CHEMICAL ENGINEERING TRANSACTIONS
VOL. 92, 2022

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Rubens Maciel Filho, Eliseo Ranzi, Leonardo Tognotti

ISBN 978-88-95608-90-7; **ISSN** 2283-9216

DOI: 10.3303/CET2292058

Diethyl Carbonate Production from CO_2 and Ethanol in an Isothermal PFR via Aspen Plus Simulation

Victor Hugo S. Ramos[a,*], Nahieh T. Miranda[a], Betânia H. Lunelli[b], Leonardo V. Fregolente[a], Rubens Maciel Filho[a], Maria Regina W. Maciel[a]

[a]Laboratory of Optimization, Design, and Advanced Control, School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Campinas, 13083-852, Brazil
[b]School of Chemical, Pontifical Catholic University of Campinas, Professor Dr. Euryclides de Jesus Zerbini 1516, Campinas, 13087-571, Brazil
v264227@dac.unicamp.br

In this work, diethyl carbonate (DEC) production from CO_2 and ethanol, coming from the bioethanol plant, is studied using 2-cyanopyridine (2-CP) as a dehydrating agent and CeO_2 as a catalyst. Aiming to integrate existing plants and applying the concept of circular economy, this work has the appeal of not emitting carbon dioxide and valuing renewable carbon in the production of diethyl carbonate, a compound with high added value that can be applied as lithium battery electrolyte and as an intermediate in obtaining ketones, tertiary alcohols, and heterocyclic components. The DEC production proposed in this work was simulated via Aspen Plus V10 software. The reaction system is composed of the following reagents: carbon dioxide (CO_2), ethanol (EtOH), diethyl carbonate (DEC), water (H_2O), 2-cyanopyridine (2-CP), picolinamide (2-PA), ethyl picolinimidate (EPI), ethyl picolinate (EP), ammonia (NH_3), and ethyl carbamate (EC). The mixture properties were calculated using the Non-Random-Two-Liquid (NRTL) method. The reaction mixture composition used was 10 kmol/h of ethanol, 15 kmol/h of CO_2, and 5 kmol/h of 2-CP. The reactor was simulated as a multi-tubular isothermal plug flow reactor (PFR). The kinetic reactions were modeled using power law equations. The effect of reactor operating temperature (range 130–150 °C) and reactor dimensions on ethanol conversion was studied. At 50 atm and 130 °C, 4.01 kmol/h of DEC was obtained at the output stream of the reactor, corresponding to 11.37 t/day with an ethanol conversion of 82.85 %. From the open literature, this is the first work that the DEC production from ethanol and CO_2 is simulated in a multi-tubular reactor.

1. Introduction

Diethyl carbonate (DEC) is a biodegradable colourless liquid with moderate toxicity and low bioaccumulation (Shukla and Srivastava, 2016; PubChem, 2022). Due to its high oxygen content (40.6 %), it can act as a fuel additive replacing methyl tert-butyl ether (MTBE) containing 18.2 % oxygen content, to improve gasoline octane number while requiring less additive to achieve the same effect (Wang et al., 2007; Shukla and Srivastava, 2018; De Groot et al., 2014). Among other organic carbonates, DEC has also been studied as an electrolytic solvent for lithium batteries (Zhang et al., 2020; Jote et al., 2020).

Alternative routes such as urea alcoholysis (Wang et al., 2007), transesterification of ethanol with ethylene carbonate (Iida et al., 2018), decarboxylation of diethyl oxalate (Hao et al., 2009), direct synthesis by carbonylation of ethanol using CO_2 (Giram et al., 2018) and supercritical CO_2 (Gasc et al., 2009) have been studied to obtain DEC.

Applying the concept of Circular Economy, obtaining DEC from ethanol and CO_2 from the sugarcane bioethanol plant appears as an ecologically friendly alternative to the conventional process that uses the toxic compound phosgene (Denardin and Valença, 2020; Arbeláez et al., 2020). This route's appeal is the use of renewable carbon and the reduction of CO_2 emissions applied to the integration of existing industrial plants.

Paper Received: 24 January 2022; Revised: 28 March 2022; Accepted: 25 April 2022
Please cite this article as: Ramos V.H.S., Miranda N.T., Lunelli B.H., Fregolente L.V., Maciel Filho R., Wolf Maciel M.R., 2022, Diethyl Carbonate Production from CO2 and Ethanol in an Isothermal Pfr via Aspen Plus Simulation, Chemical Engineering Transactions, 92, 343-348 DOI:10.3303/CET2292058

This work addresses the reactional step of obtaining DEC via Aspen Plus simulation in order to support future experimental activities and process design. An in-depth discussion of the parameters involving the reactor in simulating the production of DEC from ethanol and CO_2 is presented.

2. Materials and Methods

In this work, the reaction step of a DEC plant aiming at the production of 10 t/day (3.53 kmol/h) is presented. The simulation was performed using Aspen Plus V10 software. The reaction system is composed of the following components: carbon dioxide (CO_2), ethanol (EtOH), diethyl carbonate (DEC), water (H_2O), 2-cyanopyridine (2-CP), picolinamide (2-PA), ethyl picolinimidate (EPI), ethyl picolinate (EP), ammonia (NH_3), and ethyl carbamate (EC). The properties of the mixture were calculated using the Non-Random Two Liquid Activity Coefficient (NRTL) model and the missing data extracted from the database presented by Yu et al. (2020).

Table 1 shows the reaction system and the kinetics of DEC production from ethanol and CO_2 as contributions from the studies by Yu et al. (2020) and Giram et al. (2018). In this work, the reactor was simulated as an isothermal multi-tubular Plug Flow Reactor (PFR) considering the vapor-liquid equilibrium and the Power Law kinetic equations. The reactor bed was simulated assuming a CeO_2 catalyst density of 7,130 kg/m^3 (Sigma Aldrich, 2021) and 0.4 voidage. The reactor feed flowrate was set at 10 kmol/h of ethanol, 15 kmol/h of CO_2, and 5 kmol/h of 2-CP. The effect of reactor operating temperature (range 130–150 °C) on ethanol conversion was studied, as well as the influence of the length and number of tubes on the PFR.

Table 1: Reaction system and kinetic parameters of DEC production (Yu et al., 2020; Giram et al., 2018)

Reaction	Equation	E_a (kJ/kmol)	k_0 (kmol/kgcat.s)
$CO_2 + 2(EtOH) \overset{r1}{\rightarrow} DEC + H_2O$	$r_1 = k_1 \exp(-{E_{a_1}}/{RT})$	150,163	4.608×10^{14}
$DEC + H_2O \overset{r2}{\rightarrow} CO_2 + 2(EtOH)$	$r_2 = k_2 \exp(-{E_{a_2}}/{RT})\, {X_{DEC}X_{H_2O}}/{X_{CO_2}X_{EtOH}^2}$	125,359	5.550×10^{17}
$2CP + H_2O \overset{r3}{\rightarrow} 2PA$	$r_3 = k_3\, T \exp(-{E_{a_3}}/{RT}) X_{2-CP}X_{H_2O}$	258	7.048
$2CP + EtOH \overset{r4}{\rightarrow} EPI$	$r_4 = k_4 \exp(-{E_{a_4}}/{RT}) X_{2-CP}X_{EtOH}$	15,259	3.851×10^{-5}
$2PA + EtOH \overset{r5}{\rightarrow} EP + NH_3$	$r_5 = k_5 \exp(-{E_{a_5}}/{RT}) X_{2-PA}X_{EtOH}$	6,919	2.151×10^{-2}
$EP + NH_3 \overset{r6}{\rightarrow} 2PA + EtOH$	$r_6 = k_6 \exp(-{E_{a_6}}/{RT}) X_{EP}X_{NH_3}$	1,937	8.726
$DEC + 2PA \overset{r7}{\rightarrow} EC + EP$	$r_7 = k_7 \exp(-{E_{a_7}}/{RT}) X_{DEC}X_{2-CP}$	69,837	7.133×10^5
$EC + EP \overset{r8}{\rightarrow} DEC + 2PA$	$r_8 = k_8 \exp(-{E_{a_8}}/{RT}) X_{EC}X_{EP}$	12,915	3.133×10
$EPI + H_2O \overset{r9}{\rightarrow} EP + NH_3$	$r_9 = k_9\, T \exp(-{E_{a_9}}/{RT}) X_{EPI}X_{H_2O}$	14,952	1.114×10^2

3. Results and Discussion

The biggest challenge in using CO_2 to produce chemical compounds is the thermodynamic limitation due to the high stability of CO_2, a topic that has been widely discussed previously in the literature (Denardin and Valença, 2020; Tomishige et al., 2020; Wang et al., 2017). Among the technological advances in the route to obtain organic carbonates from CO_2, the use of catalysts based on CeO_2 and 2-cyanopyridine as a dehydrating agent has been consolidated as a promising route although there is still room to increase the yield and selectivity of the carbonate production (Tomishige et al., 2020; Honda et al., 2014; Pawar et al., 2020; Daniel et al., 2021; Zhang et al., 2021).

The presence of the dehydrating agent promotes a shift in the chemical balance, leads to greater formation of diethyl carbonate (DEC) and the formation of undesirable products by parallel reactions (Table 1). For the simulation via Aspen Plus, the experimental conditions presented by Giram et al. (2018) and the kinetic study presented by Yu et al. (2020) were considered. From the open literature, this is the first work that simulated the DEC production from ethanol and CO_2 in a multi-tubular reactor.

The simulation presented in this work corresponds to the DEC production stage, focusing on the variables of the reaction system and the reactor design. Thus, it is important to emphasize that the complete DEC plant also includes the steps of separation and purification of the products.

Figure 1 shows the flowsheet designed to simulate the reaction system. The liquid streams of ethanol (ETOH-F) and 2-CP-F are initially mixed in the mixer (MIX-LIQ) and then pumped up to 50 atm. The CO2-F stream is compressed up to 50 atm and sent to the MIX-F feed mixer. The FEED stream is sent to a heater to adjust the reaction temperature (range 130–150 °C) and then sent to the isothermal PFR (RPLUG).

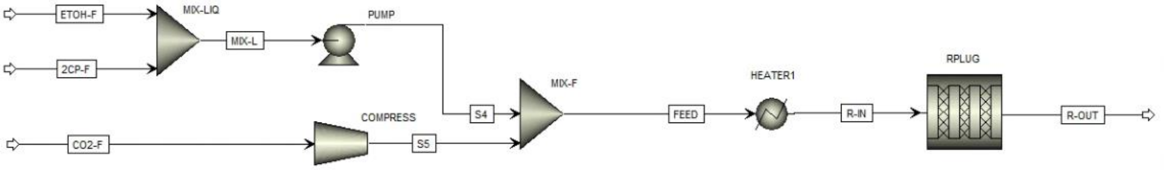

Figure 1: Flowsheet of the reactional step of DEC production – MIX-LIQ = liquid mixer; COMPRESS = compressor; PUMP = pump; MIX-F = feed mixer; HEATER1 = heater; RPLUG = plug flow reactor

Initially, the PFR was simulated in a single tube (results presented in Figure 2) to analyze the behavior of ethanol conversion and DEC production as the reactor length varies, keeping the diameter at 2.54 cm (1 in). It was observed that, in a small reactor length, the effect of temperature is relevant, favoring the conversion of EtOH as the temperature increases (Giram et al., 2018). However, as the reactor length increases from 0.5 m to 200 m, this influence decreases leading to similar levels of ethanol conversion around 90%. The use of a 200 m reactor in this plant is impractical due to the large occupied space, production and maintenance costs. Because of these impeditive values, it was proposed to use multi-tubular PFR.

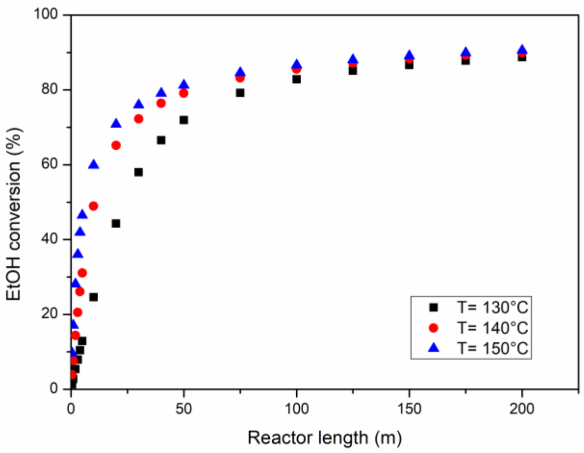

Figure 2: Influence of reactor length on ethanol conversion – Simulation conditions: 50 bar, 10 kmol/h of ethanol, 15 kmol/h of CO_2, and 5 kmol/h of 2-CP, catalyst density of 7,130 kg/m^3, and 0.4 of bed voidage and diameter of the reactor of 2.54 cm

After this preliminary study, the reactor was then simulated as a multi-tubular PFR with a tube diameter of 2.54 cm and reactor length of 5 m. Figure 3 shows the influence of the number of tubes on ethanol conversion and DEC production. Similar to the behavior observed in Figure 2, it can be seen that from 20 tubes onwards, the influence of temperature on the ethanol conversion is practically negligible. In addition to increasing ethanol conversion, increasing the number of tubes increases the reactor thermal stability since the reaction system is exothermic, favoring the cooling and control of axial and radial temperature profile of the reactant fluid (Overtoom et al., 2009).

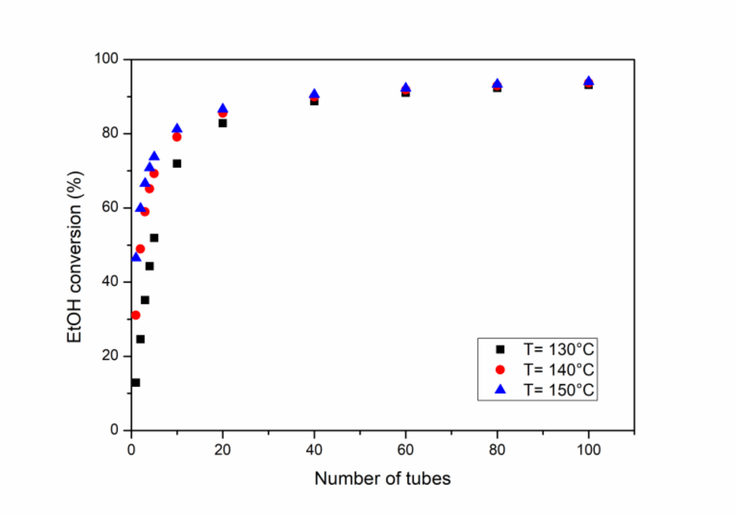

Figure 3: Influence of number of tubes on ethanol conversion – Simulation conditions: 50 bar, 10 kmol/h of ethanol, 15 kmol/h of CO_2, and 5 kmol/h of 2-CP, catalyst density of 7,130 kg/m^3, and 0.4 of bed voidage, reactor diameter of 2.54 cm, and reactor length of 5 m

In addition to the conversion of ethanol, the formation of side products throughout the reactor at different temperatures was also analyzed. Despite the complexity of the reaction system (Table 1), Figure 4 shows that the excess of the dehydrating agent 2-CP ensures the capture of water. It leads to the formation of the hydrated form 2-PA in the same proportion as the formation of DEC. The increase in temperature and number of reactor tubes showed little influence on the formation of parallel products EP, NH_3, EC, and EPI.

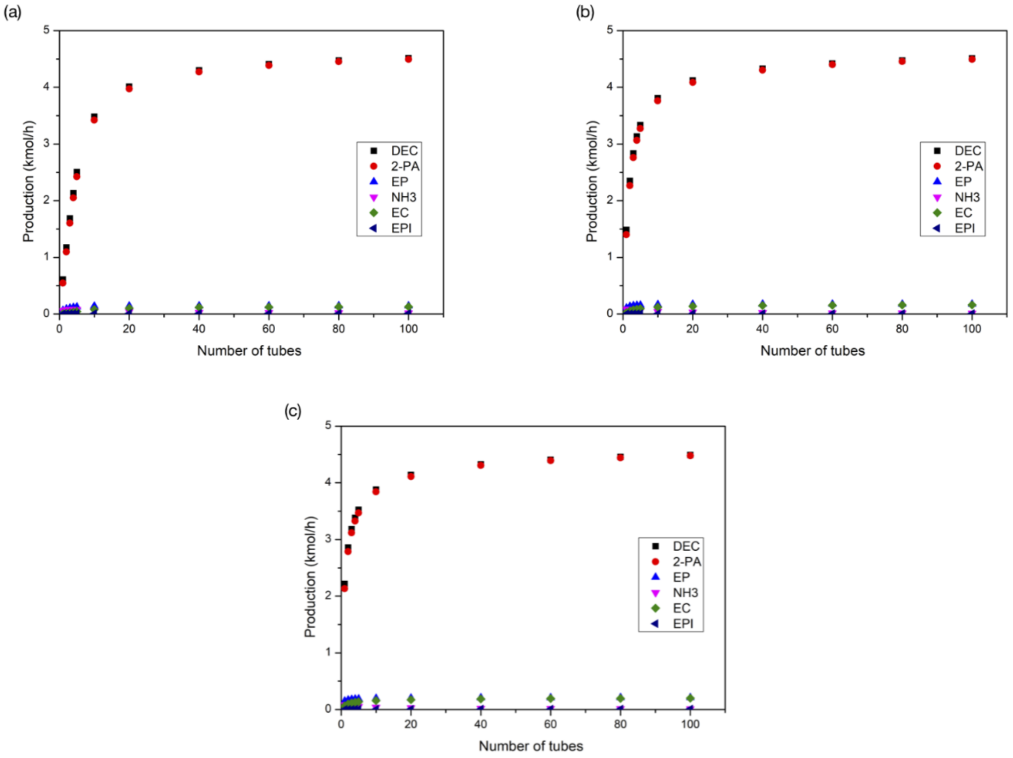

Figure 4 – Influence of product formation with the variation in the number of reactor tubes: (a) 130 °C, (b) 140 °C, and (c) 150 °C – Simulation conditions: 50 bar, 10 kmol/h of ethanol, 15 kmol/h of CO_2, and 5 kmol/h of 2-CP, catalyst density of 7,130 kg/m^3, and 0.4 of bed voidage. Reactor diameter of 2.54 cm and reactor length of 5 m

Table 2 shows the flowrate of the components in the reactor outlet stream at different temperatures. Under the simulated conditions, it was observed that the increase in temperature favors the conversion of EtOH to form DEC. However, the percentage difference of DEC flow at the reactor output at 130 °C and 150 °C was 3.07 %. Thus, it justifies the use of a lower temperature, reducing the amount of heat required. The production of 4.01 kmol/h of DEC corresponds to 474.02 kg/h of DEC or 11.37 t/day reaching the target set in the project.

Table 2: Composition of the outlet stream of the multi-tubular isothermal PFR

Components (kmol/h)	Temperature (°C)				
	130	135	140	145	150
CO_2	10.8832	10.7910	10.7412	10.7084	10.6854
EtOH	1.7153	1.5378	1.4424	1.3799	1.3360
DEC	4.0126	4.0870	4.1197	4.1349	4.1397
H_2O	0.0000	0.0000	0.0000	0.0000	0.0000
2-CP	0.8728	0.7827	0.7341	0.7020	0.6793
2-PA	3.9720	4.0511	4.0868	4.1043	4.1111
EP	0.1448	0.1579	0.1720	0.1872	0.2035
NH_3	0.0406	0.0359	0.0328	0.0305	0.0287
EC	0.1042	0.1220	0.1391	0.1567	0.1749
EPI	0.0104	0.0083	0.0071	0.0064	0.0061
Heat Duty (kW)	-117.2365	-122.2291	-126.2047	-129.9003	-133.5410
EtOH conv. (%)	82.85	84.62	85.57	86.20	86.64

Simulation conditions: 50 bar, 10 kmol/h of ethanol, 15 kmol/h of CO_2, and 5 kmol/h of 2-CP, catalyst density of 7,130 kg/m^3, and 0.4 of bed voidage. Reactor diameter of 2.54 cm, reactor length of 5 meters, number of tubes equal to 20

This study allowed to evaluate the influence of temperature on the production of DEC when simulated in a multi-tubular reactor. In addition to dimensioning the reactor to increase the production of DEC, it was also observed that the temperature has less influence in a multi-tubular reactor than when simulated in a single tube reactor, justifying the use of a lower temperature. Thus, it allows the reduction of the energy expenditure. Quantifying energy expenditure in the energy supply to heat the reagents in comparison to the DEC production is suggested as future work.

4. Conclusions

In this work, the production of DEC from ethanol and CO_2 with dehydrating agent 2-cyanopyridine on CeO_2 catalyst was simulated for the first time in a multi-tubular reactor using Aspen Plus commercial software. The simulation was carried out in a multi-tubular isothermal PFR, obtaining a production of 11.37 t/day of DEC in the reactor outlet. The importance of the simulation stage in the development and advancement of process technologies was evidenced in favouring the DEC production when using a multi-tubular reactor.

Nomenclature

conv. – conversion, %
E_a – activation energy, kJ/kmol
k_0 – velocity constant, kmol/kgcat.s
r_0 – reaction number
X – mole fraction of component
R – universal gas constant, kJ/kmol.K
T – reaction temperature, °C

Acknowledgments

The authors thank CAPES (grant 8887.495488/2020-00), São Paulo Research Foundation (FAPESP) (grant #2015/20630-4), The National Council for Scientific and Technological Development (CNPq) (grant 313952/2020-5), and University of Campinas (UNICAMP).

References

Arbeláez O., Santis A., Villegas A., Villa A., Ivanova S., Centeno M., 2020. Transformation of carbon dioxide into linear carbonates and methane over Cu-Ni and Ru-Fe supported on pellets activated carbon, Chem Eng Trans, 79, 109–114.

Daniel C., Schuurman Y., Farrusseng D., 2021, Surface effect of nano-sized cerium-zirconium oxides for the catalytic conversion of methanol and CO_2 into dimethyl carbonate. J Catal, 394, 486–494.

De Groot F.F.T., Lammerink R.R.G.J., Heidemann C., Van Der Werff M.P.M., Garcia T.C., Van Der Ham L.A.G.J., et al., 2014, The industrial production of dimethyl carbonate from methanol and carbon dioxide, Chem Eng Trans, 39, 1561–1566.

Denardin F.G., Valença G.P., 2020, Synthesis of diethyl carbonate from ethanol and CO_2 over ZrO_2 catalysts, Brazilian J Chem Eng, 38, 77–87.

Gasc, F., Thiebaud-Roux, S., Mouloungui, Z., 2009, Methods for synthesizing diethyl carbonate from ethanol and supercritical carbon dioxide by one-pot or two-step reactions in the presence of potassium carbonate, J Supercrit Fluid 50, 46–53.

Giram G.G., Bokade V.V., Darbha S., 2018, Direct synthesis of diethyl carbonate from ethanol and carbon dioxide over ceria catalysts, New J Chem, 42, 17546–17552.

Hao, C., Wang, S., Ma, X., 2009, Gas phase decarbonylation of diethyl oxalate to diethyl carbonate over alkali-containing catalyst, J Mol Catal A-Chem 306, 130–135.

Honda M., Tamura M., Nakagawa Y., Nakao K., Suzuki K., Tomishige K., 2014, Organic carbonate synthesis from CO_2 and alcohol over CeO_2 with 2-cyanopyridine: Scope and mechanistic studies, J Catal, 318, 95–107.

Iida, H., Kawaguchi, R., Okumura, K., 2018, Production of diethyl carbonate from ethylene carbonate and ethanol over supported fluoro-perovskite catalysts. Catal Comun 108, 7–11.

Jote B.A., Beyene T.T., Sahalie N.A., Weret M.A., Olbassa B.W., Wondimkun Z.T., et al., 2020, Effect of diethyl carbonate solvent with fluorinated solvents as electrolyte system for anode free battery, J Power Sources 461, 228102.

Overtoom R., Fabricius N., Leenhouts W., 2009, Shell GTL, from Bench scale to World scale, 1st ed. Elsevier Ltd. Proceedings of the 1st Annual Gas Processing Symposium, 378–386.

Pawar A.A., Lee D., Chung W.J., Kim H., 2020, Understanding the synergy between MgO-CeO_2 as an effective promoter and ionic liquids for high dimethyl carbonate production from CO_2 and methanol, Chem Eng J, 395, 124970.

PubChem, Diethyl carbonate $(C_2H_5O)_2CO$ <pubchem.ncbi.nlm.nih.gov/compound/Diethyl-carbonate> accessed 05.01.2022.

Shukla K., Srivastava V.C., 2016, Diethyl carbonate: Critical review of synthesis routes, catalysts used and engineering aspects, RSC Adv, 6, 32624–32645.

Shukla K., Srivastava V.C., 2018, Synthesis of diethyl carbonate from ethanol through different routes: A thermodynamic and comparative analysis, Can J Chem Eng, 96, 414–420.

Sigma Aldrich, Cerium(IV) oxide powder, <www.sigmaaldrich.com/BR/en/product/aldrich/211575> accessed 21.09.2021.

Tomishige K., Gu Y., Chang T., Tamura M., Nakagawa Y., 2020, Catalytic function of CeO_2 in non-reductive conversion of CO_2 with alcohols, Mater Today Sustain, 9, 100035.

Wang D., Yang B., Zhai X., Zhou L., 2007, Synthesis of diethyl carbonate by catalytic alcoholysis of urea, Fuel Process Technol, 88, 807–812.

Wang J., Hao Z., Wohlrab S., 2017, Continuous CO_2 esterification to diethyl carbonate (DEC) at atmospheric pressure: application of porous membranes for in situ H_2O removal. Green Chem, 19, 3595–3600.

Yu B-Y., Wu P-J., Tsai C-C., Lin S-T., 2020, Evaluating the direct CO_2 to diethyl carbonate (DEC) process: Rigorous simulation, techno-economical and environmental evaluation, J CO2 Util, 41, 101254.

Zhang M., Xu Y., Williams B.L., Xiao M., Wang S., Han D., et al., 2021, Catalytic materials for direct synthesis of dimethyl carbonate (DMC) from CO_2, J Clean Prod, 279, 123344.

Zhang Z., Murali A., Sarswat P.K., Free M.L., 2020, High-efficiency lithium isotope separation in an electrochemical system with 1-butyl-3-methylimidazolium dicyanamide, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and diethyl carbonate as the solvents, Sep Purif Technol, 253, 117539.