ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2019-15-1-55-61

UDC 547.729

Investigation of propylene carbonate synthesis regularities by the interaction of propylene glycol with carbamide

Aleksandr V. Sulimov[@], Anna V. Ovcharova, Grigory M. Kravchenko, Yulia K. Sulimova

Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nizhny Novgorod, 603950 Russia
[@]Corresponding author, e-mail: epoxide@mail.ru

Objectives. *Cyclic carbonates are important products of organic synthesis, which are widely used as solvents, catalysts, and reagents for the production of various compounds (in particular, urethane-containing polymers) by the non-isocyanate method. The process of carbamide alcoholysis with polybasic alcohols is a promising method for the synthesis of cyclic carbonates. The purpose of this study is to determine the reaction conditions for the interaction of propylene glycol with carbamide in the presence of zinc acetate as a catalyst.*
Methods. *We conducted experiments to study the synthesis of propylene carbonate in a batch laboratory apparatus. Moreover, we analyzed the starting reagents and final products using gas–liquid chromatography.*
Results. *We studied the synthesis of propylene carbonate by carbamide alcoholysis with propylene glycol in the presence of a catalyst (zinc acetate) by varying the following parameters: initial molar ratio of propylene glycol/carbamide = (0.5–5):1, synthesis temperature 130–190°C, reagent residence time in the reactor 0.5–4 h, and the catalyst amount in the reaction mixture 0–1.5 wt %.*
Conclusions. *We determined the technological parameters of propylene carbonate synthesis in a batch reactor. Moreover, we showed that the process allowed the production of propylene carbonate with a sufficiently high yield of 80%—at the initial molar ratio of propylene glycol/carbamide = 3:1, temperature 170°C, and residence time 2 h.*

Keywords: *cyclocarbonates, propylene carbonate, propylene glycol, carbamide, catalysis.*

For citation: Sulimov A.V., Ovcharova A.V., Kravchenko G.M., Sulimova Yu.K. Investigation of propylene carbonate synthesis regularities by the interaction of propylene glycol with carbamide. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2020;15(1):55-61. https://doi.org/10.32362/2410-6593-2020-15-1-55-61

Изучение закономерностей синтеза пропиленкарбоната взаимодействием пропиленгликоля с карбамидом

А.В. Сулимов[@], А.В. Овчарова, Г.М. Кравченко, Ю.К. Сулимова

Нижегородский государственный технический университет им. Р.Е. Алексеева, Нижний Новгород, 603950 Россия
[@]Автор для переписки, e-mail: epoxide@mail.ru

Цели. *Циклические карбонаты являются важными продуктами органического синтеза, которые находят широкое применение в качестве растворителей, катализаторов и реагентов для получения ряда соединений, в частности, уретансодержащих полимеров неизоцианатным методом. Одним из перспективных методов их синтеза является процесс алкоголиза карбамида многоосновными спиртами. Цель данной работы – определение условий реакции взаимодействия пропиленгликоля с карбамидом в присутствии ацетата цинка в качестве катализатора.*
Методы. *Экспериментальное исследование процесса синтеза пропиленкарбоната на лабораторной установке периодического действия. Анализ исходных реагентов и полученных продуктов с использованием газожидкостной хроматографии.*
Результаты. *Изучены закономерности получения пропиленкарбоната алкоголизом карбамида пропиленгликолем в присутствии катализатора (ацетата цинка) при варьировании основных параметров процесса в следующих диапазонах: начальное молярное соотношение реагентов пропиленгликоль/карбамид составляло (0.5–5):1, температура синтеза 130–190 °С, время пребывания реагентов в реакторе 0.5–4 ч, содержание катализатора в реакционной смеси 0–1.5 масс. %.*
Выводы. *Рекомендованы технологические параметры синтеза пропиленкарбоната, протекающего в реакторе периодического действия. Показано, что осуществление процесса при начальном молярном соотношении пропиленгликоля и карбамида 3:1, при температуре 170 °С и времени пребывания 2 ч позволяет получать пропиленкарбонат с достаточно высоким выходом – 80%.*

Ключевые слова: *циклокарбонаты, пропиленкарбонат, пропиленгликоль, карбамид, катализ.*

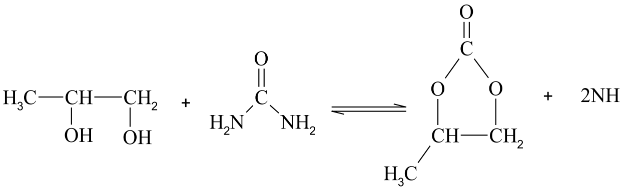
Для цитирования: Сулимов А.В., Овчарова А.В., Кравченко Г.М., Сулимова Ю.К. Изучение закономерностей синтеза пропиленкарбоната взаимодействием пропиленгликоля с карбамидом. *Тонкие химические технологии.* 2020;15(1):55-61. https://doi.org/10.32362/2410-6593-2020-15-1-55-61

INTRODUCTION

Propylene carbonate is an important product of organic synthesis. Because it possesses a number of valuable properties, it is widely used as a solvent and intermediate product in various syntheses. Its use as a solvent is attributed to the good dissolving ability, low toxicity, biodegradability, and high boiling point. Propylene carbonate is used in the production of polyacrylonitrile fibers, in the separation of CO_2 and H_2S, as a component of lubricating oils, hydraulic fluids, and electrolytes in lithium-ion batteries [1]. In addition, propylene carbonate is used as a starting component to obtain polymer compositions in pharmaceuticals [2] and in the synthesis of dimethyl carbonate [3].

Currently, propylene carbonate is commercially produced by the direct cyclocarboxylation of propylene oxide with carbon dioxide under catalysis by alkali metal salts, ammonium, phosphines, and metal complexes [4]. However, in addition to the traditional disadvantages inherent to homogeneous catalytic processes, this method is characterized by the rather stringent conditions of implementation (200°C and 5–10 MPa) [5]. Economic and environmental requirements dictate the need to develop new catalytic systems and technological processes for the synthesis of propylene carbonate.

A promising method for producing propylene carbonate is the interaction of propylene glycol and carbamide [6]:



The undoubted advantage of this process is that it is based on available raw materials, which can be obtained from renewable sources. Specifically, carbamide under industrial conditions is obtained by the interaction of ammonia and carbon dioxide; the reserves of the latter in the environment are practically inexhaustible [7, 8]. Propylene glycol is commercially produced from propylene oxide. However, even today, when the chemical market is oversaturated with bio-glycerin, many studies are published on its transformation to propylene glycol [9, 10]; in the future, the proportion of propylene glycol will only increase [11]. In general, possible options for raw materials for obtaining propylene carbonate can be represented as a diagram (Fig. 1).

The direct cyclocarboxylation of propylene oxide or propylene glycol is of considerable interest. However, this process, even when implemented on an industrial scale, is characterized by certain disadvantages (e.g., the need to use very high pressures) [5]. It is worth noting the studies regarding the catalytic systems based on ionic liquids and various metal complexes [12–14]. The use of these catalysts allows the cyclocarboxylation of propylene oxide to be carried out with carbon dioxide at low temperatures and pressures. Despite the rather high yield of propylene carbonate (greater than 90–95%), the process of obtaining such catalytic systems is complex and expensive, which casts doubt on the possibility of their industrial use, at least in the near future.

The use of propylene glycol and carbamide to produce propylene carbonate allows the process to be carried out under milder conditions at lower temperatures (130–180°C) and pressures (0.05–0.1 MPa) [15]. The possibility of its implementation is determined by the presence of effective catalytic systems. Previous studies [15, 16] have shown that metal acetates can catalyze the reaction of propylene glycol with carbamide to form propylene carbonate. Moreover, zinc acetate is most active in this process [16]. Therefore, we have investigated the synthesis of propylene carbonate by the interaction of propylene glycol with carbamide in the presence of zinc acetate as a catalyst.

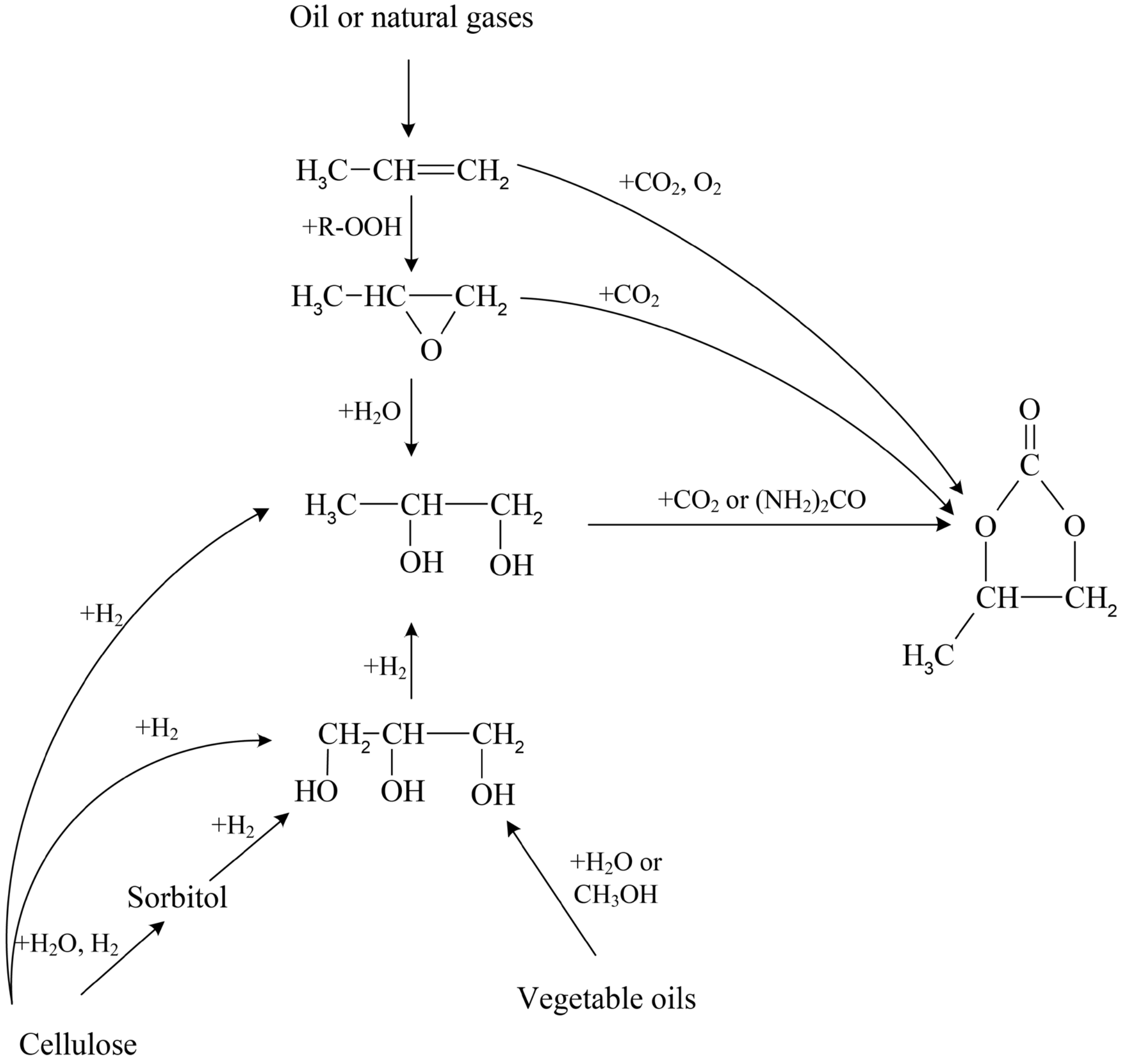


Fig. 1. Possible routes for the synthesis of propylene carbonate.

MATERIALS AND METHODS

The following reagents were used in this study (the purity grade is indicated in brackets): propylene glycol (puriss.), carbamide (p.a.), zinc acetate (p.a.).

The synthesis of propylene carbonate was carried out in a batch laboratory apparatus consisting of a glass reactor with electric heating, a reflux condenser, a temperature measurement and control system, and a magnetic mixing device. The calculated amounts of propylene glycol, carbamide, and zinc acetate were loaded into the reactor, and the heating and stirring of the reaction mixture were started. Upon reaching the set temperature, the start time of the synthesis was recorded. The reaction mass was kept for a certain time (0.5–4 h) at a constant temperature (130–190°C). At the end of the synthesis, samples (0.5 g) were taken from the reaction mass and quantitatively dissolved in the excess amount of absolute isopropyl alcohol.

The analysis of the reaction mixtures to determine the content of propylene glycol and propylene carbonate was carried out by gas chromatography on a Chromos GC-1000 instrument equipped with a flame ionization detector on a VB-1701 capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas; its flow rate through the column was 60 mL × min^{-1}. The temperatures of the evaporator and column thermostat were maintained at 200°C and 150°C, respectively. The technique was evaluated based on 5–7 parallel experiments, and their mean square error did not exceed 5%. The yield of propylene carbonate was determined relative to carbamide.

RESULTS AND DISCUSSION

On the basis of the reference data [17], the thermodynamic calculations of the reaction under standard conditions (p = 0.1013 MPa and T = 298.15 K) show that the change in enthalpy (ΔH) and the change in the Gibbs free energy (ΔG) of the reaction are 51.60 kJ/mol and 13.99 kJ/mol, respectively. A positive change in enthalpy means that the reaction between propylene glycol and carbamide proceeds with heat absorption. Thus, an increase in the temperature of the process will contribute to a shift in equilibrium toward the reaction products. However, a positive change in the Gibbs free energy indicates that the reaction cannot proceed at the temperature of 298.15 K. The dependence of ΔG on the reaction temperature is shown in Fig. 2.

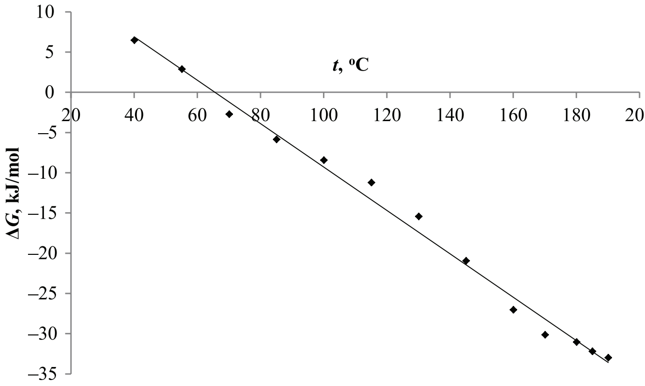


Fig. 2. Dependence of ΔG of the reaction on temperature.

The isobaric–isothermal potential decreases with an increase in the reaction temperature and becomes equal to zero at 62°C (335 K). This suggests that at temperatures higher than the abovementioned value, the reaction can proceed in the forward direction.

The equilibrium constant of the reaction at 130°C is 99.8; at 190°C, the equilibrium constant reaches 5271.3, which indicates a considerable shift in the equilibrium toward the reaction products with an increase in the temperature to 190°C.

Thus, calculations show that the synthesis of propylene carbonate from propylene glycol and carbamide is thermodynamically possible. However, to increase the speed of the process and reduce the time required to achieve equilibrium, kinetic factors should also be considered.

On the basis of the results obtained by calculation, the effect of temperature on the yield of propylene carbonate was studied in the temperature range of 130–190°C (Fig. 3).

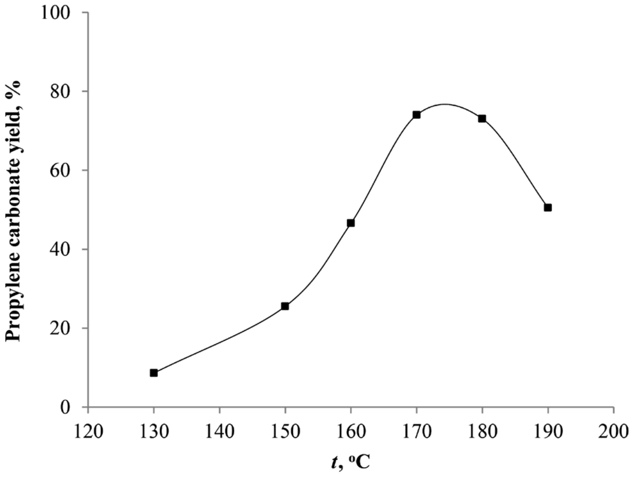


Fig. 3. Dependence of the propylene carbonate yield on the synthesis temperature (initial molar ratio propylene glycol/carbamide = 1:1, catalyst content 1 wt %, synthesis time 2 h).

The analysis of the results shows that with an increase in the temperature to 170–180°C, an increase in the yield of propylene carbonate is observed. A further increase in the temperature leads to a decrease in the yield of the target product, which is clearly associated with the occurrence of side processes (e.g., oligomerization of propylene carbonate). Thus, to implement the process, it is advisable to maintain the temperature in the range of 170–180°C. Under these conditions, the propylene carbonate yield of 74–75% is achieved.

To evaluate the effect of the initial molar ratio of propylene glycol/carbamide on the yield of propylene carbonate, a series of experiments was carried out with this indicator varying in the range of (0.5–5):1. The results are shown in Fig. 4.

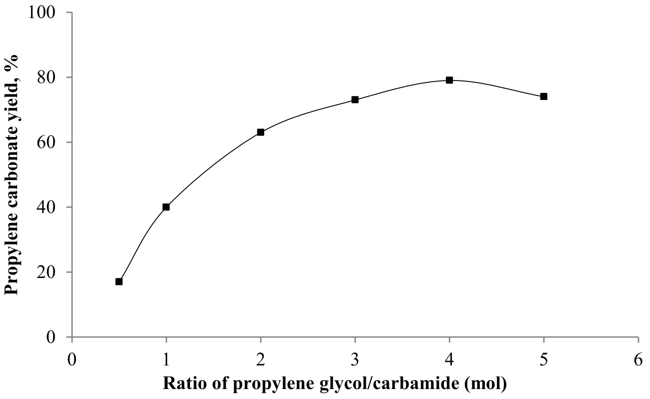


Fig. 4. Dependence of the propylene carbonate yield on the initial propylene glycol/carbamide ratio (synthesis temperature 170°C, catalyst content 1 wt %, synthesis time 2 h).

Figure 4 shows that a noticeable increase in the yield of propylene carbonate is observed with an increase in the ratio of reagents to 4:1. It is recommended to perform the synthesis of propylene carbonate in the presence of a 3–4-fold molar excess of propylene glycol. Unreacted propylene glycol is supposed to be isolated from the reaction using mass transfer processes and recycled to the chemical conversion step.

Based on the propylene carbonate yield–synthesis time dependence (Fig. 5), the optimal time was selected from 2 to 2.5 h. An increase in the reaction time beyond this value is undesirable because it leads to a certain decrease in the yield of propylene carbonate, which is most likely owing to the participation of the target product in further transformations.

Finally, we have investigated the dependence of propylene carbonate yield on the catalyst content in the reaction mixture (Fig. 6).

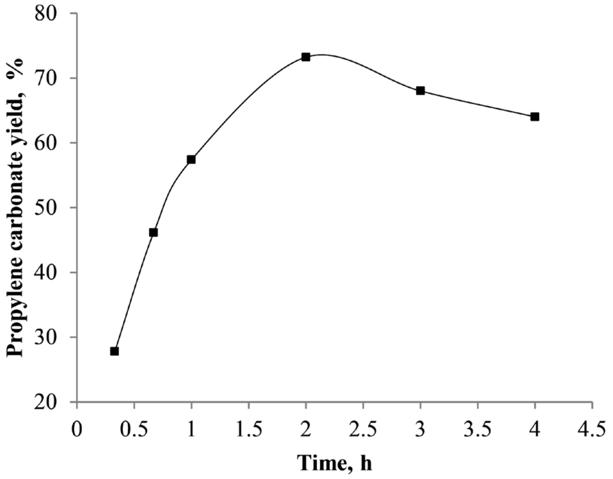


Fig. 5. Dependence of the propylene carbonate yield on the duration of the synthesis (synthesis temperature 170°C, initial molar ratio of propylene glycol/carbamide = 3:1, catalyst content 1 wt %).

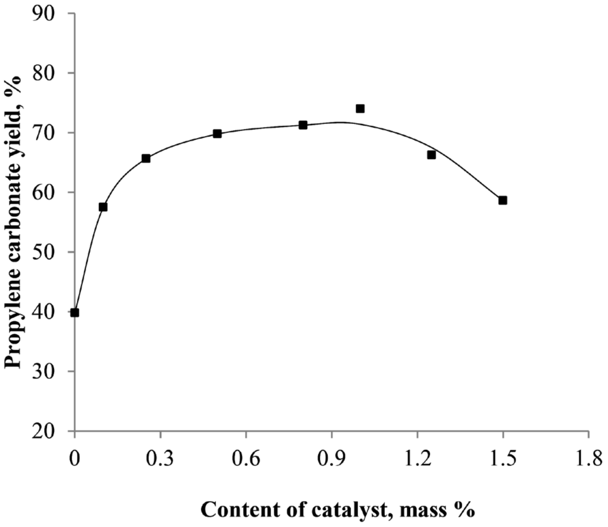


Fig. 6. Dependence of the propylene carbonate yield on the catalyst content (synthesis temperature 170°C, initial molar ratio of propylene glycol/carbamide = 3:1, synthesis time 2 h).

As expected, an increase in the catalyst amount in the reaction mixture promotes an increase in the yield of propylene carbonate. This dependence can be explained by an increase in the process rate; during the same time (2 h) a larger amount of propylene carbonate is formed with a higher catalyst content. This trend continues until the catalyst content is 1 wt %. With a further increase in the concentration of the catalyst, propylene carbonate in the reaction mixture can participate in side reactions, and its yield decreases, which is confirmed by the observed regularities.

In addition, the reaction can occur in the absence of a catalyst. At fixed parameters (temperature 170°C, propylene glycol/carbamide ratio = 3:1, contact duration 2 h), the yield of propylene carbonate does not exceed 40%. This value is relatively small, and it is unlikely that the non-catalytic process can be considered as an alternative. However, this fact is important and should be considered in further studies on the kinetics of propylene carbonate synthesis.

CONCLUSIONS

Thermodynamic calculations and kinetic studies of the reaction between propylene glycol and carbamide in the presence of zinc acetate as a catalyst allowed us to identify the range of parameters, ensuring high yields of the target product (75–80%). Based on our analysis, we recommend the following parameter values: temperature 170–180°C, initial ratio propylene glycol/carbamide (2–3):1, synthesis time between 1.5 and 2 h, and catalyst content 1 wt %.

The authors declare no conflicts of interest.

REFERENCES

1. Shaikh A.G., Sivaram S. Organic Carbonates. *Chem. Rev.* 1996;96(3):951-976. https://doi.org/10.1021/cr950067i
2. Debotton N., Dahan A. Applications of Polymers as Pharmaceutical Excipients in Solid Oral Dosage Forms. *Med. Res. Rev.* 2017;37(1):52-97. https://doi.org/10.1002/med.21403
3. Zhou J., Dongfang W., Zhang B., Guo Y. Synthesis of propylene carbonate from urea and 1,2-propylene glycol over metal carbonates. *Chem. Ind. Chem. Eng. Q.* 2011;17(3):323-331. https://doi.org/10.2298/CICEQ101123018Z
4. Suib S.L. (Ed.) *New and Future Developments in Catalysis.* Elsevier: Amsterdam; 2013. 478 p. ISBN 978-0-444-53882-6
5. Darensbourg D.J., Holtcamp M.W. Catalysts for the reactions of epoxides and carbon dioxide. *Coord. Chemi. Rev.* 1996;153:155-174. https://doi.org/10.1016/0010-8545(95)01232-X
6. Shukla K., Srivastava V.C. Synthesis of organic carbonates from alcoholysis of urea: A review. *Catal. Rev.* 2017;59(1)1-43. https://doi.org/10.1080/01614940.2016.1263088
7. Aresta M., Dibenedetto A. Utilisation of CO_2 as a chemical feedstock: opportunities and challenges. *Dalton Transactions.* 2007;28:2975-2992. https://doi.org/10.1039/B700658F
8. Mikkelsen M., Jorgensen M., Krebs F.C. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energ. Environ. Sci.* 2010;3(1)43-81. https://doi.org/10.1039/B912904A
9. Dasari M.A., Kiatsimku P.-P., Sutterlin W.R., Suppes G.J. Low-pressure hydrogenolysis of glycerol to propylene glycol. *Appl. Catal. A-G.* 2005;281(1):225-231. https://doi.org/10.1016/j.apcata.2004.11.033
10. Maris E.P., Davis R.J. Hydrogenolysis of glycerol over carbon-supported Ru and Pt catalysts. *J. Catal.* 2007;249(2):328-337. https://doi.org/10.1016/j.jcat.2007.05.008
11. Xiu Z.-L., Zeng A.-P. Present state and perspective of downstream processing of biologically produced 1,3-propanediol and 2,3-butanediol. *Appl. Microbiol. Biotechnol.* 2008;78(6):917-926. https://doi.org/10.1007/s00253-008-1387-4
12. Sulimov A.V., Ovcharova A.V., Ovcharov A.A., Ryabova T.A., Kravchenko G.M., Lysanov S.A. Synthesizing cyclic carbonates from olefin oxides and carbon dioxide. I: Catalysis with ionic liquids. *Catalysis in Industry.* 2016;8(4):300-309. https://doi.org/10.1134/s2070050416040103
13. Decortes A., Castilla A.M., Kleij A.W. Salen-Complex-Mediated Formation of Cyclic Carbonates by Cycloaddition of CO_2 to Epoxides. *Angew. Chem. Int. Ed.* 2010;49(51):9822-9837. https://doi.org/10.1002/anie.201002087
14. Sheng, X., Guo H., Qin Y., Wang X., Wang F. A novel metalloporphyrin-based conjugated microporous polymer for capture and conversion of CO_2. *RSC Advances.* 2015;5(40):31664-31669. https://doi.org/10.1039/C4RA16675B
15. Li Q., Zhao N., Wei W., Sun Y. Catalytic performance of metal oxides for the synthesis of propylene carbonate from urea and 1,2-propanediol. *J. Mol. Catal. A-Chem.* 2007;270(1):44-49. https://doi.org/10.1016/j.molcata.2007.01.018
16. Zhao X., Sun N., Wang S., Li F. Synthesis of Propylene Carbonate from Carbon Dioxide and 1,2-Propylene Glycol over Zinc Acetate Catalyst. *Ind. Eng. Chem. Res.* 2008;47(5):1365-1369. https://doi.org/10.1021/ie070789n
17. Gurvich L.V., Veyts I.V., Medvedev V.A. Thermodynamic properties of individual substances. Vol. 1, part 1. New York, United States: 1989. 551 p.

About the authors:

Aleksandr V. Sulimov, Dr. of Sci. (Engineering), Professor, Department of Chemical and Food Technologies, Nizhny Novgorod State Technical University n.a. R.E. Alekseev (49, Gaidara ul., Dzerzhinsk, Nizhny Novgorod oblast, 606000, Russia). Scopus Author ID 56497239500, ResearcherID K-5437-2015, https://orcid.org/0000-0002-8399-6231

Anna V. Ovcharova, Cand. of Sci. (Chemistry), Associate Professor, Department of Chemical and Food Technologies, Nizhny Novgorod State Technical University n.a. R.E. Alekseev (49, Gaidara ul., Dzerzhinsk, Nizhny Novgorod oblast, 606000, Russia). Scopus Author ID 55263080200

Grigory M. Kravchenko, Master Student, Department of Chemical and Food Technologies, Nizhny Novgorod State Technical University n.a. R.E. Alekseev (49, Gaidara ul., Dzerzhinsk, Nizhny Novgorod oblast, 606000, Russia).

Yulia K. Sulimova, Master Student, Department of Chemical and Food Technologies, Nizhny Novgorod State Technical University n.a. R.E. Alekseev (49, Gaidara ul., Dzerzhinsk, Nizhny Novgorod oblast, 606000, Russia). https://orcid.org/0000-0003-4417-884X

Об авторах:

Сулимов Александр Владимирович, доктор технических наук, профессор кафедры «Химические и пищевые технологии», Нижегородский государственный технический университет им. Р.Е. Алексеева (606000, Россия, Нижегородская обл., г. Дзержинск, ул. Гайдара, д. 49). Scopus Author ID 56497239500, ResearcherID K-5437-2015, https://orcid.org/0000-0002-8399-6231

Овчарова Анна Владимировна, кандидат химических наук, доцент кафедры «Химические и пищевые технологии», Нижегородский государственный технический университет им. Р.Е. Алексеева (606000, Россия, Нижегородская обл., г. Дзержинск, ул. Гайдара, д. 49). Scopus Author ID 55263080200

Кравченко Григорий Михайлович, магистрант кафедры «Химические и пищевые технологии», Нижегородский государственный технический университет им. Р.Е. Алексеева (606000, Россия, Нижегородская обл., г. Дзержинск, ул. Гайдара, д. 49).

Сулимова Юлия Константиновна, магистрант кафедры «Химические и пищевые технологии», Нижегородский государственный технический университет им. Р.Е. Алексеева (606000, Россия, Нижегородская обл., г. Дзержинск, ул. Гайдара, д 49). https://orcid.org/0000-0003-4417-884X

Submitted: December 23, 2019; Reviewed: February 07, 2020; Accepted: February 17, 2020.

Translated from Russian into English by S. Durakov

Edited for English language and spelling by Enago, an editing brand of Crimson Interactive Inc.