

Limonene carbonate synthesis from CO₂: Continuous flow catalysis with integrated product separation

Ana B. Paninho^{a,b}, Christian Westhues^b, Daniel Geier^b, Ana V. M. Nunes^{a,*},
Manuel Nunes da Ponte^a, Walter Leitner^b, Giancarlo Franciò^{b,*}

^a. LAQV, REQUIMTE, Dep. Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

^b. RWTH Aachen University, Institut für Technische und Makromolekulare Chemie,
Worringerweg 2, 52074 Aachen, Germany

* francio@itmc.rwth-aachen.de * ana.nunes@fct.unl.pt

The cycloaddition of CO₂ to epoxides is one of the most attractive route to use CO₂, as a C₁ building block. This reaction has been object of an intensive research in the last years as documented by the growth in the number of publications [1]. The resulting cyclic organic carbonates are important low energy molecules, which find application as electrolytes for lithium batteries, pharmaceutical intermediates and monomers in polymer production [1].

Recent developments comprise the replacement of fossil-based epoxides by bio-derived epoxides for the production of entirely renewable cyclic carbonates. Bio-derived epoxides are however, less reactive and, thus, more challenging substrates due to their complex structure and substitution patterns [2]. In this context, process intensification strategies are particularly important in view of future large-scale industrial applications.

Limonene epoxide is a bio-derived building block obtained from the epoxidation of limonene, a natural compound widely available as by-product of the citrus industry. In this work, the continuous flow production of limonene carbonate from limonene epoxide and CO₂ was explored using a biphasic reaction system composed of CO₂ and an ionic liquid (IL) in a high-pressure set-up apparatus. The working principle of CO₂/IL biphasic systems is based on the fact that supercritical CO₂, used as the carrier, has high solubility in ILs, while ILs have no measurable solubility in CO₂ and cross-contamination is avoided [3]. The IL phase (Aliquat Br and TBABr) was used as the catalyst, while supercritical CO₂ was used as the reactant and mobile phase. Phase behaviour studies both for the reagent and the product were first performed to identify suitable operating conditions for the flow-system. Continuous-flow experiments were then conducted using a continuous stirred tank reactor. The results under continuous-flow conditions will be discussed and compared with those obtained for reactions operated at batch conditions.

References : [1] H. Buuttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, Recent Developments in the Synthesis of Cyclic Carbonates from Epoxides and CO₂, *Top. Curr. Chem.*, **2017**, 375, 50. [2] A.S. Reis Machado, A.V.M. Nunes, M.Nunes da Ponte, Carbon dioxide utilization—Electrochemical reduction to fuels and synthesis of polycarbonates, *J. Supercrit Fluids*, **2018**, <https://doi.org/10.1016/j.supflu.2017.12.023>. [3] J. Walkowiak, G. Franciò, W. Leitner, “Supercritical Fluids as Advanced Media for Reaction and Separation in Homogeneous Catalysis” in *Applied Homogeneous Catalysis with Organometallic Compounds*, 3rd Edition (Eds.: B. Cornils, W. A. Herrmann, M. Beller, R. Paciello) Vol. 4, pag. 1221-1258, Wiley-VCH Weinheim 2018, ISBN: 978-3-527-32897-0.

Acknowledgements : Financial support by the European Regional Development Fund (ERDF) and the state of North Rhine-Westphalia, Germany. Fundação para a Ciência e a Tecnologia – FCT (Portugal), through the project UID/QUI/50006/2013. A.V.M. Nunes is thankful to FCT for contract IF/01374/2014. A.B. Paninho is thankful to FCT for the doctoral fellowship PD/BD/52497/2014. Portuguese NMR spectrometers are part of The National NMR Facility, supported by FCT (RECI/BBB-BQB/0230/2012).