-78[6]), toluene (analytical grade, 99%, GOST 14710-78[7]), 1% alcoholic solution of phenolphthalein (indicator), potassium hydroxide (analytical grade, 99%), as well as sodium hydroxide (analytical grade, 99%).

The consumption of carboxylic acid during the esterification process was determined by the titrimetric method with visual indication. For titration,

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[2] GOST 6259-75. Interstate Standard. Reagents. Glycerin. Specifications. Moscow: IPK Izdatelstvo standartov; 2001 (in Russ.).

[3] GOST 9262-77. State Standard of the USSR. Reagents. Calcium hydroxide. Specifications. Moscow: IPK Izdatelstvo standartov; 1996 (in Russ.).

[4] GOST 22688-77. State Standard of the USSR. Lime for building purposes. Test methods. Moscow: IPK Izdatelstvo standartov; 1997 (in Russ.).

[5] GOST R 55878-2013. National Standard of the Russian Federation. Rectified hydrolytic technical ethyl alcohol. Specifications. Moscow: Standartinform; 2014 (in Russ.).

[6] GOST 6006-78. Interstate Standard. Reagents. 1-Butanol. Specifications. Moscow: IPK Izdatelstvo standartov; 2002 (in Russ.).

[7] GOST 14710-78. Interstate Standard.Petroleum toluene. Specifications. Moscow: IPK Izdatelstvo standartov; 2004 (in Russ.).

a 0.1 N alcoholic solution of potassium hydroxide and a 1% alcoholic solution of phenolphthalein (indicator) were used.

The esterification product of glycerol and carboxylic acids was identified using chromato-mass spectrometric analysis (GC–MS) on a Saturn 2100T GC/MS instrument (*Varian*, USA) equipped with a VF-1ms 30 M × 0.25 mm quartz capillary column × 0.25 µm (*Agilent Technologies*, USA). Carrier gas was helium grade 6.0 (with an impurity content not more than 0.00001%), carrier gas flow rate—1.2 cm^3/min; split injection 1:10; injector temperature—280°C. When programming the capillary column temperature, the initial temperature was 80°C, isotherm time—3 min, final temperature—300°C, isotherm time—2 min; temperature rise rate—10.0°C/min; total analysis time—30 min. An ion trap mass-spectrometric detector was used. Electron ionization (EI) mass spectra (70 eV) were recorded in the full mass spectrum scanning (SCAN) mode in the range from 40 to 650 *m*/*z* at a rate of 1 mass spectrum per second.

Elemental analysis was performed using an Elementar Vario EL cube universal elemental analyzer (*Abacus Analytical Systems GmbH*, Germany).

The infrared (IR) spectra of the obtained basic catalysts were recorded in air at room temperature (20°C) on a Nicolet-6700 IR-Fourier spectrometer (*Thermo Scientific*, USA) in the region of 400–4000 cm^{-1} with a scanning step of 0.5 cm^{-1}.

Synthesis of calcium oleate

Into a glass reactor equipped with a reflux condenser, a Dean-Stark trap, and an overhead stirrer, 0.177 mol (50 g) of oleic acid, 0.088 mol (4.96 g) of calcium oxide, and 50 mL of toluene were loaded. The reaction mixture was refluxed for 16 h at a stirring speed of 400 ± 10 rpm. Reaction water was removed by azeotropic distillation in a Dean–Stark trap. The obtained calcium oleate was purified by repeated reprecipitation with diethyl ether from toluene. Melting point 82–83°C (~80°C [18]). IR spectrum, $\tilde{\nu}$, cm^{-1}: 3404 w (OH), 2917 s (C–H), 2849 s (C–H), 1573 s (COO$^-$), 1536 s (COO$^-$), 3644 w (Ca–O).

Synthesis of calcium ethoxide

Calcium ethoxide [19] was synthesized in a 250 mL glass reactor equipped with an overhead stirrer and a reflux condenser protected from air moisture. Mixing speed was 300 ± 10 rpm. Calcium metal in an amount of 5 g was placed in a reactor with 100 mL of absolute ethanol and refluxed for 8–16 h air moisture. The resulting calcium ethoxide was stored in a desiccator under argon over solid sodium hydroxide (NaOH). IR spectrum, $\tilde{\nu}$, cm^{-1}: 3645 m (OH), 2951 w (C–H), 2802 w (C–H), 2701 w (C–H), 1059 s (C–O), 3645 w (Ca–O).

Synthesis of calcium butoxide

Calcium butyrate was similarly synthesized to calcium ethylate using 5 g of metallic calcium and 100 mL of butyl alcohol. The resulting calcium butoxide was stored in a desiccator under argon over solid NaOH. IR spectrum, $\tilde{\nu}$, cm^{-1}: 3645 m (OH), 2958 w (C–H), 2910 w (C–H), 2873 w (C–H), 1077 w (C–O), 3644 w (Ca–O).

Synthesis of calcium glyceroxide

The synthesis of calcium glyceroxide [20] was carried out by the interaction of glycerol with calcium hydroxide (Fig. 1). 1.36 mol (125 g) of glycerol, 0.22 mol (16.6 g) of calcium hydroxide, and 30 mL of toluene as azeotrope-forming agent were loaded into a reactor equipped with a Dean–Stark trap for removing reaction water by azeotropic distillation, as well as a reflux condenser and an overhead stirrer. The reaction mixture was stirred at 450 ± 10 rpm. After distilling off the calculated amount of reaction water (duration about 7 h), the reaction mass was cooled. The formed precipitate was filtered off under vacuum, washed with ethanol until completely removal of unreacted glycerol, and dried for 1 h at 105°C. The resulting calcium glyceroxide was stored in a desiccator under argon over solid NaOH. IR spectrum, $\tilde{\nu}$, cm^{-1}: 3229 w (OH), 2874 m (C–H), 2836 w (C–H), 1128 w (C–O), 1091 m (C–O), 3641 w (Ca–O), 1370 w [δ(C–O–H)], 1306 s [δ(C–O–H)]. Elemental analysis: obtained C (29.9 ± 3.0%), H (6.0 ± 0.6%) [$Ca(C_3H_7O_6)_2$]; calculated C (32.4%), H (6.3%).

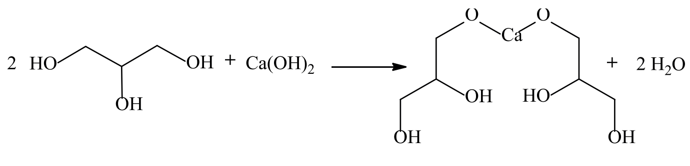

Fig. 1. Scheme of calcium glyceroxide synthesis.

Carrying out catalytic experiments

1) To study the effect of the main catalysts on the rate of esterification of glycerol with oleic acid, the following calcium-containing catalysts were chosen: calcium oxide, calcium hydroxide, calcium oleate, calcium ethoxide, calcium butoxide,

and calcium glyceroxide. 1 mol (92.09 g) of glycerol, 1 mol (282.46 g) of oleic acid, and 70 mL of toluene were used. After loading one of the catalysts from the above list (Table 1) with stirring in an amount of 1.5 mol %, the temperature of the reaction mass was raised to the boiling point of the azeotrope and kept at this temperature for 4 h. The reaction water was collected in a Dean–Stark trap.

2) To study the effect of the amount of calcium glyceroxide on the rate of esterification of glycerol with oleic acid, esterification was carried out under similar conditions. The only difference was in the amounts of catalyst used in each experiment—from 1 to 6 mol % (Table 2)—as well as the longer period of synthesis (10 h). Following the end of the synthesis, unreacted glycerol was separated in a separating funnel and the azeotrope-forming agent (toluene) was distilled off in a vacuum water jet pump.

Products were identified by chromato-mass spectrometry. Oleic acid monoglyceride: m/z (I_{rel}, %): 356 (3.2) $[M]^+$, 339 (23.7), 264 (99.9), 166 (15.7), 137 (24.9), 112 (23.3), 98 (45.9), 83 (31.8), 69 (32.4), 55 (60.3), 41 (55.7). Oleic acid diglyceride: m/z (I_{rel}, %): 339 (11.8), 265 (8.6), 185 (51.2), 129 (99.9), 97 (14.3), 83 (21.4), 69 (28.2), 55 (59.1), 41 (42.4). Oleic acid: m/z (I_{rel}, %): 282 (5.5) [M]+, 264 (41.9), 151 (18.9), 123 (24), 111 (30.3), 97 (65), 83 (67.8), 69 (66.4), 55 (99.9), 41 (80).

The material balance of laboratory syntheses of the esterification of glycerol with oleic acid was calculated to determine the technological parameters (conversion and selectivity) on the basis of the data obtained by gas chromatography-mass spectroscopy.

RESULTS AND DISCUSSION

Three groups of calcium compounds were tested as catalysts: the first group being calcium oxide and hydroxide, the second comprising a salt of calcium and oleic acid, while the third group is made up of calcium alcoholates: ethyl alcohol, butyl alcohol, and glycerol. The catalytic activity of the obtained basic catalysts based on calcium compounds was studied using the model of esterification of glycerol with oleic acid.

Esterification reactions are known to occur at several hydroxyl groups of glycerol with the formation of mixtures of products. The interaction of glycerol with oleic acid proceeds according to the scheme of successive reactions. Once sufficient amounts of oleic acid monoglyceride have been accumulated, it becomes available for consumption in the formation of diglyceride.

Calcium oxide and hydroxide were used to achieve a conversion for glycerol of 27.07% and 28.66%, respectively; for oleic acid, the equivalent conversion rates were 28.65% and 30.17% under the same conditions (Fig. 2). The use of calcium oleate turned out to be even more efficient: the conversion for glycerol was 35.54%, while, for oleic acid, the equivalent conversion was 37.36%. However, the highest value was achieved when using calcium alcoholates: for calcium glyceroxide, the conversion rate was 48.48% for glycerol and 49.56% for oleic acid. At the same time, no significant difference was found between ethoxide, butoxide and calcium glyceroxide. It is likely that calcium ethoxide and butoxide are converted during synthesis to calcium glyceroxide.

Table 1. Loads of calcium-containing catalysts

Catalyst	CaO	$Ca(OH)_2$	$Ca(C_{17}H_{33}COO)_2$	$Ca(C_2H_5O)_2$	$Ca(C_4H_9O)_2$	$Ca(C_3H_7O_3)_2$
Amount, mol %	1.5	1.5	1.5	1.5	1.5	1.5
Amount, g	0.84	1.11	9.04	1.95	2.79	3.33

Table 2. Loading amounts of calcium glyceroxide, catalyst $Ca(C_3H_7O_3)_2$

Amount, mol %	1	1.25	1.5	2	4	6
Amount, g	2.22	2.78	3.33	4.44	8.88	13.33

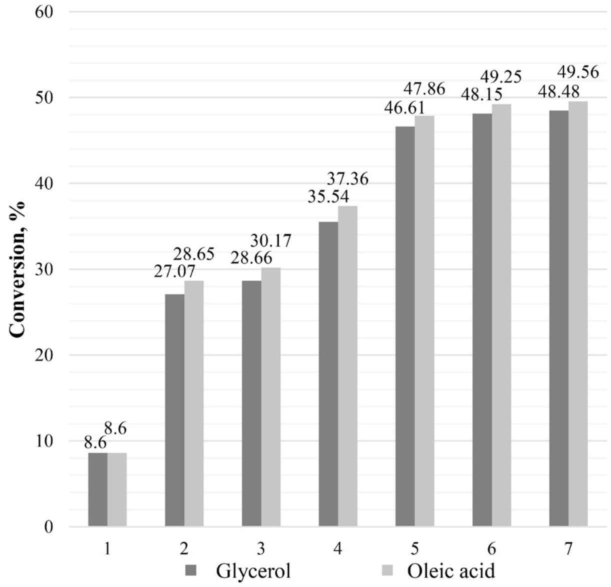

Fig. 2. Influence of a catalyst on the reagent conversion: 1 – no catalyst used, 2 – calcium oxide CaO, 3 – calcium hydroxide $Ca(OH)_2$, 4 – calcium oleate $Ca(C_{17}H_{33}COO)_2$, 5 – calcium ethoxide $Ca(C_2H_5O)_2$, 6 – calcium butoxide $Ca(C_4H_9O)_2$, 7 – calcium glyceroxide $Ca(C_3H_7O_3)_2$.

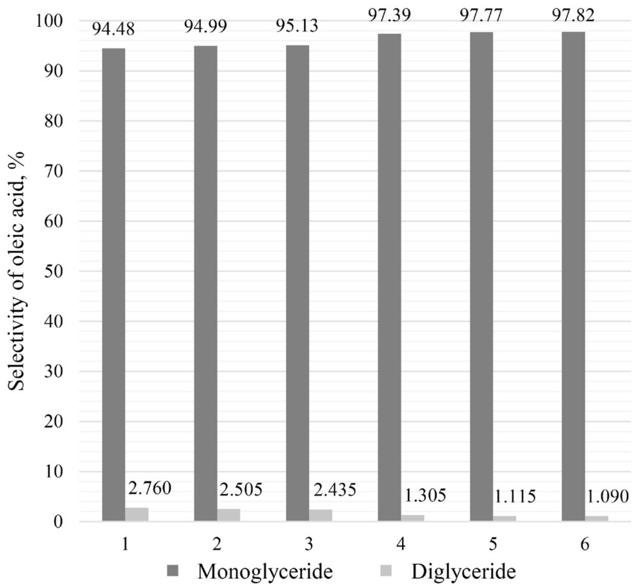

Fig. 3. Influence of the catalyst type on the selectivity for the oleic acid consumption: 1 – calcium oxide CaO, 2 – calcium hydroxide $Ca(OH)_2$, 3 – calcium oleate $Ca(C_{17}H_{33}COO)_2$, 4 – calcium ethoxide $Ca(C_2H_5O)_2$, 5 – calcium butoxide $Ca(C_4H_9O)_2$, 6 – calcium glyceroxide $Ca(C_3H_7O_3)_2$.

In none of the experiments was the formation of triglycerides detected. The use of $Ca(C_{17}H_{33}COO)_2$, $Ca(OH)_2$, and CaO showed similar selectivities for the formation of mono- and diglycerides – at about 95% and 2.5%, respectively (Fig. 3). The highest selectivity (above 97%) for the formation of monoglycerides was achieved when calcium alcoholates were used as catalysts.

Studies of the influence of the amount of calcium glyceroxide on the process of esterification of glycerol with oleic acid have been carried out. The amount of catalyst was changed in the range from 1 to 6 mol %. The initial data on the loading of reagents and catalyst are presented in Table 2.

During the reaction, the change in the degree of conversion of oleic acid in the reaction system over time was monitored. Samples were taken during 10 h of synthesis. The results of changing the conversion of oleic acid for each catalyst concentration are shown in Fig. 4.

The study of the effect of the amount of calcium glyceroxide on the conversion of oleic acid showed that the conversion of oleic acid increases with a change in the amount of catalyst from 1 to 1.5 mol % from 58% to 86% for 10 h of synthesis. No further increase in catalyst concentration has a significant effect on the course of the synthesis. Thus, the optimal concentration of the catalyst—equal to 1.5 mol %—was used to achieve the maximum value of the conversion of oleic acid with a minimum catalyst content.

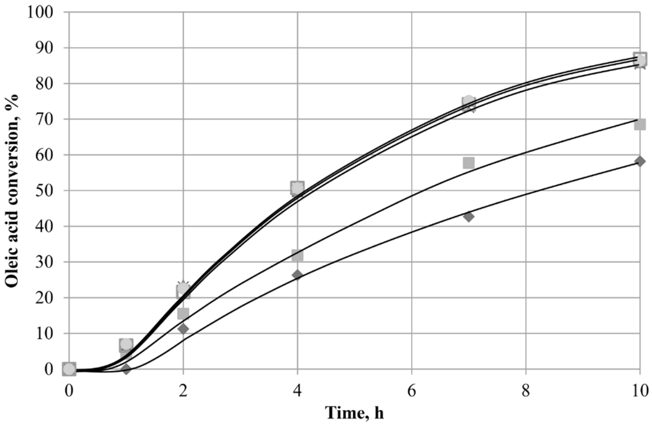

Fig. 4. Time dependence of oleic acid conversion. The amount of calcium glyceroxide, mol %: ♦ 1; ■ 1.25; × 1.5; ▲ 2; ● 4; □ 6.

A multifunctional additive for polymer processing was obtained using the proposed method for esterification of glycerol with oleic acid in the presence of calcium glyceroxide as a catalyst. This additive combines plasticizing agents in the form of mono- and diglycerides of oleic acid and calcium-containing compounds that have a thermally stabilizing effect on chlorine-containing polymers [7]. The main characteristics of the obtained multifunctional additive according to the developed method are presented in Table 3.

Table 3. Main characteristics of the obtained multifunctional additive

Analytically controlled components	Value
Content of oleic acid monoglycerides, %	82–86
Content of diglycerides of oleic acid, %	1.5–5
Mass fraction of calcium, %	<0.2
Acid number, mg KOH/g	20–25

The developed additive is assigned to hazard class 4 by the sanitary service of the Russian Federation, which permits the use of this additive without restrictions in any PVC products, including plastic compounds for medical purposes.

A sample of the multifunctional additive was tested in a model formulation of a medical plastic compound based on ultra-high molecular weight PVC-S8059U [21] produced by *Kaustik*, Volgograd, Russia. The introduction of the additive was carried out by partial replacement (5%) of dioctyl terephthalate in the formulation without changing the total mass of the composition. The production of the PVC composition in the P-600 mixer of the Brabender complex (*Brabender Technologie*, Germany) permits automatical control of changes in temperature and load on the mixing device during the process [22].

The parameters for obtaining PVC compositions in the mixer of the Brabender complex are presented in Table 4: temperature—93–94°C; mixing time—20 min; stirring device rotation speed—100 min^{-1}.

When using the studied additive in the production of PVC compositions, no technological difficulties were observed. Both the control and experimental compositions comprised free-flowing powders without agglomerates. Since the torque has a lower value (0.39 N·m) compared to the control composition (0.41 N·m) upon reaching the dry point of the experimental composition, the resistance exerted by the composition during operation of the mixer is lower. Moreover, by introducing the developed additive, it was possible to reduce the time taken to reach the dry point. Taken together, these factors confirm the effectiveness of the additive, which reduces energy costs for the production of a PVC composition by more than 11%.

Table 4. Production mode for polyvinyl chloride (PVC) compositions

Torque on the mixing device, N·m	Experimental composition	Control composition
Maximum	0.81	0.86
At the dry point	0.39	0.41
At the end of the test (12 min)	0.34	0.44
Time to reach the dry point, s	240	246
Specific energy consumption during the production of PVC composition, N·m/g	6.8	7.7

Table 5. Indicators of PVC composite materials

Indicator	Experimental composition	Control composition
Thermal stability at 190°C, (Congo red method), min	122	86
Melt flow rate at 190°C and a load of 10 kg through a capillary with a diameter of 2 mm, g/10 min	17.7	11.1

The resulting PVC compositions were poured out of the loading device into the working area of the extruder, where a strand was formed from the powder, from which granules were subsequently obtained for further testing.

Indicators of the material obtained from the control and experimental compositions are given in Table 5.

The obtained results showed a significant increase in the thermal stability of the PVC composition. The increase in the thermostabilizing effect is due to the presence of calcium-containing compounds in the composition of the additive, which provides its multifunctionality.

Thus, the developed method can be used to obtain an additive, which acts as a processing additive in the production of medical products and improves processing performance. As well as reducing internal friction and preventing sticking to metal parts of processing machines, the additive improves thermal stability and melt flow rate.

CONCLUSIONS

Calcium alcoholates are shown to catalyze the reaction of esterification of glycerol with oleic (or higher) acid, increasing the conversion of the initial substances and the selectivity of monoglyceride formation as compared to calcium oxide, hydroxide and oleate. The obtained optimal ratio of components—glycerol : oleic acid : calcium glyceroxide, 1:1:0.015, respectively—achieves the maximum conversion of oleic acid (up to 86%) over 10 h of synthesis. The proposed method for the esterification of glycerol with higher carboxylic acids in the presence of a calcium-containing catalyst also obviates the stage of purification from the catalyst when obtaining a composition having the properties of a multifunctional additive for the processing of polyvinyl chloride.

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Authors' contributions

Yu.L. Zotov – design of the research concept, development of the experiment, discussion and analysis of the results, and writing the text of the article;

D.M. Zapravdina – design of the research concept, planning and conducting experimental studies, processing the data obtained, and preparation of the data obtained for publication;

E.V. Shishkin – consultation on conducting individual stages of the study, scientific editing.

Yu.V. Popov – consultation on conducting individual stages of the study, scientific editing.

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