2nd International Symposium on Green and Sustainable Chemistry

8th International Conference on Biocatalysis in Non-Conventional Media

CARTAGENA (SPAIN) MAY 25–28, 2026

BOOK OF ABSTRACTS

Edited by:

Susana Nieto,
Eduardo García-Verdugo,
Andrés R. Alcántara
& Pedro Lozano

Susana Nieto, Eduardo García-Verdugo, Andrés R. Alcántara, Pedro Lozano

Universidad de Murcia, Universidad Jaume I Castellón, Universidad Complutense de Madrid.

ISBN: 978-84-09-86742-4 Nº Registro: 2026032669
Formato digital
2026

Dear colleagues,

On behalf of the Organizing Committee, the Scientific Committee, the Green Chemistry Division (GEQV, https://geqv.rseq.org/) of the Spanish Royal Society of Chemistry (RSEQ) and the European Society of Applied Biocatalysis (ESAB, https://esabweb.org/), it is a privilege to invite you to participate in the dual conference:

2nd International Symposium on Green and Sustainable Chemistry, and

8th International Conference on Biocatalysis in Non-Conventional Media,

which will take place the Polytechnical University of Cartagena (Spain, https://www.upct.es/) between May 25-29, 2026

We are truly convinced that this meeting will be an extraordinary discussion forum to learn about and enjoy the research carried out by our community, both national and international, in all areas of Green and Sustainable Chemistry and Biocatalysis, as interdisciplinary platforms that offer to academic and industrial researchers a privileged environment to exchange on the latest scientific advances in these fields, to show your recent innovations, to share on tomorrow's scientific and technological hurdles, and to facilitate public-private and private-private partnerships.

This dual Symposium will bring together young researcher (i.e. Master, PhD students, Postdocs, and professional of the chemical industry), and leading experts in the field of Green and Sustainable Chemistry and Biocatalytic transformation. The goal of the Symposium is to disseminate novel concepts and latest trends in these disciplines to enable a sustainable present and future by providing a comprehensive training for young scientists.

Pedro Lozano

Chair of the Organizing Committee

President of the Green Chemistry Division – Spanish Royal Society of Chemistry

Organizing and Local Committee

- **Pedro Lozano -** University of Murcia - Spain (Chairman)
- **Eduardo Garcia-Verdugo -** University Jaume I - Spain
- **Maria J Hernáiz -** Complutense University of Madrid - Spain
- **Arjan W. Kleij -** ICIQ & ICREA, Tarragona - Spain
- **Belén Altava -** University Jaume I - Spain
- **Jose L. Serrano -** Polytechnical University of Cartagena - Spain
- **Juan. A. Madrid -** National Reference Centre in Chemistry – Spain
- **Andres R Alcantara –** Complutense University of Madrid - Spain
- **Susana Nieto -** University of Murcia - Spain
- **Rocio Villa -** University of Murcia – Spain
- **Francisco Velasco -** University of Murcia – Spain

Scientific Committee

- **Pedro Lozano -** University of Murcia – Spain (Chairman)
- **Eduardo Garcia-Verdugo -** University Jaume I - Spain
- **Maria J Hernáiz -** Complutense University of Madrid - Spain
- **Arjan W. Kleij -** ICIQ & ICREA, Tarragona - Spain
- **Belen Altava –** University Jaume I - Spain
- **Andres R Alcantara –** Complutense University of Madrid - Spain
- **Elena Ibanez – I**nstitute of Food Science Research CSIC in Madrid
- **Joaquin García-Álvarez –** University of Oviedo
- **Maria J. Sabater –** ITQ/UPV Valencia
- **Pedro Cintas –** University Extremadura
- **Beatriz Giner –** University San Jorge Zaragoza
- **Uwe Pischel –** University Huelva
- **Rene Rodriguez –** OLON Derivados Químicos S.A.
- **Juana M. Bernal –** TAHE Productos Cosméticos S.L - Spain
- **Roland Wohlgemuth -** Lodz University of Technology - Poland
- **Elisabeth Jacobsen -** NTNU, Trondheim, Norway
- **Sergio Riva -** Institute of Chemical Sciences and Technologies "Giulio Natta". Milan. Italy
- **Daniela Ubiali -** University of Pavia. Italy
- **Francesco Molinari -** University of Milan. Italy
- **Francesco Secundo -** National Council of Research, Milan. Italy

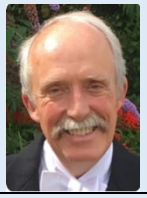
Technical Secretariat

- **Vértice Sur**(congresos@verticesur.es)

https://isgreensc2026bncm.org/

SCIENTIFIC PROGRAM

Monday, May 25th, 2026

17:00 – 18:15	**REGISTRATION**
18:15 – 18:30	**WELCOME AND INTRODUCTION** (Isaac Peral Room) Chairs: Pedro Lozano, Eduardo García-Verdugo and Andrés R. Alcántara
18:30 – 19:15	**Opening Lecture.** Chairman: Eduardo García-Verdugo **PL-1.** The role of chemists in a sustainable world  **David Cole-Hamilton** Professor of Sustainable Chemistry Scholl of Chemistry. University of Saint-Andrews. UK EuChemS Past President
19:15 – 20:30	**WELCOME COCKTAIL**

Tuesday, May 26th, 2026

	SESSION 1 (Isaac Peral Room)
8:30 – 9:15	Chair: Pedro Lozano  **PL-2.** The Intergovernmental Panel for Chemicals, Waste and Pollution **Tom Welton** Professor of Sustainable Chemistry Imperial College London – UK RSC Past President, RSC Sustainability, Editor-in-Chief
9:15 - 9:30	**OPENING CEREMONY**
9:30 – 10:00	Chair: David Cole-Hamilton  **KN-1** – Ionic-Liquid–Modified Semiconductor Interfaces for Artificial Photosynthesis **Jairton Dupont** Professor of Organic Chemistry-Distinguished Researcher Faculty of Chemistry. University of Murcia. Spain

	SESSION 2	
	Symposium 1 (Isaac Peral Room) *Plastic Depolymerization and Circular Chemistry#1* *Chairs: Maria J. Hernáiz / Elena Ibañez*	**Symposium 2** (Salón de Grados) *Non conventional Reaction Media for (Bio)catalysis)* *Chairs: Andrés R. Alcántara / Susana Nieto*
10:30 – 11:00	**KN-2** - Biocatalytic Alcoholysis of Polyurethanes Using Short-Chain Alcohols.  **F. Lopez-Gallego** Group leader at CIC biomaGUNE	**KN-3** - Entrapment of Enzymes in Ionic Liquid Gels, Towards Biocatalytic NaturIL Gels  **A. C. Marr** Professor of Inorganic Chemistry Queen's University of Belfast - UK
11:00 – 11:20	**COFFEE + POSTER SESSION**	
11:20-11:40	**OC-1** - Toward Sustainable Plastic Recycling using Supercritical CO_2 A. Cabañas	**OC-6** - Exploring hydrolase promiscuity towards chitosan in hydrated DES media D. A. Durante-Salmerón
11:40 - 12:00	**OC-2** - Ionic Liquids and Superbase Catalysts for the Sustainable Depolymerization of Polyurethane Foam Waste R. Villa	**OC-7** - Application of DESs as cosolvents in redox biocatalysis G. de Gonzalo
12:00 – 12:20	**OC-3** - Integrating enzyme kinetics and biocatalyst engineering for sustainable PET degradation J.M. Bolivar	**OC-8** - Rational DESs design for unspecific peroxygenase (UPO) stabilization N. Yilmaz
12:20 – 12:40	**OC-4** - Magnetically recoverable catalysts for polymer wastes recycling C. Martin	**OC-9** - Bifunctional Uncoupled Catalysis Enabled by Deep Eutectic Solvent Systems for C-4 Functionalization of Isoquinolines A. Cores
12:40 – 13:00	**OC-5** - Synthesis and Chemical Recycling of Crosslinked Poly(ether-co-carbonates D. Rigo	**OC-10** - Modulating enzymatic phloretin gluycosylation through deep eutectic solvents (DES) D. Rodriguez-Garcia
13:00- 15:00	**LUNCH**	

	SESSION 3 (Isaac Peral Room)	
15:00 -15:45	Chair: Andrew C. Marr  **PL-3** – Enzymatic Synthesis in Deep Eutectic Solvents: Catalysis Across Hydrophilic and Hydrophobic Realms **Selin Kara** Professor of Biocatalysis and Bioprocess Engineering Head of the Institute of Technical Chemistry Leibniz University Hannover (DE) and Aarhus University (DK)	
	Symposium 3: (Isaac Peral Room) *Sustainable Chemical Processes#1* *Chairs: Belén Altava / Jesús Esteban*	**Symposium 4** (Salón de Grados) *CO_2 capture and/or Transformation#1* *Chairs: Rocio Villa / David Cole-Hamilton*
15:45 -16:05	**OC-11** - Laboratory to Market: Development of Water-Soluble Catalysts For Solving Key Research Problems A. N. Kapdi / J. L. Serrano	**OC-15** - Efficient and Sustainable CO_2 Conversion into Fuels and High-Value Products L. C. Branco
16:05-16:25	**OC-12** - Mechanism-driven sustainable Pd-catalyzed cross-coupling reaction methodologies I. J. S. Fairlamb	**OC-16** - Green synthesis of Limonene-based NIPUs precursors: A comparative catalytic study in supercritical CO_2 P. Cruza-Rodelgo
16:25-16:45	**OC-13** - Designing Renewable Functional Ionic Liquids: Toxicity, Catalytic performance, and Green metrics evaluation A. Leal-Duaso	**OC-17** - Unlocking the Potential of Biocatalysis-driven CCU: A sustainable production of valuable chemicals from industrial feedstocks O. Romero
16:45-17:05	**OC-14** - Uncatalyzed aerobic epoxidation of liquid alkyl alkenes J. Oliver-Meseguer	**OC-18** - Electrochemical biogas upgrading: Direct CO2 to CH4 conversion employing Cu-based MOFS Jose Antonio Abarca
17:05-17:30	**COFFEE + POSTER SESSION**	

	SESSION 4 (Isaac Peral Room)
17:30-18:15	Chair: Selin Kara  **PL-4** – Discovery and engineering of enzymes for the depolymerization of polyurethanes **Uwe T. Bornscheuer** Professor of Biotechnology & Enzyme Catalysis Institute of Biochemistry. University of Greifswald, Germany
18:15 – 20:15	**VISIT TO CARTAGENA**
20:30 – 24:00	**PhD & Young Researchers Night** Cocktail Dinner + Drinks + Live Music Symposium Building Courtyard

Wednesday, May 27th, 2026

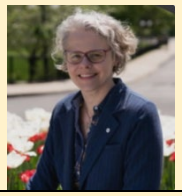
	SESSION 5 (Isaac Peral Room)	
8:45- 9:30	Chair: Tom Welton  **PL-5.** Valorization of whatever comes out of the eggs **Joao M. C. A. P. Coutinho** Professor of Chemistry Director of CICECO – Aveiro Institute of Materials University of Aveiro, Portugal.	
	Symposium 5 (Isaac Peral Room) *Plastic Depolymerization and Circular Chemistry#2* *Chairs: Eduardo García-Verdugo / Joaquín García-Álvarez*	**Symposium 6** (Salón de Grados) *Sustainable (Bio)catalytic and down-stream processes* *Chairs: Martina L. Contente / Vicente Gotor Fernández*
9:30-9:50	**OC-19** - Advancing circular economy through sustainable metal recovery from waste tantalum capacitors. F. Braga	**OC-23** - Sustainable Biocatalytic Production of Bio-Based Diethyl Succinate in Ionic Liquids S. Nieto
9:50-10:10	**OC-20** - Py-GC-MS-based methodology for the environmental assessment of PHB in agricultural soils. M. Alcaraz-Dolera	**OC-24** - Enhancing Laccase-Driven Poly(vinyl alcohol) Depolymerization Using Polyol-Based Biosolvents. M. I. S. Aguiar
10:10 – 10:30	**OC-21** - Circular enzymatic biobleaching: revalorization of high-polluted waste streams Y. Fredes	**OC-25** - Redesign of cheese whey permeate upcycling: a biocatalytic approach guided by green metrics M. S. Robescu
10:30 – 10:50	**OC-22** - DOZN™3.0 - A Quantitative Green Chemistry Evaluator for a Sustainable Future E. Ponnusamy	**OC-26** - Sustainable biocatalytic processes in green solvents for the production of bioactive compounds M. Bigliardi
10:50 - 11:10	**COFFEE + POSTER SESSION**	

	SESSION 6 (Isaac Peral Room)	
11:10 – 11:40	Chair: Selin Kara  **KN-4.** Can biocatalysis be even greener? **Francesca Paradisi** Professor of Sustainable Pharmaceutical Chemistry University of Bern, Switzerland.	
	Symposium 7 (Isaac Peral Room) *Sustainable Chemical Processes#2* *Chairs: Marcileia Zanatta / Tom Welton*	**Symposium 8** (Salón de Grados) *Biomass and Bioresources* *Chairs: Marina Cvjetko / Uwe Bornscheuer*
11:40 – 12:00	**OC-27** - Synthesis and Solubilization Potential of Glycerol-Derived Solvents: A Sustainable Approach to Green Chemistry E. Pires	**OC-32** - A Sweet Flow: HMF Production and in-situ Valorization into Valuable Nitrile-containing Compounds via Telescopic Flow Chemistry. J. E. Sanchez-Velandia
12:00 - 12:20	**OC-28** - Cu-catalyzed stereodivergent decarboxylative amination of bicyclic carbamates: Access to cyclobutane-1,3-diamine synthons Y. Ren	**OC-33** - Effect of chao- and kosmotropic natural deep eutectic solvents on the chitin separation and from h. Illucens pupae molt shells G. A. Portillo Perez
12:20 – 12:40	**OC-29** - Closing the Loop: Flow Platform for the Sustainable Synthesis, Application and Electrochemical Recovery of Nickel Catalysts Charlotte Willans	**OC-34** - Extraction and purification of Phlorotannins from Sargassum muticum using natural deep eutectic solvents M. X. Zhang
12:40 – 13:00	**OC-30 -** Visible Light-Induced Catalyst-Free Decarboxylative Povarov-Type Reaction of N-Aryl Glycines with Maleimides in Deep Eutectic Solvents J. A. Ñiguez-Elena	**OC-35** - Evaluation of different surfactants in the etherification of glycerol with tert-Butanol using microemulsions F. Perez
13:00 – 13:20	**OC-31** - Sustainable approaches to sulfur containing polymers through the exploitation of carbon disulfide as a sulfur-rich feedstock C. J. Whiteoak	**OC-36** - Sustainable Valorization of Insect Biomass: Optimized Oil Recovery Using Green Solvents L. C. Branco
13:20- 15:00	**LUNCH**	

	SESSION 7 (Isaac Peral Room)	
15:00-15:45	Chair: Joao Coutinho  **PL-6**. Catalysis and Sustainability from Atom to Planetary Scale **Javier Perez-Ramirez** Professor of Catalysis Engineering at the Institute for Chemical and Bioengineering ETH Zürich, Switzerland Green Chemistry, Editorial Board Chair	
	Symposium 9 (Isaac Peral Room) *Flow, Biphasic and Multi-phase green catalytic systems* *Chairs: Juan M. Bolívar / Selin Kara*	**Symposium 10** (Salón de Grados) *CO_2 capture and/or Transformation#2* *Chairs: Jairton Dupont / Fernando López-Gallego*
15:30-16:00	**KN-5** - Biphasic production of HMF and furfural: lessons learned from green alternative solvent use and macrokinetic studies  J. Esteban	**KN-6** - Sustainable Decarbonization Pathways for CO_2 Conversion  M. Zanatta
16:00-16:20	**OC-37** - Green in Motion: Biocatalysis–Reactor Synergy in Sustainable Manufacturing M. L. Contente	**OC-40** - Green metal-organic framework for CO_2 fixation F. G. Cirujano
16:20-16:40	**OC-38** - 3D printed biocatalytic flow reactors A. Pordea	**OC-41** - Redefining Sustainable Synthesis: Mechanochemistry as a Driver for Advanced Coordination Chemistry and Green Catalysis J. F. Reynes
16:40-17:00	**OC-39** - Pickering Emulsion-Templated Ultra-Porous Films from Biopolymers as Supports for Enzyme Immobilization W. Dang	**OC-42** - An Iron-Based MOF as a Versatile Catalyst for CO_2 Valorization and Renewable Feedstok Transformation I. M. Pastor
17:00-17:15	**COFFEE + POSTER SESSION**	

GEQV 2025 AWARDS (Isaac Peral Room)	
17:15-17:50	Chair: Pedro Lozano  **Lecture "2025 GEQV Medal"** **Avelino Corma** CSIC Reseach Professor -Distinguished Researcher Polytechnical University of Valencia. Spain
17:50-18:30	Chairs: Pedro Lozano / Belen Altava **GEQV 2025 AWARDS CEREMONY**
18:30-19:30	***BEER -POSTER SESSION***
20:00 – 24:00	**GALA DINNER** Restaurante Alviento – Pier of Cartagena https://www.espacioalviento.com/restaurante-alviento

Thursday, May 28th, 2026

	SESSION 8 (Isaac Peral Room)	
8:45 – 9:30	Chair: Elena Ibañez **PL-7**. Mechanochemistry and Aging-Based as Innovative Methods for the Valorization of Biomass into Nanocrystals and Nanofibers  **Audrey Moores** Professor of Chemistry, Materials group of the McGill Sustainable Systems Initiative (MSSI). McGill University. Montreal, QC, Canada.	
	Symposium 11 (Isaac Peral Room) *Green Energies* *Chairs: Andrew C Marr / Pedro Cintas*	**Symposium 12** (Salón de Grados) *Bio-based materials* *Chairs: Andrés R. Alcántara / Joao Coutinho*
9:30 – 9:50	**OC-43** - Catalytic higher ether synthesis and characterization: elevating Power-to-liquids higher alcohol products to a drop-in e-fuel D. De Baker	**OC-46** - Xylose and glucose recovery from sunflower stalks by microwave-based pretreatment R. García Barranco
9:50 – 10:10	**OC-44** - Exploring the role of zeolite structure and acidity on Cu-based catalysts for dimethyl ether steam reforming J. J. Lopez-Martin	**OC-47** - Bioengineering Lysozyme-Loaded Alginate/Chitosan Films for Therapeutic Applications M. H. Ribeiro
10:10 – 10:30	**OC-45** -Hollow Rotating Disk Electrode (h-RDE): Bridging Conventional RDE and GDE Testing for Gas-Fed Electrocatalysis F. Santos	**OC-48** - Choline-Based Ionic Liquids as Selective Cytotoxic Agents Against Cervical Cancer Cells J. J. Delgado-Marin
10:30 -10:50	**COFFEE + POSTER SESSION**	
	SESSION 9	
	Symposium 13 (Isaac Peral Room) *Sustainable Chemical Processes#3* *Chairs: Nuria Martín / Audrey Moores*	**Symposium 14** (Salón de Grados) *Enzyme Stability and Stabilization* *Chairs: Gonzalo de Gonzalo / Francesca Paradisi*

10:50 – 11:20	 **KN-7** - Design of One-Pot Chemoenzymatic Cascades Merging Polar Organometallic Reagents (RLi/RMgX) with Laccases and ADHs J. Garcia-Alvarez	 **KN-8** - Recent progress on gold-enzyme cascades for the synthesis of optically active organic molecules V. Gotor-Fernández
11:20 - 11:40	**OC-49** - Highly active Metathesis Catalysts for Industrial Applications T. Gazdag	**OC-54** - Eutectozymes: a novel platform based on solid eutectic matrices for advanced biocatalysis A. Beloqui
11:40 – 12:00	**OC-50** - Electrocatalytic Access to Quinoline Sulfones under Sustainable Conditions in Deep Eutectic Solvents D. Adsuar	**OC-55** - Coimmobilization of enzymes with different stabilities. How to re-use of the most stable immobilized enzyme after the inactivation of the least stable enzyme using the glutaraldehyde chemistry. P. Abellanas-Perez
12:00 - 12:20	**OC-51** - Chemical Valorization of Lindane Residues J. M. Fraile	**OC-56** - Engineering of rubber degrading enzymes A. Pordea
12:20 – 12:40	**OC-52** - Earth abundant catalysts for the sustainable production and upcycling of biobased polyesters with advanced properties M. E. G. Mosquera	**OC-57** - Levoglucosenone-derived solvents prevent aggregation and tune substrate accessibility of immobilized CALB M. Mangiagalli
12:40 – 13:00	**OC-53-** Synthesis of C4 α-hydroxyesters from C2-biomass derived glycolaldehyde with Sn-β V. de Blas-Sanchez	**OC-58** - Designing Designer Solvents: Optimizing Protein Stability in Deep Eutectic Solvents through a Combined Experimental and Computational Approach A. Damjanović
13:00 – 13:20	***AWARDS AND CLOSING CEREMONY*** (Isaac Peral Room)	
13:20- 15:00	***CLOSING LUNCH***	

CONFERENCES

The role of chemists in a sustainable world

D. Cole-Hamilton
EaStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, Scotland, UK
Email: djc@st-and.ac.uk

The world is at a crossroads. It has come from a time where fossil fuel resources provided the raw materials for almost everything and most things were used and thrown away. Because fossil fuels are finite and their burning causes global changes in climate, and because most other resources are finite, we must move to a world where renewable resources are used to make reusable and recyclable objects in a circular economy for sustainable development. The renewable resources must no compete for land with food production.

The United Nations has defined seventeen goals for sustainable development In this talk we shall explore the huge role chemistry must play in achieving all of these goals.

With only 4 years to go to the target date of 2030, urgent action is required and chemists must provide it.

[1] D. J. Cole-Hamilton, Chem. Eur. J, **2020**, *26*, 1894-1899

The Intergovernmental Panel for Chemicals, Waste and Pollution

Prof Tom Welton

Department of Chemistry, Imperial College London and The Royal Society of Chemistry

Email: t.welton@imperial.ac.uk

The products of the chemicals industries are essential to our everyday lives. However, we also know that many of these can lead to negative environmental and health effects. Concepts of humankind's ability to impact our environment have changed dramatically since the advent of the industrial revolution. Initially, it was believed that there was no human activity that could have any widespread or lasting impact on the environment. Today, we know that is not true and that human activities are having global impacts. This talk tracks these changes and looks at how the United Nations is seeking to bring together the best possible science to provide the crucial societal services that come from chemical products without compromising the environment and the health of current and future generations. I will also show how scientists may become involved in this process.

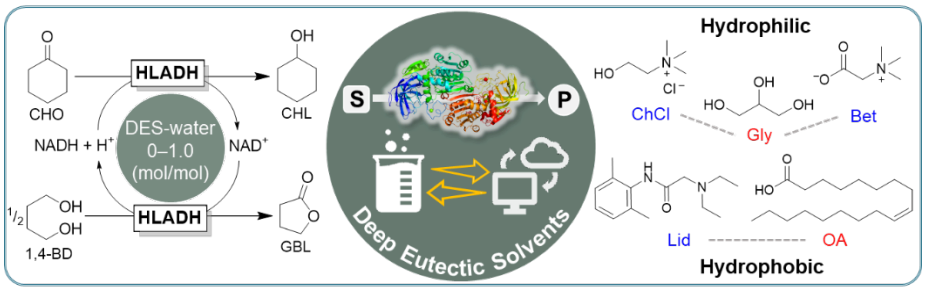
Enzymatic Synthesis in Deep Eutectic Solvents: Catalysis Across Hydrophilic and Hydrophobic Realms

Selin Kara,[a,b]

a Callinstr. 5, 30167 Hannover, Germany, Leibniz University Hanover.
b Gustav Wieds Vej 10, 8000 Aarhus C, Denmark, Aarhus University.

E-mail: selin.kara@bce.au.dk, selin.kara@iftc.uni-hannover.de

Biocatalysis has been shifting from conventional aqueous media to non-aqueous media in line with the principles of Green Chemistry.1a Deep eutectic solvents (DESs) represent a new class of greener solvents with high tunability.1b,c The rational design of biocatalysis in DESs requires a comprehensive knowledge of the DES effects on enzymes. The impact of DESs on oxidoreductases has been holistically studied by assessing the catalytic performance of alcohol dehydrogenases (ADHs) in DES-water mixtures (e.g., choline chloride-glycerol, ChCl-Gly, 1:2) with the aid of experimental analyses and molecular dynamics (MD) simulations.2a,b The individual DES components showed a discrepant impact, e.g., positive of Gly or negative of ChCl, promoting the generation of an enzyme-compatible eutectic mixture by increasing the Gly fraction (ChCl-Gly, 1:9).2c Furthermore, replacing ChCl with betaine (Bet) led to identifying a more enzyme-friendly Bet-Gly system (Scheme 1).



Scheme 1. Analysis of horse liver alcohol dehydrogenase in glycerol-based deep eutectic solvents containing various water contents (0–100 vol.%) by combining experiments and simulations.

The fact that enzyme activity is positively related to water activity due to the solvation changes surrounding enzymes promoted the use of hydrophobic DES, lidocaine-oleic acid, leading to the 1st outperformance of DES-buffer mixture over pure buffer at 100 g/L substrate loading.[3]

---

[1] a) M. van Schie, J. D. Sporing, M. Bocola, P. Domínguez de María, D. Rother, *Green Chem*. **2021**, *23*, 3191-3206. b) M. Pätzold, S. Siebenhaller, S. Kara, A. Liese, C. Syldatk, D. Holtmann, *Trends Biotechnol.* **2019**, *37*, 943-959. c) N. Zhang, P. Domínguez de María, S. Kara, *Catalysts* **2024**, *14*, 84.
[2] a) L. Huang, J.P. Bittner, P. Domínguez de María, S. Jakobtorweihen, S. Kara, *ChemBioChem* **2018**, *21*, 811-817; b) J. P. Bittner, I. Smirnova, S. Jakobtorweihen, Molecules 2024, 29, 703. c) J. P. Bittner, N. Zhang, L. Huang, P. Domínguez de María, S. Jakobtorweihen, S. Kara, *Green Chem*. **2022**, *24*, 1120-1131.
[3] N. Zhang, V. Lahmann, J. P. Bittner, P. Domínguez de María, S. Jakobtorweihen, I. Smirnova, S. Kara, *ChemSusChem* **2024**, e202402075.

Discovery and engineering of enzymes for the depolymerization of polyurethanes

Uwe T. Bornscheuer

Institute of Biochemistry, University of Greifswald, Greifswald, Germany

E-mail: uwe.bornscheuer@uni-greifswald.de

This lecture will cover recent achievements in the discovery, protein engineering [1] and application of enzymes in the depolymerization of plastics with a focus on polyurethanases. To address the global problem of plastic waste, we have performed extensive research for the recycling of PET, for which we have improved different esterases and also recently established a protocol enabling a fair comparison PETases reported in literature [2]. We also designed enzyme cascades to degrade poly(vinylalcohols) and low molecular weight polyethylene [3]. Very recently, we have identified the first three urethanases in a metagenomic library able to degrade polyurethanes [4]. The initially found three enzymes can indeed hydrolyze the carbamate bond in (poly)urethanes, which now makes it possible to recycle these polymers as this enables the isolation of the aromatic amine monomers. In addition, we have solved the X-ray structures of all three enzymes [5], performed biochemical characterization and could broaden their substrate scope. This also guided our search for further urethanases which led to the discovery of interesting amidases and nylonases [6].

[1] R. Buller et al., *Science* **2023**, *382*, eadh8615; T. Bayer et al., *Angew. Chem. Int. Ed.*, **2025**, *64*, e202505976.
[2] G. Arnal et al., *ACS Catal.*, **2023**, *13*, 13156-13166.
[3] T. Oiffer et al., *Angew. Chem. Int. Ed.*, **2024**, *63*, e202415012.
[4] Y. Branson et al. *Angew. Chem. Int. Ed.*, **2023**, *62*, e202216220.
[5] T. Bayer et al. *Angew. Chem. Int. Ed.*, **2024**, *63*, e202404492; Z. Li et al., *Adv. Sci.*, **2025**, *12*, 2416019; L. Rotilio et al., *Angew. Chem. Int. Ed.*, **2024**, *63*, e20241953.
[6] I. Somvilla et al., *Adv. Sci.*, **2025**, *13*, e17740 (2025); I. Somvilla et al., *ACS Catal.*, **2025**, *15*, 8902-8912.

Valorization of whatever comes out of the eggs

João A. P. Coutinho[a,*], Mara G. Freire[a]

[a] *CICECO - Aveiro Institute of Materials, Dep. of Chemistry, University of Aveiro, Aveiro, Portugal*

E-mail: jcoutinho@ua.pt

Chicken eggs and poultry waste have been the focus of much of our study, as they appear to be unsuspected, rich sources of valuable compounds when treated with ionic liquids. Primarilly we addressed the eggs. In Aveiro, a city proud of its egg-yolk-based sweets, the excess egg white is a by-product that is hard to valorise. We will show how to extract the albumin from the egg white [1] and how we learnt to fibrillate proteins from this rich and cheap source [2] using a technique that was later successfully applied to human platelet lysates, allowing us to produce nanofibrils that were used to produce free-standing membranes for cell self-aggregation.[3] But the egg yolk was no less interesting. Rich in IgY antibodies it became the object of an ERC grant aimed at their recovery to be used as biopharmaceuticals.[4] Eggs can undoubtedly be used for purposes other than making tortillas.

Recently, we became interested in chicken feathers. Millions of tonnes of this unpleasant waste are generated each year, with little use. Feathers are rich in keratin (90 wt %), a fibrous protein with higher stability and lower solubility than most proteins. The conversion of an unavoidable biowaste into value-added products became our purpose. The processing conditions (keratin concentration, plasticiser, and IL type) were optimised to achieve the biomaterial's best properties. The results demonstrated that the processing conditions have a substantial effect on the biomaterial properties. To achieve a sustainable process, IL recovery and reuse were also evaluated. Our results demonstrate that chicken feathers can be efficiently valorised to produce keratin-based biomaterials for use in, among others, the biomedical field.[5,6]

[1] Pereira et al., *Process Biochem*, **2016**, 51, 781
[2] P. Bharmoria et al., *Comm Mat,* **2020**, 1, 34
[3] Monteiro et al. *ACS Nano* **2024**, 24, 15815
[4] Almeida et al., Sep Pur Tech, **2022**, 299, 121697
[5] Polesca et al., *Green Chem*, **2023**, 25, 1424
[6] Polesca et al., *ACS Materials Lett*, **2025**, 10, 3370

Catalysis and Sustainability from Atom to Planetary Scale

J. Pérez-Ramírez

Institute for Chemical and Bioengineering and NCCR Catalysis, ETH Zurich, Switzerland

E-mail: jpr@chem.ethz.ch

Ensuring a sustainable future for the chemicals and energy industries is a pressing global concern that has far-reaching impacts on the environment, human health, quality of life, and the economy. Catalysis plays a crucial role in this journey, constantly pushing the boundaries of conventional design to spearhead the transition towards defossilized and circular chemical manufacturing. This talk aims to illustrate the interdisciplinary and cross-scale mindset required to design catalysts that meet the ever-evolving sustainability criteria, bridging the gap between atom and planet. Delving into the latest research from my laboratory, I will showcase how a deeper understanding of catalyzed processes is driving revolutionary technological advancements. Through case studies in key areas such as CO2 valorization, polymer manufacture, and organic synthesis, I will exemplify how nanoscale engineering and the availability of increasingly powerful tools to access structural variations and mechanism under relevant conditions aid catalyst discovery. At the forefront of design, I will demonstrate the importance of precisely controlling the architecture, speciation, and dynamics of supported metals in low-nuclearity catalysts, highlighting the impact that even the smallest changes can have on performance. The presentation will touch on current frontiers in catalyst synthesis and characterization, and emphasize the critical role of quantitative metrics in guiding low-carbon strategies.

Mechanochemistry and Aging-Based as Innovative Methods for the Valorization of Biomass into Nanocrystals and Nanofibers

Galen Yang,[a] Tony Jin,[a] Austin Richard,[a] Jasmine Hong,[a] Edmond Lam,[a] and Audrey Moores[a,*]

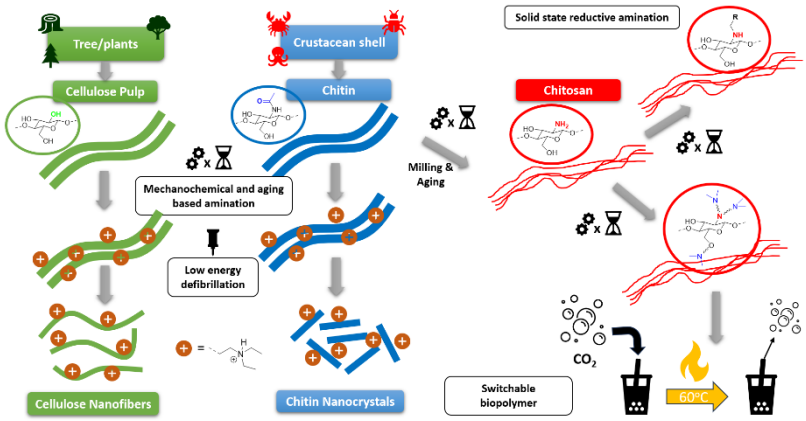
[a] *Centre in Green Chemistry and Catalysis, 801 Sherbrooke Street West, Montréal, QC, H3A 0B8, Canada*

E-mail: audrey.moores@mcgill.ca

Mechanochemistry and aging-based methodologies (Mecha&Ag) are emerging as powerful alternatives to conventional solution-based synthesis, enabling transformations that are difficult, inefficient, or wasteful under solvothermal conditions. By leveraging mechanical force and controlled solid-state reactivity, these approaches offer reduced solvent use, improved process mass intensity (PMI), and access to highly functionalized materials with unique properties.

Our group has developed Mecha&Ag platforms for the transformation of renewable feedstocks and polymeric materials, including chitin, chitosan, cellulose, and more recently synthetic polymers. We established solvent-minimized protocols for the extraction[1] and deacetylation[2] of chitin and controlled depolymerization chitosan,[3] as well as the preparation of nanochitin and nanochitosan.[4-6] Building on this foundation, we demonstrated highly efficient solid-state functionalization strategies that overcome long-standing limitations in polysaccharide chemistry. These include reductive alkylation of chitosan with unprecedented degrees of substitution and excellent PMI,[7] as well as a one-pot SN2-type aminoalkylation affording tertiary amine-functionalized chitosan with high substitution, yielding CO_2-switchable materials.[8] We further extended this strategy to introduce cationic functionality directly onto cellulose pulp to enable low-energy defibrillation to nanofibers.[9]

Beyond biopolymers, we recently applied mechanochemistry to the controlled synthesis of microplastics, demonstrating that solid-state processing can provide reproducible and scalable particle formation with key features of naturally occurring ones.[10] Together, these studies illustrate how Mecha&Ag strategies can overcome the intrinsic limitations of solution chemistry and provide scalable, low-footprint routes to advanced materials from both biomass and waste streams._



[1]. F. Hajiali, et al., *ACS Sustainable Chem. Eng.* **2022**, *10, 34*, 11348–11357.
[2]. T. Di Nardo, et al., *Green Chem.* **2019**, 21, 3276-3285
[3]. G. Yang, et al., *ACS Sustainable Chem. Eng.* **2023** *11 (20)*, 7765-7774
[4]. T. Jin, et al., *Nanoscale Horiz.* **2021**, *6*, 505-542
[5]. T. Jin, et al., *Angew. Chem. Int. Ed.* **2022**, *61 (42)*, e202207206
[6]. T. Jin, et al., *Green Chem.* **2021**, 23, 6527-6537
[7]. G. Yang, et al., *Green Chem.* **2024**, *26*, 5386-5396.
[8]. G. Yang, et al., *ChemSusChem.* ***2025,*** *18 (19), e202501187*
[9]. G. Yang, et al., *Biomacromolecules* **2026**, *27(1)*, 451–458.
[10]. J. Hong, et al., *Env. Sci. Tech.* **2025** *59 (30)*, 15956–15965.

Ionic-Liquid–Modified Semiconductor Interfaces for Artificial Photosynthesis

Jairton Dupont,[a]

[a] *Departamento de Bioquímica y Biología Molecular "B" e Inmunología. Facultad de Química. Universidad de Murcia, E-30.100, Murcia, Spain.*

E-mail: j.dupont@um.es

Artificial photosynthesis represents a central challenge for green and sustainable chemistry,[1] as it requires the activation of thermodynamically stable CO_2 using solar energy while maintaining selectivity and material sustainability.[2] Conventional semiconductor photocatalysts are often limited by unfavorable band-edge positions, fast charge recombination, and dominant proton reduction. In this contribution, we present recent results from our research group on ionic-liquid (IL)-modified semiconductor photocatalysts,[3] focusing on IL@TiO_2, IL@Bi-based materials, and IL@Fe_2O_3, as a unified strategy to address these limitations.

We show that immobilization of tailored ILs at semiconductor surfaces generates structured interfacial nanoenvironments that modulate band energetics, enhance charge separation, and increase local CO_2 availability (Figure 1). For IL@TiO_2, ILs induce interfacial electronic restructuring that facilitates CO_2 activation under solar irradiation to generate CO. In IL@Bi-based systems, IL organization stabilizes reduced CO_2 intermediates and promotes selective two-electron reduction pathways to CO. IL@Fe_2O_3 further illustrates how ILs can mediate interfacial electron transfer and proton management, enabling visible-light-driven CO_2 reduction to formate/formic acid despite intrinsic limitations of hematite.

Across these systems, we identify IL anion basicity, hydration level, and interfacial organization as key parameters governing activity and product selectivity, enabling preferential formation of CO or formic acid/formate while suppressing parasitic hydrogen evolution. These findings establish IL-modified semiconductors as tunable platforms for artificial photosynthesis and provide general design principles relevant to the development of sustainable solar-driven CO_2 conversion processes.

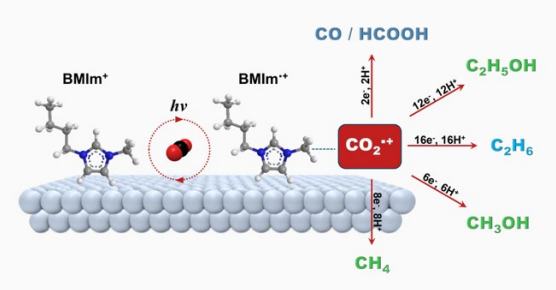


Figure 1. Cartoon of the CO_2 photo-reduction mediated by imidazolium ionic liquids.

Acknowlegements. This work has been partially supported by MICIU-AEI-FEDER 10.13039/501100011033 (PID2024-159264OB-C21/C22, and CPP2023-010883) and FAPERGS (22/2551-0000386-9).

[1] A. Machin, M. Cotto, J. Duconge and F. Marquez, *Biomimetics*, 2023, **8**, 298.
[2] J. Dupont and P. Lozano, *Angew. Chem. Int. Ed. Engl.*, 2025, **64**, e202416459.
[3] M. I. Qadir, et. al., *ChemSusChem*, 2020, **13**, 5580-5585.

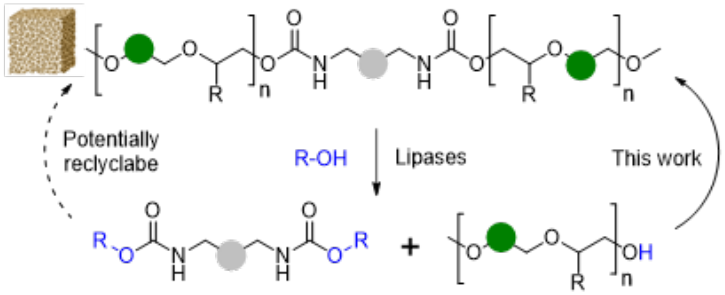
Biocatalytic Alcoholysis of Polyurethanes Using Short-Chain Alcohols

Fernando López-Gallego[1,3], Riccardo Moro[1], Andrea Rizzo[1] and Haritz Sardon[2]

[1] Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramon 182, 20014, Donostia, Spain
[2] POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizábal, 3, 20018 Donostia-San Sebastián, Spain.
[3] Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain

E-mail: flopez@cicbiomagune.es

No efficient bioprocess currently exists for recycling polyether polyurethane foams albeit they are widely used materials in everyday life. Lastly, enzymes have revolutionized plastic recycling, but their application to polyurethanes remains in its infancy. In this work, we find two lipases from *Thermomyces lanuginosus* and *Rhizopus oryzae* capable of cleaving urethane bonds through alcoholysis using short-chain primary alcohols. This mechanism outperforms conventional enzymatic hydrolysis. As result, these lipases successfully degrade polyether polyurethane foams, releasing polyols and alkyl carbamates. The polyols are isolated and subsequently reused in a new polymerization process, generating partially recycled foams. This enzymatic approach in alcohol media was extended to non-isocyanate polyurethane foams, opening new paths for depolymerizing and recycling complex plastics, thereby contributing to a more circular plastic economy.



Scheme 1. Lipase-driven alcoholysis to recycle polyols and dicarbamates

Entrapment of Enzymes in Ionic Liquid Gels, Towards Biocatalytic NaturIL Gels.

Ramatu Seidu,[a] Gareth Brown,[b] Stefan Mix,[b] Patricia C. Marr,[a*] Andrew C. Marr [a*]

[a] *School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, UK*

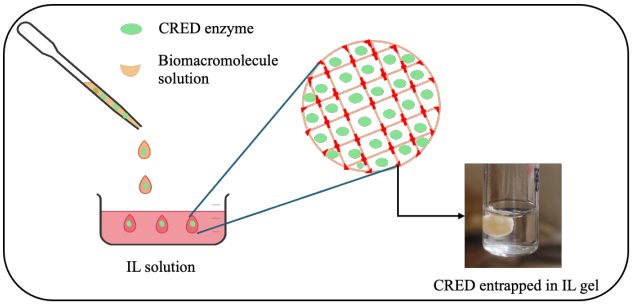
[b] *Almac Group, Almac House, 20 Seagoe Industrial Estate, Craigavon BT63 5QD, UK.*

Email: p.marr@qub.ac.uk, a.marr@qub.ac.uk

Enzyme immobilization greatly improves separations in enzyme-catalyzed processes, reducing solvent use, energy consumption and waste. The entrapment of enzymes within ionic liquid (IL) gels[1] offers the additional opportunity to tune the environment around the enzyme and optimise performance and lifetime.[2] Lipases have been entrapped in polymer[3] (polyacrylamide) and supramolecular[4] (organic molecule) IL gels for operation in solvent and aqueous environments respectively. The IL gel produces a robust and reuseable immobilized enzyme.

NaturIL gels are defined as gels that comprise, a liquid containing ions that can be derived from nature, coupled with a biomacromolecular solid matrix.[5,6] Entrapment of an enzyme in a NaturIL gel produces a tuneable all-natural heterogeneous catalytic system.

Some of the latest developments in IL gel entrapped lipases and carbonyl reductases (CREDs) will be presented.



Keywords

Ionic liquid gels, Enzymes Entrapment, Lipase, Carbonyl Reductase

[1] Marr, P. C.; Marr, A. C. Ionic Liquid Gel Materials: Applications in Green and Sustainable Chemistry. *Green Chem.* **2016**, *18*, 105–128. https://doi.org/10.1039/C5GC02277K.

[2] Imam, H. T.; Marr, P. C.; Marr, A. C. Enzyme Entrapment, Biocatalyst Immobilization without Covalent Attachment. *Green Chem.* **2021**, *23*, 4980–5005. https://doi.org/10.1039/D1GC01852C.

[3] Pérez-Tomás, J. Á.; Brucato, R.; Griffin, P.; Kostal, J.; Brown, G.; Mix, S.; Marr, P. C.; Marr, A. C. Entrapment in HydrIL Gels: Hydro-Ionic Liquid Polymer Gels for Enzyme Immobilization. *Catal. Today*, **2024**, *432*, 114595. https://doi.org/10.1016/j.cattod.2024.114595.

[4] Imam, H. T.; Hill, K.; Reid, A.; Mix, S.; Marr, P. C.; Marr, A. C. Supramolecular Ionic Liquid Gels for Enzyme Entrapment. *ACS Sustain. Chem. Eng.* **2023**, *11*, 6829–37. https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00517.

[5] Marr, P. C.; Marr, A. C. Ionic liquid gels: catalysts for sustainability in synthesis, energy, electronics and medicine, *Phil. Trans. R. Soc. A*, **2026**, *384*, 20240301. https://doi.org/10.1098/rsta.2024.0301.

[6] Bailie, P. A.; Walsh, P. J.; Marr, A. C.; Marr, P. C. NaturIL Gels: Gels Formed from the Synergy of Alginates and Bioderived ions. Comparison of ChAAIL Gels and Hydrogels, *ACS Sustain. Chem. Eng.* **2026**, *in press*.

.

Can biocatalysis be even greener?

Francesca Paradisi[a]

[a] *Dept. of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern (Switzerland)*

E-mail: francesca.paradisi@unibe.ch

The move towards sustainable syntheses is a widespread effort which sees academia and industry developing new strategies and solutions.[1] But why is it that biocatalysis, in general, is still not part of the standard toolbox of a chemist? Enzymes are felt to be challenging to work with, they would require a major revolution of the set-up of an existing process, it appears easier to just replace the catalyst with a more efficient newer one which can be just slotted in, in a well-established multi-step chemical cascade. In addition, the requirement for aqueous conditions for the biocatalysts is often limiting in terms of concentrations and scalability. From a process point of view, water is not so green if one needs ten times the volume. And what do we do with the dirty water? Our recent work has focussed on finding ways to make enzymatic steps just another possibility to be at least considered as an option when designing a multi-step synthesis. The ability to immobilize enzymes through versatile chemistries and supports, is a pillar of our group, which has enabled very successful continuous flow processes (Fig. 1). But again, we started thinking at the additional waste we generate when we discard the immobilized biocatalyst. Can we do better? Here I will present our latest efforts in the field. [2-4]

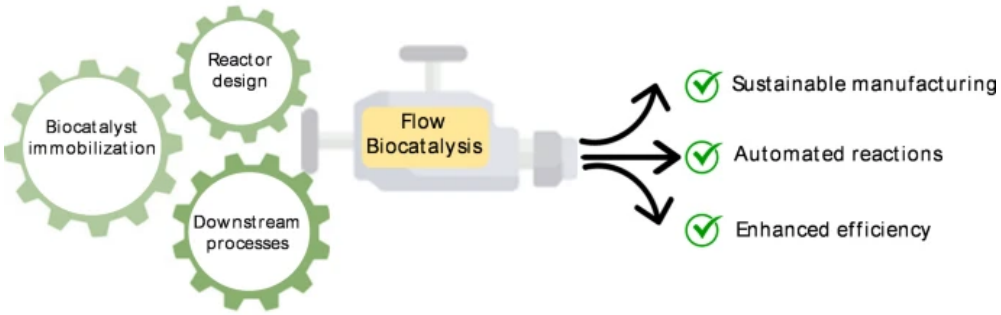


Figure 1. *Flow biocatalysis and sustainability*

[1] Benítez-Mateos, A. I.; Roura Padrosa, D.; Paradisi, F. *Nat. Chem.* **2022**, *14*, 489–499.
[2] Díaz-Kruik, P.; Roura Padrosa, D.; Hegarty, E.; Lehmann, H.; Snajdrova, R.; Paradisi, F. *Org. Process Res. Dev.* **2024**, *28*, 2683–2691
[3] Rassati, B.; Reusser, J.; Robustini, L.; Ben Mariem, O.; Pavlova, A.; Eberini, I.; Paradisi, F. *ACS Catal.* **2025**, *15* (24), 21115–21123
[4] Bojanov, G; Swit J.; Paradisi, F. *Chem. Sci.* **2026**, in press

Biphasic production of HMF and furfural: lessons learned from green alternative solvent use and macrokinetic studies

Dominik Soukup-Carne,[a] Nico Thanheuser,[b] Christopher M.A. Parlett,[a] Walter Leitner,[b] Xiaolei Fan,[a] Andreas J. Vorholt,[b] Jesús Esteban,[c,a,b*]

[a] *Department of Chemical Engineering, School of Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*

[b] *Max-Planck-Institute for Chemical Energy Conversion, Stiftstraße 34, 45470 Mülheim an der Ruhr, Germany*

[c] *Department of Chemical and Materials Engineering, Faculty of Chemical Sciences, Complutense University of Madrid, Avda. Complutense s/n, Madrid 28040, Spain*

E-mail: jeesteba@ucm.es; jesus.estebanserrano@manchester.ac.uk

5-hydroxymethylfurfural (HMF) and furfural (Fur) have attracted attention as key compounds for the development of bioeconomy, serving as building blocks to produce biofuels, solvents and biobased plastics. Their production through the acid-catalyzed dehydration of C6 and C5 lignocellulosic biomass derived sugars, typically taking place in aqueous media, is prone to the generation of undesired by-products like humins as well as levulinic and formic acids, the latter by the rehydration of HMF. For this reason, biphasic systems for the production with *in situ* extraction of HMF and Fur represent an interesting reaction system [1,2]. Despite numerous studies using this approach, there have been scarce systematic efforts to (a) select solvents with a high extractive capability towards HMF and Fur showing adequate environmental, health and safety profiles and [3] and (b) propose thorough microkinetic models to describe the progress of the reactions in biphasic systems using recyclable catalysts [4,5]. This work proposes (a) the COSMO-RS [3] and CHEM21 [4] based solvent selection for furan extraction, concluding that MIBK and cyclohexanone are green solvents showing high partition coefficients [5]; and (b) the modelling of the reactions to produce HMF with EDTA as highly recoverable thermoresponsive catalyst [6] and Fur with sulfated zirconia as heterogeneous catalyst [7] considering the mass balances and phenomena involved in these biphasic reaction systems. Finally, as an additional strategy to mitigate the generation of levulinic and formic acids from HMF rehydration, we present the use of a biphasic systems based on a self-consuming deep eutectic solvent (DES) as reaction phase, with excellent selectivity towards the product and recyclability of the reaction and extraction solvents [8,9].

This communication covers the work of two doctoral theses completed at the University of Manchester and the Max Planck Institute for Chemical Energy Conversion.

[1] J. Esteban, A.J. Vorholt, W. Leitner. *Green Chem.* **2020**, *22*(7), 2097-2128

[2] D. Soukup-Carne, X. Fan, J. Esteban. *Chem. Eng. J.* **2022**, *442*(2), 136313

[3] A. Klamt, A. *J. Phys. Chem.* **1995**, *99*(7), 2224– 2235

[4] D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shehada, P.J. Dunn. *Green Chem* **2016**, *18*(1), 288-296

[5]D. Soukup-Carne, P. López-Porfiri, F.S. Bragagnolo, C.S. Funari, X. Fan, M. González-Miquel, J. Esteban. *ACS Sustain. Chem. Eng.* **2024,** *12*, 3766-3779

[6] N. Thanheuser, S. Püschel, A.J. Vorholt, J. Esteban. *Fuel* **2026**, *410*, 137934

[7] D. Soukup-Carne, C.M.A. Parlett, X. Fan, J. Esteban. *React. Chem. Eng.* **2025**, *10*,839-895

[8] N. Thanheuser, J. Groteguth, W. Leitner, J. Esteban, A.J. Vorholt. *ChemSusChem* **2025,** *18*, e202401485

[9] N. Thanheuser, W. Leitner, J. Esteban, A.J. Vorholt. *RSC Sustain.* **2025,** *3*(4), 1848-1858

Sustainable Decarbonization Pathways for CO_2 Conversion

Marcileia Zanatta[a,b*], Julian E. Sánchez-Velandia[c], Vitoria Gonçalves Pina,[a,b] Cristopher Tinajero[a], Víctor Sans[a], Eduargo García-Verdugo[c]

[a] *Institute of Advanced Materials (INAM), Universitat Jaume I, Avda Sos Baynat s/n, 12071, Castellón, Spain*
[b] *Departament de Química Física i Analítica, Universitat Jaume I, Avda Sos Baynat s/n, 12071 Castellón de la Plana, Spain*
[c] *Departamento de Química Inorgánica y Orgánica, Grupo de Química Sostenible y Supramolecular,Universidad Jaume I, Castellón, Spain*

E-mail: zanatta@uji.es

The increasing concentration of atmospheric CO_2 represents a major environmental and technological challenge, driving the development of sustainable decarbonization strategies. Among these, carbon capture combined with catalytic conversion has emerged as a promising pathway to transform CO_2 into value-added chemicals and energy carriers.

This work explores integrated approaches for CO_2 capture and utilization, covering pathways from cyclic carbonate formation to formic acid production. Different absorbent systems, including basic media and tailored solvent platforms such as ionic liquids (ILs), were investigated for efficient CO_2 capture from diluted streams. Beyond their role as absorbents, these media can facilitate downstream catalytic transformations by stabilizing reactive intermediates and active catalytic species.

Captured CO_2 was subsequently converted through catalytic processes, including hydrogenation routes leading to formate/formic acid and other carbon-containing products. The performance, stability, and recyclability of the catalytic systems were evaluated, highlighting the importance of reaction medium design in enhancing activity and selectivity. Additionally, coupling chemical catalysis with complementary transformation routes broadens the product spectrum and improves overall process flexibility.

This integrated platform demonstrates a versatile and scalable approach for CO_2 valorization, contributing to industrial decarbonization efforts and sustainable chemical production. By combining efficient capture systems with catalytic conversion strategies, this work supports the development of circular carbon technologies aimed at closing the carbon loop and reducing greenhouse gas emissions.

[1] M. Zanatta, E. García-Verdugo, V. Sans, ACS Sustainable Chem. Eng., 2023, 11, 9613–9619.
[2] J. E. Sanchez-Velandia, V. Gonçalves Pina, M. Oliva, V. S. Safont, C. Echeverría-Arrondo, E. Garcia-Verdugo, V. Sans, M. Zanatta, ChemSusChem, 2025, 18, e202501284.
[3] Tinajero, C., Zanatta, M., Sánchez-Velandia, J. E., García-Verdugo, E. & Sans, V. Nat. Commun. 200, 16, 9062.
[4] M. Bruch, J. E. Sanchez-Velandia, J. Rodríguez-Pereira, M. Rich, N. Pearcy, T. Narancic, E. Garcia-Verdugo, V. Sans, K. O'Connor, M. Zanatta, Green Chem., 2024, 26, 11885–11898.

Design of One-Pot Chemoenzymatic Cascades Merging Polar Organometallic Reagents (RLi/RMgX) with Laccases and ADHs

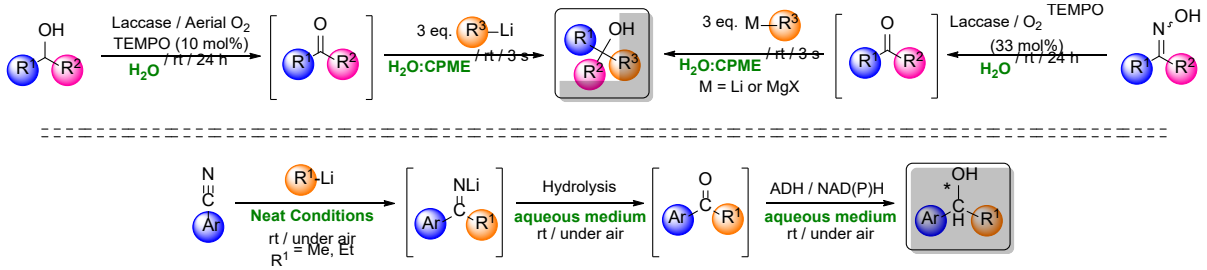
Gloría Morís-Menendez,[a] Marina Ramos-Martín,[a] Nicolas Ríos-Lombardía,[a] Vicente Gotor-Fernández,[b,*] Alejandro Presa Soto,[a,*] and Joaquín García-Álvarez.[a,*]

[a] Laboratorio de Química Sintética Sostenible (QuimSinSos). Departamento de Química Orgánica e Inorgánica, (IUQOEM). Facultad de Química. Univesidad de Oviedo. Spain
[b] Departamento de Química Orgánica e Inorgánica, (IUQOEM). Facultad de Química. Univesidad de Oviedo. Spain

E-mail: garciajoaquin@uniovi.es

The merger of highly reactive polar organometallic reagents (RLi/RMgX) with enzymes within a single reaction vessel remains one of the most challenging frontiers in the design of chemoenzymatic protocols due to their intrinsically incompatible operational windows. While biocatalysis typically requires aqueous media, room temperature and aerobic conditions, organolithium and Grignard reagents (RLi/RMgX) are traditionally restricted to: *i*) strictly anhydrous *VOC*-solvents; *ii*) inert environments (N_2 or Ar); and *iii*) cryogenic conditions (-78 ºC). Thus, overcoming this long-standing dichotomy would unlock unprecedented opportunities for the design of sustainable one-pot chemoenzymatic cascades.

Building on our previous advances which demonstrates that RLi/RMgX reagents can operate under air, at room temperature and in green protic media [1] (the aforementioned typical conditions employed in biocatalysis), we report herein the first examples of direct combinations of polar organometallic reagents with enzymes in one-pot processes, integrating both laccase-mediated bioxidations [2] and alcohol dehydrogenase (ADH)-catalyzed asymmetric bioreductions within the same aqueous reaction environment [3].



Scheme 1. Design of one-pot chemoenzymatic cascades merging RLi/RMgX reagents with Laccases and ADHs in aqueous media, under air and at room temperature.

[1] (a) C. Vidal, J. García-Álvarez, A. Hernán-Gómez, A. R. Kennedy, E. Hevia, *Angew. Chem. Int. Ed.* **2014**, *53*, 5969-5973; (b) C. Vidal, J. García-Álvarez, A. Hernán-Gómez, A. R. Kennedy, E. Hevia, *Angew. Chem. Int. Ed.* **2016**, *55*, 16145-16148.
[2] (a) M. Ramos-Martín, R. Lecuna, L. Cicco, P. Vitale, V. Capriati, N. Ríos-Lombardía, J. González-Sabín, A. Presa-Soto, J. García-Álvarez, *Chem. Commun.* **2021**, *57*, 13534-13537; (b) D. Arnodo, M. Ramos-Martín, L. Cicco, V. Capriati, N. Ríos-Lombardía, J. González-Sabín, A. Presa Soto, J. García-Álvarez, *Org. Biomol. Chem.* **2023**, *21*, 4414-4421.
[3] N. Ríos-Lombardía, G. Morís-Menéndez, I. Lavandera, V. Gotor-Fernández, J. García-Álvarez, *Adv. Synth. Catal.* **2024**, *366*, 3144-3152.

Recent progress on gold-enzyme cascades for the synthesis of optically active organic molecules

Vicente Gotor-Fernández, * **Lorena Escot, Sergio González-Granda, and Iván Lavandera**

Organic and Inorganic Chemistry Department. Instituto Universitario de Química Organometálica Enrique Moles. University of Oviedo. Avenida Julián Clavería, s/n, 33006 Oviedo (Asturias, Spain)

E-mail: vicgotfer@uniovi.es

The design of multicatalytic transformations allows the increasing of molecular complexity, while at the same time it is possible to induce chirality under mild reaction conditions. In this context, the combination in one-pot of metal species and enzymes is receiving great attention.[1,2] Particularly, gold(I) catalysts have emerged as useful catalysts for the activation of alkynes that can be compatible with the use of enzymes such as alcohol dehydrogenases,[3-5] transaminases,[6-7] or alkene reductases.[8]

Herein, we will summarize our latest achievements in the combination of gold species for the acceleration of Meyer-Schuster rearrangements and hydration reactions using propargylic systems as starting materials. Thus, the highly selective formation of different families of ketone intermediates is possible, which are susceptible to react under the same reaction conditions for the preparation of a wide series of chiral molecules.

The compatibility of organometallic and biocatalytic processes, in the same reaction vessel and under a predominantly aqueous medium, will determine the selection of sequential or concurrent process to achieve the synthesis of the desired targets with high conversions and stereoselectivities.

[1] S. González-Granda, L. Escot, I. Lavandera, V. Gotor-Fernández, *Chem. Rev.* **2023**, *123*, 5297-5346.
[2] S. González-Granda, L. Escot, I. Lavandera, V. Gotor-Fernández, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217713.
[3] S. González-Granda, I. Lavandera, V. Gotor-Fernández, *Angew. Chem. Int. Ed.* **2021**, *60*, 13945-13951.
[4] S. González-Granda, L. Escot, I. Lavandera, V. Gotor-Fernández, *ACS Catal.* **2022**, *12*, 2552-2560.
[5] L. Escot, S. González-Granda, V. Gotor-Fernández, I. Lavandera, *Org. Biomol. Chem.* **2022**, *20*, 9650-9658.
[6] S. González-Granda, N. V. Tzouras, S. P. Nolan, I. Lavandera, V. Gotor-Fernández, *Adv. Synth. Catal.* **2022**, *364*, 3856-3866.
[7] S. González-Granda, G. Steinkellner, K. Gruber, I. Lavandera, V. Gotor-Fernandez, *Adv. Synth. Catal.* **2023**, *365*, 1036-1047.
[8] L. Escot, S. González-Granda, D. Méndez-Sánchez, Y. Wang, H. C. Hailes, I. Lavandera, V. Gotor-Fernández, *Adv. Synth. Catal.* **2024**, *366*, 4737-4746.

ORAL COMMUNICATIONS

Toward Sustainable Plastic Recycling using Supercritical CO_2

Albertina Cabañas,[a,*] Ramiro Olmos-Greco[a], Eduardo Pérez[a], Lourdes Calvo[b]

[a] Department of Physical Chemistry, [b] Department of Chemical and Materials Engineering, Complutense University of Madrid, 28040 Madrid, Spain

E-mail: a.cabanas@quim.ucm.es

The increase in global plastic production and inadequate waste management have intensified environmental contamination and associated health risks. Advancing toward a **sustainable circular plastics economy**, therefore, requires innovative recycling technologies. This study examines the use of supercritical carbon dioxide ($scCO_2$) as a tunable medium for plastic recycling.

Carbon dioxide becomes supercritical above 31 °C and 73.8 bar. $scCO_2$ combines liquid-like solvating properties with gas-like diffusivity, enabling efficient mass transfer and polymer plasticization, lowering Tg and Tm. Furthermore, it is non-toxic, non-flammable, inexpensive, and can be fully removed by depressurization leaving no residue, so it is considered a green solvent. In this communication we present examples of $scCO_2$ utilization in plastic recylcing in three different areas: (i) Cleaning and disinfection, (ii) delamination of multilayer plastic films and (iii) chemical recycling.

$scCO_2$ can be used to *remove unwanted substances from polymeric materials*. Furthermore, thanks to its *disinfecting* properties, $scCO_2$ can also be used to decontaminate biological waste. We have used this approach in the sterilisation of Personal Protective Equipment (masks, gowns, gloves, ...) made of plastics [1], demonstrating that, after the supercritical treatment, these materials can be either reused or safely recycled.

Multilayer plastic films, composed of two or more different layers, are materials widely used in food packaging. The varied composition of the layers, linked to their different functions (providing barrier properties, mechanical strength, lightness, flexibility, or antimicrobial properties), makes this type of waste extremely difficult to recycle. We present a new process based on $scCO_2$ to delaminate these multilayer materials[2], improving their sorting as a crucial first step towards effectively recycling.

Finally, $scCO_2$ can be used to improve mass transfer processes, increasing the conversion yield in chemical recycling processes. We present our most recent results on the methanolysis of polyethene terephthalate from plastic bottles. We forecast a significant increase in the use of supercritical fluids for polymer recycling in the coming years.

Acknowledgements: financial support from MICIU project PID2022-137847OB-100.

[1] H.K. Ruiz, J.M. Gómez-Salazar, L. Calvo, A. Cabañas, *J. CO_2 Utilization*, **2025**, *92*, 103029
[2] R.J. Olmos-Greco, E. Pérez, L. Calvo, A. Cabañas, *J. Supercrit Fluids*, **2026,** *29*, 106813

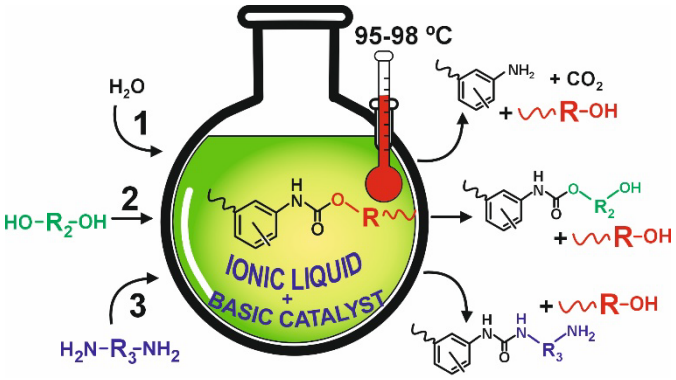
Ionic Liquids and Superbase Catalysts for the Sustainable Depolymerization of Polyurethane Foam Waste

Rocio Villa,[a*] Francisco Velasco,[a] Maite Nuño,[a] Carlos Sotillo,[a] Susana Nieto,[a] Maria Macia,[b] Eduardo Garcia-Verdugo,[b] Jairton Dupont[a] and Pedro Lozano[a]

[a] Department of Biochemistry and Molecular Biology B and Immunology, Faculty of Chemistry, University of Murcia, Murcia, Spain.
[b] Department of Organic and Inorganic Chemistry, Faculty of Chemistry, University Jaime I, Castellón, Spain
E-mail: rocio.villa@um.es

Polyurethane (PU) represents a highly versatile class of polymers distinguished by their physicochemical properties, which support their application in numerous industrial sectors, including foams, coatings, adhesives, and elastomeric materials. Due to their extensive commercial applications, PUs have become the sixth most manufactured plastic globally.[1] Within this polymer family, polyurethane foams (PUFs) highlight as thermosetting materials whose inherent chemical robustness significantly difficult their recycling and end-of-life management.

In this work, it is reported for the first time a sustainable depolymerization approach of PUFs at temperatures below 100 °C *via* hydrolysis, alcoholysis, and/or aminolysis (Figure 1). This strategy is based on the combination of water-miscible ionic liquids (ILs) such as 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and superbase catalysts (*e.g.*, 1,8-Diazabicycloundec-7-ene DBU), enabling the efficient recovery of recycled products for the re-synthesis of new PUF.[2] In contrast to traditional chemical depolymerization approaches described in the literature, which typically require organic solvents and harsh conditions (>300 °C, [3] the proposed process provides a white solid product at moderate conditions. The reaction is followed by an easy protocol based on water-washing and centrifugation cycles, which directly allows the efficient separation of the recycled product from the depolymerization medium. Notably, the depolymerization system can be reused for up to five consecutive cycles without practically unchanged performance. Finally, the recovered product is successfully used in the synthesis of new PUFs, demonstrating its potential for industrial implementation.



Scheme 1. *Superbase-catalyzed depolymerization of PUF via hydrolysis (1), glycolysis (2) or amynolysis (3) approach in the presence of water-miscible ILs.*

[1] EUROPUR. The End-of-Life of flexible polyurethane foam from mattresses and furniture brochure. 2020. https://europur.org/flexible-pu-foam/sustainability/.
[2] R. Villa, R. Salas, M. Macia, F. Velasco, B. Altava, E. Garcia-Verdugo and P. Lozano. *Angew. Chem. Int. Ed.* **2025**, 64, e20241803.
[3] G. Rossignolo, G. Malucelli and A. Lorenzetti, *Green Chem.*, **2024**, 26, 1132-1152.

Acknowledgements
This work has been partially supported by MICIU-AEI-FEDER 10.13039/501100011033 (PID2024-159264OB-C21/C22, and CPP2023-010883) grants. F.V. has a MICIU PhD-fellowship (FPU23/03041).

Integrating enzyme kinetics and biocatalyst engineering for sustainable PET degradation

Juan M. Bolivar*, Diego Carballares Navarro, Alberto García Martín, Miguel Ladero Galan

FQPIMA group, Department of Chemical and Materials Engineering, Faculty of Chemical Sciences, Complutense University of Madrid, Madrid, Spain

E-mail: juanmbol@ucm.es

The widespread accumulation of polyethylene terephthalate (PET) micro- and nanoplastics in terrestrial and aquatic environments represents a major environmental challenge. Conventional recycling strategies remain insufficient to close the materials loop or effectively address dispersed plastic pollution in water systems. Enzymatic depolymerization has emerged as a promising green alternative; however, limitations in enzyme stability, catalyst recovery, and reaction rates continue to hinder practical implementation.

In this contribution, we present the development of reaction engineering strategies for PET degradation based on quantitative kinetic analysis and the rational design of heterogeneous biocatalysts. We investigate the hydrolysis of PET-derived oligomers and PET nanoparticles catalyzed by different hydrolases, with particular emphasis on identifying kinetic bottlenecks within the consecutive reaction network leading to monomer formation. Systematic kinetic modeling is employed to analyze intermediate accumulation, pH-dependent behavior, and potential inhibitory or inactivation effects that limit overall degradation efficiency.

To translate kinetic understanding into practical systems, different immobilization strategies are evaluated to enhance operational stability, enable catalyst reuse, and facilitate integration into continuous-flow configurations. The interplay between enzyme formulation, support material, and reaction conditions is analyzed to design robust biocatalytic systems suitable for realistic operating environments.

This approach integrates enzyme kinetics, immobilization engineering, and reactor concepts as complementary tools to advance sustainable PET degradation and upcycling. The methodology is adaptable to emerging PET hydrolases and extendable to applications involving soluble oligomers as well as PET micro- and nanoplastic substrates.

This work is involved in the BMRex project (Biocatalytic membranes for micro/nano plastic degradation within waste water effluents) that has received funding from Pathfinder Open 2022, a European Innovation Council (EIC) work programme that is part of Horizon Europe.

.

Magnetically recoverable catalysts for polymer wastes recycling

Carmen Martín,[a]* Maite Perfecto,[b] Garikoitz Beobide,[b] David Ávila[a] and Israel Cano[a]*

[a]Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid. Avda. Complutense s/n. 28040-Madrid.
[b]Departamento de Química Orgánica e Inorgánica, Universidad del País Vasco, UPV/EHU, Apartado 644, E-48080, Bilbao.

E-mail: mariad80@ucm.es

Plastics made from non-renewable fossil fuels have become a ubiquitous material in our daily life. For example, PET used as packaging materials, nylon found in clothing, or polyurethane employed as thermal/acoustic insulation materials. However, the manufacture and their subsequent use present many drawbacks: the requirement of non-renewable fossil fuel precursors, the CO_2/NO_x emissions associated with their synthesis and disposal, and the overwhelming amount of waste produced. Therefore, the recycling of post-consumer polymers is key to save energy and conserve the environment.

Among the different methods for recycling plastics, chemical processes (glycolysis, aminolysis, utilization of a gas splitting agent, etc.) are simple and inexpensive depolymerization pathways that involve the selective depolymerisation of plastics to produce useful molecules with industrial applications.

The main goal of our work is the development of a new family of magnetically recoverable nanocatalysts through magnetic separation that allow the chemical recycling of post-consumer polymer wastes, leading to the production of high added value compounds. In this contribution it is described the synthesis and characterization of materials based on silica-coated (SiO_2), magnetite (Fe_3O_4) nanoparticles in which a catalyst consisting of a metal-containing ionic liquid (mim)[MCl_n]) is anchored "Fe_3O_4@SiO_2@(mim)[MX_n] (Figure 1)". Interestingly, catalysts were easily recovered with an external magnetic field, providing nearly 100% yield and selectivity in polyester depolymerization for 12 consecutive reaction cycles (Figure 1). [1][2]

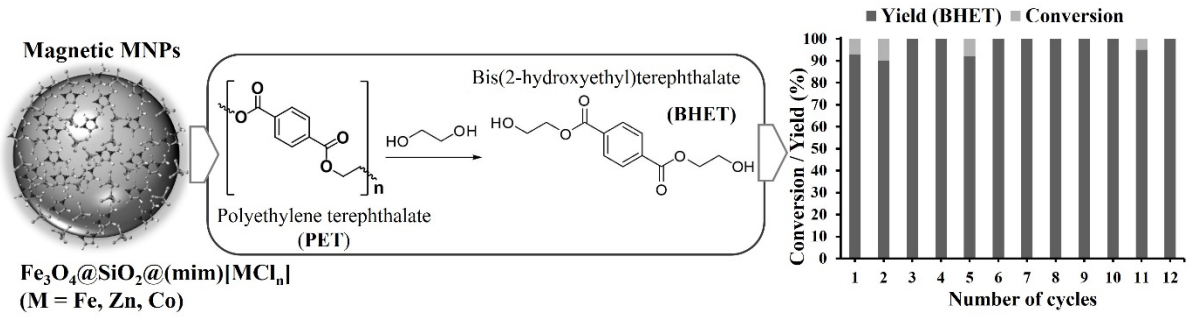


Figure 1. Example of nanocatalyst reuse in the glycolysis of PET.

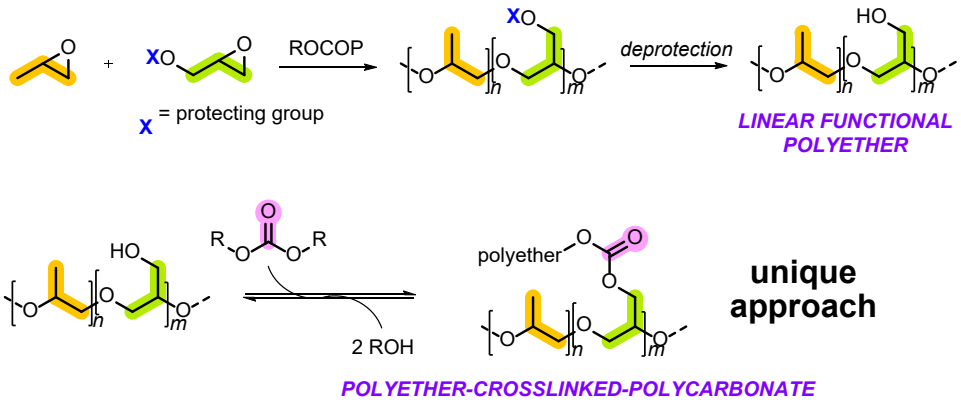
[1] I. Cano, C. Martín, J. Alaves Fernandes,R. W. Lodgea, J. Dupont, F. A. Casado-Carmona, R. Lucena, S. Cardenas, V. Sans, I. de Pedro, *App. Catal. B Environ.* **2020**, *260*, 118110.
[2] C. Martín, M. Perfecto-Irigaray, G. Beobide, E. Solana-Madruga, D. Ávila-Brande, M. Laso-Quesada, I. de Pedro, F. A. Casado-Carmona, R. Lucena, S. Cardenas, I. Cano, *ACS Sustain. Chem. Eng.* **2025**, *13*, 7890-7903.

Synthesis and Chemical Recycling of Crosslinked Poly(ether-*co*-carbonates)

Davide Rigo,[a] Sara Faoro,[a,b,c] Lilas Aubel,[a,b,c] Angelo Scopano,[a,d] Alejandro Delgado,[a] and Arjan Kleij[a,e]

[a]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona (ES).*
[b] *Universitat Rovira i Virgili (URV), Tarragona (ES)*
[c]*Center for Education and Research on Macromolecules (CERM), University of Liège (BE)*
[d]*University of Groningen (RUG), Engineering and Technology Institute Groningen (NL)*
[e]*Catalan Institute of Research and Advanced Studies (ICREA), Barcelona (ES)*
E-mail: drigo@iciq.es

Plastic pollution and recycling are global problems posing an imminent challenge to mankind.[1] One option to mitigate these environmental issues is the development of sustainable routes to biobased plastics (*i.e.*, bioplastics)[2] and their concomitant recycling/upcycling.[3] The chemical recycling of plastics is key especially for thermosets (crosslinked polymers) as inherently they cannot be recycled with conventional "melt-and-reshape" methods. Polyethers and polycarbonates are a class of polymers interconnected by C–O and C–C bonds which are used in a wide variety of applications.[4,5]



The presence of C–O based (ether and carbonate) bonds within the polymer architecture provides better bio/photo/chemo-based degradability compared to, for instance, conventional rubbers and polyolefins. This makes the development of poly-ether/carbonates with reversible crosslinks very attractive in the context of sustainable development. We thus envisioned to prepare polyethers with suitable (reversible) carbonate crosslinking groups that can be installed via a novel and modular synthesis approach using an in house developed catalytic system.[6] The obtained crosslinked poly(ether-*co*-carbonates) could be chemically recycled via methanolysis with no appreciable loss of properties/performance detected after recycling.

[1] https://www.unep.org/plastic-pollution#:~:text=Every%20minute%2C%20the%20equivalent%20of,-up%20in%20landfills%20or%20dumped (accessed on 27/01/2026)
[2] S. Spierling, S. Springer, S. Albrecht, C. Herrmann, H.-J. Endres et al. *J. Clean. Prod.* **2018**, *185*, 476-491.
[3] L. D. Ellis, N. A. Rorrer, K. P. Sullivan, G. T. Beckham et al. *Nat. Catal.* **2021**, *4*, 539–556.
[4] J. Herzberger, K. M. Worm, F. R. Wurm, H. Frey et al. *Chem. Rev.* **2016**, *116*, 2170−2243.
[5] H. Wang, F. Xu, Z. Zhang, M. Feng, M. Jiang, S. Zhang, *RSC Sustainability*, **2023**, *1*, 2162-2179.
[6] C. J. Whiteoak, N. Kielland, V. Laserna, A. W. Kleij et al. *J. Am. Chem. Soc.* **2013**, *135*, 1228−1231.

Exploring hydrolase promiscuity towards chitosan in hydrated DES media

Daniel Alonzo Durante-Salmerón,[a]* Isabel Fraile-Gutiérrez,[a,b], Isabel Rodríguez-Veiga[a], Inmaculada Aranaz[a,b] and Andrés R. Alcántara[b]*

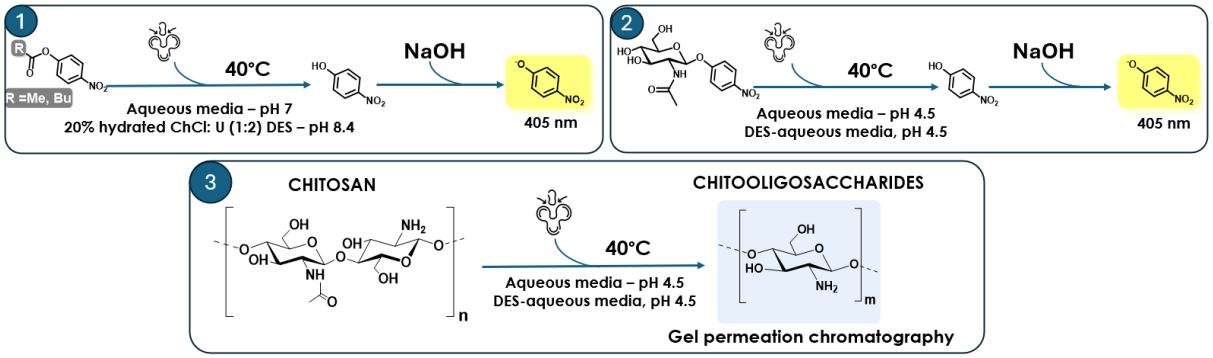
[a] *Instituto Pluridisciplinar. Complutense University of Madrid. Paseo Juan XIII, 1, Madrid, Spain*

[b] *Department of Chemistry in Pharmaceutical Sciences, Pharmacy Faculty, Complutense University of Madrid (UCM), Madrid, Spain.*

E-mail: ddurante@ucm.es

The controlled hydrolysis of chitosan results in the formation of products known as chitooligosacharides (COS), which have desirable biomedical properties [1]. Although the enzymatic hydrolysis of chitosan is mediated in nature by chitosanases [2], these enzymes are very expensive, limiting their widespread application. Thus, cheaper hydrolases with "promiscuous" chitosanolytic activity would be beneficial from an economic point of view to produce COSs [3]. In recent years, Deep Eutectic Solvents (DESs) have emerged as cost-effective media for biocatalysis, enhancing lipase activity and stability [4]. Hence, this project seeks to explore a potential synergy between the use of DESs-based media and promiscuous enzymes to eventually achieve an upscaled production of COSs.

Initial experiments focused on determining whether DES-based media could influence enzyme activity. Thus, a comparative study of the hydrolysis of para-nitrophenol (*p*NP) derived substrates by different commercial lipase formulations in either aqueous media or in 20% hydrated DES-based media was carried out. Results prompted the authors to explore the potential of the different screened enzymes to hydrolyze chitosan samples dissolved in DES-based media (**Scheme 1**). Preliminary findings suggest that certain DESs may provide an environment where chitosan can effectively be dissolved and hydrolyzed.



Scheme 1. Schematic representation of the reactions explored in this work employing commercial lipase formulations in either aqueous or DES-based media. ChCl: Choline chloride, U: Urea

[1] S. Jagdale, B. Agarwal, A. Dixit, S. Gaware, *Int. J. Biol. Macromol.* **2024**, *257*.
[2] S. Sinha, S. Chand, P. Tripathi, *Appl. Biochem. Biotechnol*. **2016**, *180*, 883-99
[3] D. N. Poshina, et al., *Polym. Degrad. Stabil*. **2018**, *10*, 127-129
[4] S. M. Taklimi, et al., *J. Mol. Liq*. **2023**, *377*, 121562

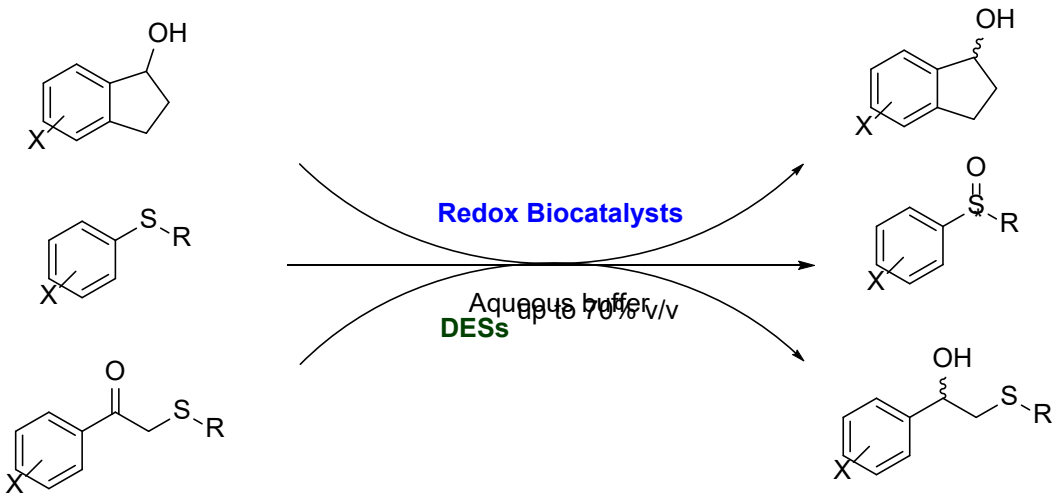
Application of DESs as cosolvents in redox biocatalysis

Gonzalo de Gonzalo,[a] Chiara Falcini,[a] Juan Carvajal-Bárcena,[a] Nikola Loncar,[b] and Marco W. Fraaije[c],

[a] Department of Organic Chemistry, University of Seville, c/ Profesor García González 1, 41012, Seville, Spain
[b] GECCO Biotech, Groningen, the Netherlands
[b] Author affiliation: address, country, workplace. (Times New Roman, italics, size 12 points)

E-mail: gdegonzalo@us.es

Deep eutectic solvents (DESs) have emerged as sustainable and valuable alternatives to conventional organic solvents for use as reaction media in biocatalytic transformations [1]. Among the various classes of biocatalysts employed for the synthesis of high-value compounds, oxidoreductases are particularly prominent due to their ability to catalyze a wide range of redox reactions. Since the seminal report describing the use of Baker's yeast for the bioreduction of ethyl acetoacetae in the presence of ChCl:Gly (1:2) [2], numerous studies have demonstrated the applicability of DESs as cosolvents in oxidoreductase-catalyzed processes [3].
In the present study, we investigated the influence of different DESs on the activity and selectivity of oxidases, monooxygenases, and ketoreductases in the enantioselective synthesis of chiral alcohols and sulfoxides. Careful selection of both the DES composition and the biocatalyst enabled, in many cases, enhanced catalytic performance in these non-conventional media compared to conventional aqueous buffer systems. Furthermore, key parameters affecting biocatalyst properties in DES-containing systems were systematically analyzed, highlighting the potential of DESs as valuable and versatile cosolvents in biocatalysis.



Scheme 1. Biocatalytic redox processes in presence of Deep Eutectic Solvents as cosolvents.

[1] S. Nieto, R. Villa, F. J. Ruiz, F. Velasco, P. Lozano, *Biocat. Biotrans*. **2026**, DOI: 10.1080/10242422.2026.2622470.
[2] Z. Maugeri, P. Domínguez de María, *ChemCatChem.* **2014**, *6*, 1535-1537.
[3] C. Aranda, G. de Gonzalo, *Molecules*, **2020**, *25*, 3016.

Rational DESs design for unspecific peroxygenase (UPO) stabilization

Nina Yilmaz,[a] Marina Cvjetko Bubalo,[b*] Miguel Alcalde,[c] and Selin Kara,[a,d,*]

[a] Callinstr. 5, 30167 Hannover, Germany, Leibniz University Hanover.
[b] Pierottijeva 6, 10000 Zagreb, Croatia, University of Zagreb.
[c] Campus Cantoblanco, 28049 Madrid, Spain, Institute of Catalysis, CSIC.
[d] Gustav Wieds Vej 10, 8000 Aarhus C, Denmark, Aarhus University.

E-mail: nina.yilmaz@iftc.uni-hannover.de

Unspecific peroxygenases (UPOs) are often described as the "Swiss Army knife" of biocatalysis due to their broad substrate scope and ability to catalyze selective oxyfunctionalization reactions without requiring costly cofactors or auxiliary proteins. However, their industrial application remains limited by enzyme inactivation at elevated cosubstrate H_2O_2 concentrations and poor water solubility of hydrophobic substrates. [1] Although organic solvents can improve the solubility of challenging substrates, they often reduce the enzyme's activity. Deep eutectic solvents (DESs) have emerged as promising alternative reaction media that can be tailor-designed to enhance both substrate solubility and enzyme stability. [2] In this study, a rational DES-based medium engineering strategy was developed for the UPO mutant PaDa-I through comprehensive experimental screening combined with Screening Model for Real Solvents (COSMO-RS)-based *in silico* modeling.

First, the thermal stability of PaDa-I was systematically analyzed using nano differential scanning fluorimetry (nanoDSF), a high-throughput method for rapid stability screening and formulation assessment, in individual DES component solutions and corresponding DES-based media. Sarcosine, sugars, amino acids, and polyols were identified as effective stabilizers, either alone or within DESs, supporting a component-driven rationale for DES design. Furthermore, residual activity assays were conducted at 25 °C, 40 °C, and 50 °C. Notably, PaDa-I retained full catalytic activity after eight weeks of incubation at 25 °C in 60 wt.% sarcosine-sorbitol (1:4), whereas activity decreased by 25% in the pure buffer. Additionally, more than 50% residual activity was maintained after ten days at 50 °C in sarcosine-xylose (1:4) and sarcosine-glycine-alanine (1:2:0.5) DESs, while buffer-incubated enzyme showed less than 20% residual activity after 24 hours. Finally, molecular descriptors derived from COSMO-RS were used to develop mathematical models that successfully predicted enzyme stability in DESs. For data evaluation, FAIR data tools, developed by the team of Prof. Dr. Jürgen Pleiss (University of Stuttgart), were implemented. These tools facilitated data analysis and management while ensuring compliance with FAIR data principles, thereby improving the accessibility and reproducibility of results and helping to address the reproducibility crisis in scientific research. [3]

[1] M. Hobisch, D. Holtmann, P. Gomez de Santos, M. Alcalde, F. Hollman, S. Kara, *Biotechnol. Adv.* **2021**, *51*, 1-13.
[2] N. Zhang, P. Domínguez de María, S. Kara, *Catalysts* **2024**, *14*, 1-29.
[3] S. Malzacher, D. Meißner, J. Range, Z. Findrik Blažević, K. Rosenthal, J. M. Woodley, R. Wolgemuth, P. Wied, B. Nidetzky, R. T. Giessmann, K. Prakinee, P. Chaiyen, A. S. Bommarius, J. M. Rohwer, R. O. M. A. de Souza, P. J. Halling, J. Pleiss, C. Kettner, D. Rother, *Nat. Catal.* **2024**, *7*, 1245-1249.

Bifunctional Uncoupled Catalysis Enabled by Deep Eutectic Solvent Systems for C-4 Functionalization of Isoquinolines

Alejandro Cores,[a] Xavier Marset,[b] Diego J. Ramón,[a] and Gabriela Guillena.[a]

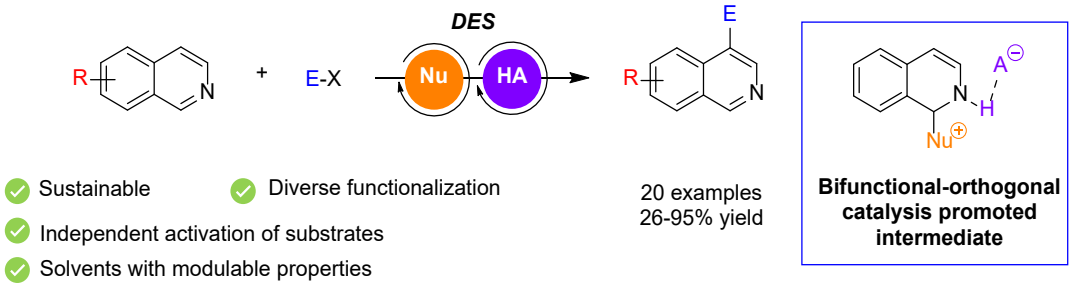
[a]*Departamento de Química Orgánica e Instituto de Síntesis Orgánica, University of Alicante.*

[b]*Departamento de Química Orgánica e Instituto Universitario de Electroquímica, University of Alicante.*

E-mail: alejandro.cores@ua.es

The extensive reliance on volatile organic solvents within the medicinal chemistry industry represents a major source of its well-recognized environmental burden. As a result, identifying sustainable substitutes for these solvents is crucial for the advancement of synthetic methodologies consistent with the Sustainable Development Goals and Green Chemistry principles.[1] Among the proposed alternatives, eutectic mixtures have emerged as particularly attractive due to their tunability, low toxicity, safety, and renewable nature.[2]

Within Medicinal Chemistry, heterocyclic scaffolds play a central role owing to their frequent occurrence in pharmaceutical compounds. Herein, we report a C4-functionalization of isoquinolines promoted by a eutectic mixture that acts simultaneously as the reaction medium and a bifunctional catalyst (Scheme 1). Sustainability metrics were evaluated and benchmarked against a previously reported protocol employing conventional solvents,[3] revealing a marked enhancement in both sustainability and overall process efficiency.



Scheme 1. Isoquinoline C4-functionalization .

[1] Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev*. **2010**, *39*, 301–312.

[2] Marset, X.; Guillena, G. Deep Eutectic Solvents as À-La-Carte Medium for Transition-Metal-Catalyzed Organic Processes. *Molecules* **2022**, *27*, 8445–847

[3] Day, A. J.; Jenkins, T. C.; Kischkewitz, M.; Christensen, K. E.; Poole, D. L.; Donohoe, T. J. Metal and Activating Group Free C-4 Alkylation of Isoquinolines via a Temporary Dearomatization Strategy. *Org. Lett.* **2023**, *25*, 614–618.

Modulating enzymatic phloretin gluycosylation through deep eutectic solvents (DES)

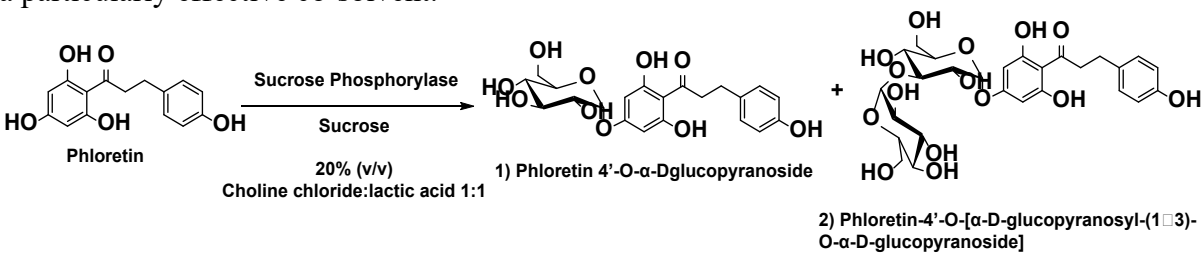
David Rodríguez-García, Carlos Uceda-Dominguez, Jose Luis Gonzalez-Alfonso, and Francisco J. Plou

Instituto de Catálisis y Petroleoquímica (ICP-CSIC), Madrid, Spain

E-mail:davidr@csic.es

Enzymatic glycosylation is an effective strategy to improve the solubility and stability of polyphenolic compounds. In the case of phloretin, a well-known antioxidant polyphenol from apple, sucrose phosphorylase from *Thermoanaerobacterium thermosaccharolyticum* (variant TtSPP_R134A) has been reported to catalyze its α-glucosylation with a strong solvent-dependent selectivity [1]. The glucosylated antioxidants exhibit improved aqueous solubility and may overcome the bioavailability issues associated with the aglycone [2]. While reactions performed in aqueous buffer mainly yield the diglucoside, the use of 10% (v/v) acetone as a co-solvent favors the formation of the monoglucoside. The diglucoside is produced via consumption of the monoglucoside, suggesting that the effect of acetone is associated with enhanced solubilization of the phloretin.

In this work, non-conventional solvents were explored as reaction modulators to control phloretin glucosylation (Scheme 1). Several green co-solvents were compared, including carbonate- and lactate-based compounds, as well as a variety of deep eutectic solvents (DES). Among the systems evaluated, the DES choline chloride:lactic acid (1:1 mol/mol) emerged as a particularly effective co-solvent.



Scheme 1. Phloretin glucosylation reaction. The use of DES co-solvent accelerates the reaction and improves the kinetic control to produce **1** and **2**.

Notably, the beneficial effects of DESs cannot be exclusively attributed to enhanced polyphenol solubility, as the sucrose hydrolysis reaction—where polyphenol is absent—is also significantly accelerated. Regarding phloretin, the reaction time required to obtain each product in the presence of the DES is substantially shorter than the reported for conventional aqueous or organic co-solvent systems. Furthermore, by applying kinetic control, selective formation of either mono- or diglucosylated phloretin can be achieved.

[1] J. L. González Alfonso, Z. Ubiparip, E. Jimenez-Ortega, A. Poveda, C. Alonso, L. Coderch, J. Jimenez-Barbero, J. Sanz-Aparicio, A. O. Ballesteros, T. Desmet, F. J. Plou, *Adv. Synth. Catal.* **2021**, *363*, 3079–3089.

[2] J. L. Gonzalez-Alfonso, L. Barahona, S. Garcia-Benlloch, M. Martinez-Ranz, B. Gracia-Gomez, M. A. Iñiguez, B. Viadel, M. Fernandez-Lobato, F. J. Plou, *Food Res. Int*. **2026**, *226*, 118238.

Laboratory to Market: Development of Water-Soluble Catalysts For Solving Key Research Problems

Prof. Anant R. Kapdi[a,*], Dr. Rajesh Sahua, Prof. Jose Luis Serrano[b]
[a]Institute of Chemical Technology, Matunga, Mumbai-400019, India
[b]Departamento de Ingeniería Química y Ambiental. Área de Química Inorgánica, Universidad Politécnica de Cartagena, 30203 Cartagena, Spain.
Email: ar.kapdi@ictmumbai.edu.in

The problems associated with the consistent and large-scale use of organic solvents for performing synthetic and catalytic reactions, as well as for purification is not a feasible or sustainable option anymore. Industries are looking for innovative development of catalytic systems that can avoid the excessive usage of volatile organic solvents and promote these processes in solvents that are environmentally benign, especially water. Over the past decade, our research group has been working on the development of sustainable catalytic solutions to promote catalytic processes, especially C—N, C—O, and C—S bond formation reactions under mild conditions, possibly at ambient temperature in water as the reaction medium for substrates such as nucleosides, heteroarenes, and amino acids. Water-solubility and subtle electronic control of the developed catalytic systems are the key features that have allowed us to solve many key research problems, as well as a few industrially relevant problems. Accordingly, a series of water-soluble phosphine-based as well as phosphine-free palladium catalysts have been developed and applied extensively for these transformations. Late-stage functionalization strategies on ribose nucleic acids (RNA in buffer) and peptides have also been achieved, providing ample evidence about their versatility.

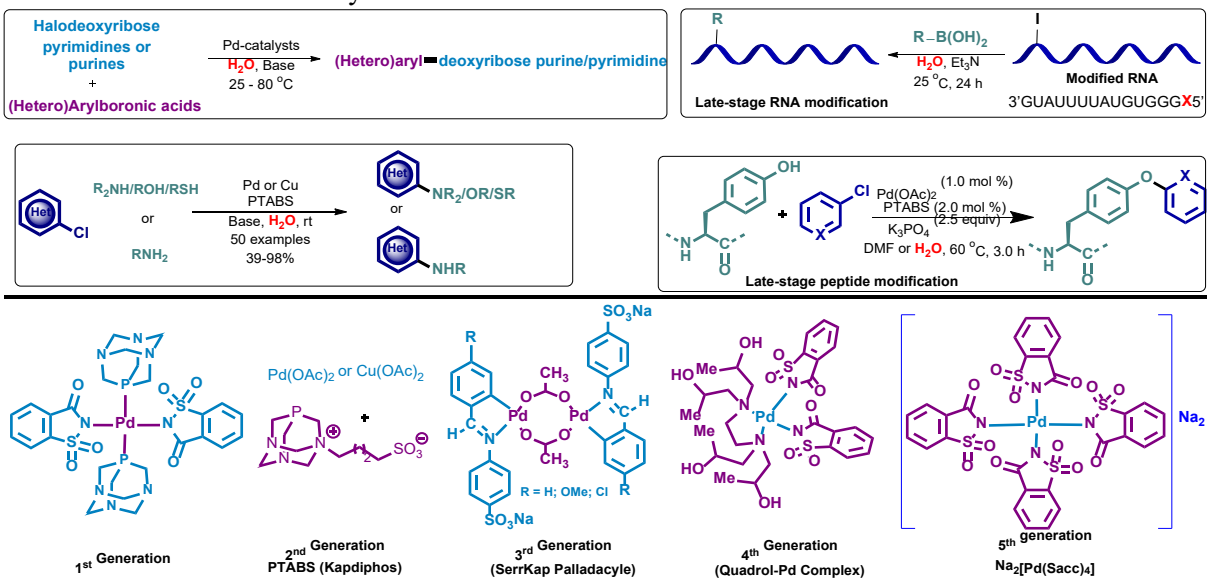


Figure 1: Generations of phosphine-based and phosphine-free water-soluble catalytic systems.

1. **1st Generation**: A. R. Kapdi, A. Ardhapure, Y. S. Sanghvi, J. L. Serrano, J. Sánchez, J. García, P. Lozano, *RSC Adv*. **2015**, *5*, 24558-24563.
2. **2nd Generation**: a) H. Shet, S. Bhilare, Y. S. Sanghvi, A. R. Kapdi, *Molecules,* **2020**, *25*, 1645. b) S. Bhilare, S. Murthy Bandaru, C. Schulzke, A. R. Kapdi, *Chem. Rec.,* **2021**, *21*, 188-203. c) A. R. Kapdi, R. Sahu, *Synlett*, **2022**, *34*, 912-930 (account on KapdiPhos). d) U. Parmar, D. Somvanshi, S. Kori, A. Desai, R. Dandela, D. K. Maity, A. R. Kapdi, *J. Org. Chem*. **2021,** *86,* 8900-8925.
3. **3rd Generation**: J. L. Serrano, L. Garcia, J. Perez, P. Lozano, J. Correia, Y. S. Sanghvi, A. R. Kapdi, *Organometallics* **2020**, *39*, 4479-4490.
4. **4th Generation**: J. L. Serrano, A. Pérez, J. Pérez, P. Lozano, S. Gaware, S. Kori, R. Dandela, Y. S. Sanghvi, A. R. Kapdi, *Dalton Trans.* **2022**, *51*, 2370-2384.
5. 5th Generation: J. L. Serrano, J. Pérez, J. A. Pérez, I. da Silva, R. Sahu, K. Pal, A. R. Kapdi, P. Lozano and Y. S. Sanghvi, *Catal. Today* **2024,** *430*, 114549.

Mechanism-driven sustainable Pd-catalyzed cross-coupling reaction methodologies

Ian J. S. Fairlamb*

[a] *Department of Chemistry, University of York, Heslington, York, YO10 5DD, United Kingdom*

E-mail: ian.fairlamb@york.ac.uk

Over the past 25 years we have been interested in the role played by higher order Pd species, initially in allylic alkylation reactions and then in cross-coupling reactions, especially Suzuki-Miyaura reactions and C-H bond functionalisations.[1] In this presentation I will first explain why Pd catalyst speciation needs to be recognized in cross-coupling chemistry,[2] with a focus placed on simple phosphine ligands, e.g. PPh_3 and P(*o*-tolyl)$_3$, showing how higher order clusters form, which are catalytically competent.[3,4] Furthermore, I will show how detailed mechanistic studies can reveal the behaviour of Pd catalyst systems under differing reaction conditions, from traditional solvents to greener solvent alternatives. Valuable mechanistic information can be gathered from studying solvents that are defined as "green".

I will further discuss how we have deployed high throughput experimentation (HTE) and data science[5] to decipher the hidden complexities of a Pd-catalyzed C-H bond functionalization reaction, which forms many products.[6] Using appropriate data science tools, underpinned by traditional mechanistic studies, we have been able to rapidly identify an intricate network of catalytic cycles which explain the different paths to the products formed. The approach developed could be useful for those interested in characterizing complete catalytic reaction manifolds, particularly with efficiency in mind and ensuring that deep-delve mechanistic studies implement green and sustainable practices. There is further value in examining published HTE reaction datasets using data science tools, directing reaction understanding and guiding mechanistic experiments.[7]

[1] (a) In C-H and C-X Bond Functionalization: Transition Metal Mediation, ed. X. Ribas, The Royal Society of Chemistry, Cambridge, **2013**. (b) A. J. Reay, I. J. S. Fairlamb, *Chem. Commun.* **2015**, *51*, 16289-16307. (c) I. J. S. Fairlamb, M. J. Ford, *Chem. Catal.* **2025**, *5*, 101255. (d) M. J. Ford, I. J. S. Fairlamb, *Chem. Catal.* **2025**, *5*, 101256.
[2] I. J. S. Fairlamb *et al. ACS Catal.* **2022**, *12*, 11615-11638.
[3] (a) I. J. S. Fairlamb *et al. J. Am. Chem. Soc.* **2021**, *143*, 9682-9693. (b) I. J. S. Fairlamb *et al. Chem. Sci.* **2019**, *10*, 7898-7906.
[4] (a) I. J. S. Fairlamb *et al. ACS Catal.* **2024**, *14*, 12769-12782. (b) I. J. S. Fairlamb *et al. Chem. Sci.* **2024**, *15*, 18627-18633.
[5] (a) S. M. Mennen, *et al. Org. Process Res. Dev.* **2019**, *23*, 1213-1242. (b) A. W. Dombrowski, *et al. ACS Med. Chem. Lett.* **2020**, *11*, 597-604. (c) I. J. S. Fairlamb *et al. Dig. Discov.* **2024**, *3*, 1467-1495.
[6] I. J. S. Fairlamb *et al. Nature Comm.* **2024**, *15*, 3968, 1-15.
[7] B. A. Franklin, J. Hargreaves, I. J. S. Fairlamb *et al.*, *Org. Proc. Res. Dev.* **2026**, *in press*.

Designing Renewable Functional Ionic Liquids: Toxicity, Catalytic performance, and Green metrics evaluation

Alejandro Leal-Duaso,[a,*] Jorge Cambronero-Arregui,[a] Alberto Clemente,[a] José A. Aínsa,[b] Elísabet Pires,[a] and José A. Mayoral[a,*]

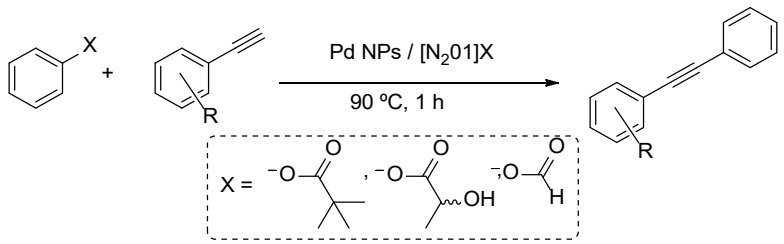
[a] *Instituto de Síntesis Química y Catálisis Homogénea. CSIC-University of Zaragoza, Faculty of Science, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain.*

[b] *Department of Microbiology, Faculty of Medicine, and BIFI, University of Zaragoza, C/ Domingo Miral s/n, E-50009, Zaragoza, Spain.*

E-mail: alduaso@unizar.es

Green chemistry is a pivotal point in the development of more sustainable and efficient processes.[1] The synergy between the development of safer solvents, coming from renewable raw materials, such as glycerol, and the application of catalytic processes leads in many cases to new, more sustainable strategies for conventional chemical reactions.[2,3] In this communication, we present the first use of renewable functional ionic liquids (ILs) in efficient and recoverable palladium nanoparticle-based catalytic systems to promote copper-free Sonogashira coupling reactions in the absence of any external base.

The design of novel task-specific ILs has focused on two aims: 1) the functionalization of the solvent by incorporating basic nature in the IL anion, and 2) the valorization of glycerol, by its conversion into the IL [$N_2$01] cation,[4] minimizing both the carbon footprint and the solvent toxicity. These systems achieved the coupling of a scope of differently-substituted substrates in 1 h, in the absence of Cu co-catalyst and base, thus minimizing waste generation. Also, different product selectivities were observed, as a result of the IL hydrophilic nature. Besides the catalytic performance study, greenness has been carefully evaluated through the calculation of different green metrics and compared with the state-of-the-art, opening the door to design functional solvents for more sustainable cross-coupling transformations. Finally, the low toxicological impact of the developed glycerol-derived ILs has been tested at different concentrations in a selection of bacteria (*E. coli, S. epidermidis*) and a fungal strain (*S. cerevisiae*).



Scheme 1. C–C coupling reaction catalyzed by Pd NPs/glycerol IL in absence of Cu and base.

Acknowledgments: We thank the financial support from Agencia Española de Investigación (PID2021-125762NB-I00) and Gobierno de Aragón (group 23_37R)

[1] P. Anastas, N. Eghbali. *Chem. Soc. Rev*. **2010**, *39(1)*, 301–312.
[2] A. Leal-Duaso, J. A. Mayoral, E. Pires. *ACS Sust. Chem. Eng*. **2020**, *8(34)*, 13076–13084.
[3] A. Leal-Duaso, J. A. Mayoral, E. Pires et al. *ACS Sust. Chem. Eng*. **2021**, *9(19)*, 6875–6885.
[4] S. Gracia, J. Barrio, A. Leal-Duaso, J. A. Mayoral, E. Pires. *RSC Sust*. **2025**, *3*, 5225–5240.

Uncatalyzed aerobic epoxidation of liquid alkyl alkenes

Judit Oliver Meseguer,[a,*] Susi Hervàs-Arnandis,[a] Silvia Rodríguez-Nuévalos,[a] Francisco Garnes-Portolés,[a] Antonio Leyva-Pérez[a,*]

[a] *Instituto de Tecnología Química (ITQ), Consejo Superior de Investigaciones Científicas-Universitat Politècnica de València, 46022, Valencia, Spain*

E-mail: joliverm@itq.upv.es

Alkyl epoxides are essential building blocks across multiple industrial sectors, including surfactants, construction materials, polymers, electronics and adhesives.[1] Their strategic importance is reflected in a global market estimated at ~€70 billion in 2024 and projected to exceed €90 billion by 2028, with a compound annual growth rate (CAGR) between 3 and 6% which implies that megaton amounts of these epoxides are to be manufactured. Meeting this growing demand requires the large-scale manufacture of megaton quantities of epoxides. Current industrial epoxidation technologies rely predominantly on stoichiometric oxidants- H_2O_2, organic peroxides and hydroperoxides—typically in the presence of catalysts and organic solvents. The only major exception is the epoxidation of ethylene with O_2/air over Ag catalysts at >500 °C.[2] Consequently, the development of a general epoxidation of alkenes with air has been a long-standing challenge in synthetic chemistry.

Here we show that a selective aerobic epoxidation of alkyl alkenes in liquid phase occurs without any catalyst, just placing the neat alkene under 3–5 bar of O_2 and heating. The reaction can be performed in either an autoclave, a stirring vessel with air bubbling or even a simple open flask, provided that any metal piece is present.[3] Alkyl epoxides are directly obtained in yields and selectivity up to 90%. The simplicity of the set-up allows to engage the epoxidation reaction with either a previous alkene formation or a later epoxide opening reactions, to achieve a variety of industrially-relevant organic products (one-pot synthesis of laurolactam).[4] These results are a practical outcome of more than 75 years of research in the direct oxidation of alkenes with air.

[1] Y Meng, F. Taddeo, A. Freites Aguilera, X. Cai, V. Russo, P. Tolvanen, S. Leveneur, *Catalysts* **2021**, *11*, 765.
[2] T. Berndt, O. Böge, *Ind. Eng. Chem. Res.* **2005**, *44*, 645–650.
[3] S. Hervàs-Arnandis, F. Garnes-Portolés, S. Rodríguez-Nuévalos, J. Oliver-Meseguer, A. Leyva Pérez, *Nat. Commun.* **2025**, *16*, 6542.
[4] S. Hervàs-Arnandis, S. Rodríguez-Nuévalos, J. Oliver-Meseguer, A. Leyva Pérez, *Catal. Sci. Technol*. **2026**, Advance Article.

Efficient and Sustainable CO_2 Conversion into Fuels and High-Value Products

L. C. Branco,* V. Paz, C. Melo, S. Messias, A. S. Reis Machado, A. Nunes
LAQV-REQUIMTE, Chemistry Department, NOVA School of Science and Technology, NOVA University of Lisbon, 2829-516 Caparica, Portugal
E-mail: l.branco@fct.unl.pt

Efficient utilization of carbon dioxide (CO_2) is essential to mitigate greenhouse gas emissions and advance carbon capture and utilization (CCU). The Sabatier reaction, converting CO_2 to methane, provides both carbon mitigation and renewable fuel production, and is increasingly applied in Power-to-Gas (P2G) technologies. P2G integrates surplus renewable electricity into chemical fuels, producing methane that can be directly injected into existing natural gas infrastructure. Its high storage capacity ensures reliable energy supply and helps balance intermittent renewable generation [1]. Ruthenium-based catalysts demonstrate superior efficiency in CO_2 hydrogenation compared to other metals [2]. Previous studies from our group showed that [Ru(COD)(2-methylallyl)$_2$] catalyzes CO_2 methanation effectively in fluorinated ionic liquids (ILs), with activity strongly dependent on the in-situ formation, stabilization, and particle size distribution of ruthenium nanoparticles (Ru NPs) [3]. Building on these results, alternative green solvents, including deep eutectic solvents (DES), were explored, leading to enhanced catalytic performance and stability. Using these systems, CO_2 conversion reached 99% with CH_4 selectivity at 150 °C.

Preliminary photothermo catalysis studies using 2 wt% Ru/TiO_2 in DES achieved 94% CO_2 conversion and a turnover frequency (TOF) of 441.71 mmol·g^{-1}·h^{-1}. Methane production was quantified via gas chromatography, while Transmission Electron Microscopy (TEM) confirmed in-situ formation of Ru NPs with sizes ranging from 3 to 6 nm.

Complementary strategies include biphasic systems combining CO in the gas phase with imidazolium-based ILs and covalent organic frameworks (COFs) as porous catalytic supports. Alternative CO_2 valorization approaches, such as photocatalytic CO_2 reduction using Ni(II) and Co(II) cryptates in IL media, electroreduction to syngas in aqueous IL media and cyclic carbonate synthesis via IL-based catalysis, are also under investigation [4-6].

These findings highlight the potential of Ru-based catalysts combined with ILs and DES to develop sustainable, high-performance, and scalable CO_2 methanation platforms. Such technologies enable efficient CCU, integration of renewable energy, and advancement toward low-carbon energy systems..

Acknowledgements: This work was supported by the InsectERA, nºC64491739300000032, co-financed by PRR - Recovery and Resilience Plan of the European Union (Next Generation EU). The authors also thank the support from FCT/MCTES (UIDB/50006/2020, LA/P/0008/2020 and UIDP/50006/2020 of the Associate Laboratory for Green Chemistry – LAQV).

---

1. W. Li et al, *RSC Advances* **2018**, 8(14), 7651.
2. C. I. Melo et al. *ChemSusChem* **2016**, 9(10), 1081.
3. C. I. Melo et al. *ACS Sustain. Chem. Eng.* **2019**, 7(14), 11963.
4. A. I. Paninho et al *Molecular Catalysis* **2021**, 499, 111292.
5. S. Messias et al. *Energy Adv.* **2022**, 1, 277.
6. R. T. Marques et al. *ChemCatChem* **2025**, 17, e202402036.

Green synthesis of Limonene-based NIPUs precursors: A comparative catalytic study in supercritical CO_2

Patricia Cruza Rodelgo [a], María Jesús Ramos[a], Ignacio Gracia[a], María Teresa García[a], Juan Francisco Rodríguez[a], Jesús Manuel García-Vargas[a]

[a]Faculty of Chemical Science and Technologies, Department of Chemical Engineering, University of Castilla-La Mancha, Ciudad Real, 13071, Spain

E-mail: patricia.cruza@uclm.es

The growing demand for sustainable alternatives to isocyanates in polyurethane production has led to the development of isocyanate-free polyurethanes (NIPUs), obtained by reacting cyclic carbonates with amines to form urethane bonds. This study present a strategic route for the synthesis of these polymers from cyclic carbonates derived from limonene, a renewable agro-industrial by-product from Castilla-La Mancha [1],[2]. This is the first study to describe the carbonation of epoxidized limonene with supercritical CO_2 ($scCO_2$) to efficiently produce limonene carbonates, fixing CO_2 and transforming it into products of economic interest, helping to reduce greenhouse gas emissions.

The influence of pressure (50–120 bar), temperature (100–140 °C), and time (8–72 h) was evaluated with different catalytic systems. Among the homogeneous catalysts, TBAB outperformed TBAI [3], achieving a yield of 91.8% under optimized conditions of higher temperature, pressure, and time. In addition, the activity and reuse of heterogeneous catalysts based on Y and ZSM-5 zeolites impregnated with KI and KBr [4] were evaluated. The use of $scCO_2$ as a reaction medium allows for the valorization of both CO_2 and local renewable resources, aligning with the principles of green chemistry and the circular economy.

a) b)

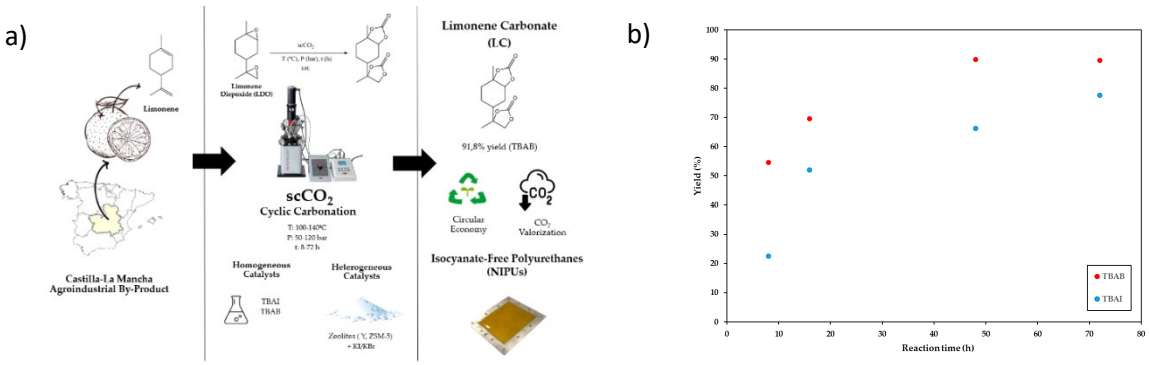


Figure 1. a) Graphical Abstract b) Effect of catalyst and reaction time on the yield of the carbonation reaction (TBAI/TBAB (5%), 100ºC, 80 bar)

[1] A. Cornille, R. Auvergne, O. Figovsky, B. Boutevin, and S. Caillol, *Eur Polym J*, Feb. **2017**, 87, 535–552

[2] Responsible Forest Management S.L., "Study and characterization of Pinus pinaster Ait. pine forests in the Autonomous Community of Castilla-La Mancha with resin potential," **2022**.

[3] Catalá, J., Caballero, M. P., de La Cruz-Martínez, F., Tejeda, J., Castro-Osma, J. A., Lara-Sánchez, A., García-Vargas, J. M., García, M. T., Ramos, M. J., Gracia, I., & Rodríguez, J. F. *Journal of CO_2 Utilization*, 61, **2022**.

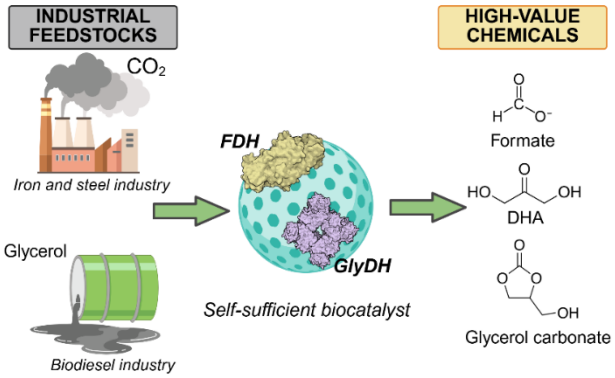
[4] Ozorio, L. P., Henrique, F. J. S., Comerford, J. W., North, M., & Mota, C. J. A. Zeolite-mediated production of cyclic organic carbonates: Reaction of CO2 with styrene oxide on zeolite y impregnated with metal halides. *Reaction Chemistry and Engineering*, **2021**, 672–678

Unlocking the Potential of Biocatalysis-driven CCU: A sustainable production of valuable chemicals from industrial feedstocks

Sady Roberto Rodríguez, Marina Guillén and Oscar Romero.
Department of Chemical, Biological and Environmental Engineering. Engineering School. Universitat Autónoma de Barcelona. 08193 Barcelona, Spain.
E-mail: oscar.romero.ormazabal@uab.cat

Decarbonizing industry requires a transition from energy-intensive fossil carbon processes to more sustainable green technologies that valorize CO_2 as a valuable waste. Biocatalysis offers a promising approach for integrating Carbon Capture and Utilization (CCU) technologies with the conversion of industrial waste into value-added chemicals [1, 2]. To meet the demanding conditions of industrial environments, enzyme immobilization plays a key role by enhancing biocatalyst stability, reusability, and overall reaction efficiency, thus enabling scalable and robust CCU applications [3].

This work explores an industrially relevant multi-enzyme CCU platform to valorize CO_2 and glycerol by integrating formate dehydrogenase (FDH) and glycerol dehydrogenase (GlyDH) enzymes for the co-production of formate and dihydroxyacetone (DHA), with *in situ* cofactor regeneration. A self-sufficient biocatalyst was developed using a sequential one-step purification and co-immobilization strategy on Ni^{2+}-ReliZyme (Scheme 1).



Scheme 1. Multi-enzymatic Carbon Capture and Utilization (CCU) strategy

To intensify the process, the CO_2 transfer rate was optimized, achieving a formate concentration of 66.1 mM (≈3g/L) at a low volumetric flow rate (0.1 vvm) representing the highest reported enzymatic yields [3]. The system's robustness was further effectively validated under industrial conditions using a crude gas mixture mimicking iron and steel industry emissions and crude glycerol from biodiesel production, yielding 43.3mM of formate, alongside significant production of DHA and glycerol carbonate.

The immobilized biocatalyst enabled reaction intensification with significant yields for all products, improved stability and reusability over five reaction cycles, and reduced DHA inhibition. This one-pot CCU approach successfully demonstrates the scalable and sustainable co-production of three high-value molecules from industrial waste.

Acknowledgments: Generalitat de Catalunya, and the 2021 SGR 00143 and project MEPLAB-CO2 (TED2021-129732A-I00) funded by MCIN/AEI/10.13039/501100011033 and by the European Union "NextGenerationEU"/PRTR.

[1] A. Carceller, M. Guillén, G. Alvaro. Environ. Sci. Technol. 2023, 57, 51, 21727–21735
[2] S.R. Rodriguez, M. Guillén, O. Romero. ACS Sustainable Chem. Eng. 2025, 13, 4, 1440–1449.
[3] S.R. Rodriguez, O. Romero, M. Guillén. ACS Sustainable Chem. Eng. 2026, 14, 1, 86–98

Electrochemical biogas upgrading: Direct CO_2 to CH_4 conversion employing Cu-based MOFS

Jose Antonio Abarca[a,*], Guilherme Silva[b], Cátia Azenha[b], Angel Irabien[a], Adélio M. Mendes[b], Guillermo Díaz-Sainz[a]

[a]*Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Av. de los Castros, s/n, 39005, Santander, Spain*

[b]*LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

E-mail: abarcaja@unican.es

Biomethane plays a key role in the energy transition toward a sustainable economy that is not dependent on fossil sources. In biogas production, a gas stream rich in methane and CO_2 is generated, and CO_2 must be removed to upgrade biogas to a predominantly CH_4 composition. At this stage, CO_2 electroreduction can play a crucial role by converting residual CO_2 from a biogas plant into usable CH_4 [1].

In this context, the direct electrochemical conversion of CO_2 to CH_4 is evaluated using an MEA-type reactor fed with humidified CO_2. As a first step, the Cu-based catalyst Cu-UiO66 is used as a reference, and the electrode composition is optimized.

A commercial carbon-based substrate with an integrated microporous layer (MPL) (Sigracet 39 BB) is employed as the catalyst support. The catalyst is deposited onto the substrate using an automated spray-coating technique until a catalyst loading of 1.5 mg cm^{-2} is reached. The electrode composition is modified by incorporating different ionomers: a cationic ionomer (Afiton D-521) and an anionic ionomer (Sustainion XA-9).

Once prepared, the electrode is implemented in a flow cell operating in MEA configuration, using a Sustainion membrane to separate the anode (platinum coil) from the cathode, which is placed in direct contact with the membrane. A 1 M KOH solution is used as the anolyte, and the cathode is supplied with humidified CO_2 at a flow rate of 150 mL min^{-1}. Experiments are conducted at different current densities ranging from 50 to 200 mA cm^{-2}.

Preliminary results demonstrate that electrode composition strongly influences reaction selectivity [2]. When the electrode is prepared using Nafion as the ionomer, H_2 production becomes predominant, with low Faradaic Efficiencies toward CH_4 (~10 %). This behavior is attributed to the proton-conducting nature of the ionomer. In contrast, CH_4 selectivity improves significantly when Sustainion is used as the ionomer, reaching Faradaic efficiencies of up to 25% at 50 mA cm^{-2}. Once it was confirmed that electrode composition significantly affects CH_4 selectivity, additional Cu-MOF-based catalysts, such as Cu-ZIF-8, will be investigated with the aim of maximizing CH_4 production, as a preliminary step prior to testing under real biogas conditions.

Acknowledgements: This research was funded by CETPartnership, under the 2023 joint call for research proposals (CETP-FP-2023-00378), co-funded by the European Commission (GA N°101069750) and with the funding provided by the Spanish Research Agency through project PCI2024-155027-2, funded by MICIU/AEI/10.13039/501100011033. This work was financially supported by: ELECTROMET (CETP/0005/2023) financed by the Fundação para a Ciência e a Tecnologia, I.P., through national funds within the scope of the Clean Energy Transition Partnership (CETP); national funds through FCT/MECI: LEPABE, UID/00511/2025 (https://doi.org/10.54499/UID/00511/2025) and UID/PRR/00511/2025 (https://doi.org/10.54499/UID/PRR/00511/2025) and ALiCE, LA/P/0045/2020 (https://doi.org/10.54499/LA/P/0045/2020). Jose Antonio Abarca gratefully acknowledges the predoctoral research grant (FPI) PRE2021-097200

[1] T. Zhang, S. Verma, S. Kim, T.T. Fister, P.J.A. Kenis, A.A. Gewirth, *J. Electroanal, Chem.,* **2020**, 875, 113862.

[2] H. Gao, T. Yang, W. Nie, Y. Gao, Z. Wang, A. Dong, *Catal.* **2025,** 15, 328

.

Advancing circular economy through sustainable metal recovery from waste tantalum capacitors

Flavia N. Braga,[a,b] Maria C. Hespanhol,[c,*] Ana M. Ferreira,[a] Ana C. R. V. Dias,[d] Helena Passos,[b] Nicolas Schaeffer[a] and João A.P. Coutinho[a]

[a] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[b]LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
[c] Group of Analysis and Education for Sustainability (GAES), Chemistry Department, Federal University of Viçosa (UFV), Viçosa, 36570-900, Minas Gerais, Brazil
[d] CESAM – Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal
E-mail: mariacarmo@ufv.br

The rapid advancement of electronic technologies and the shortened lifespan of devices have intensified the global e-waste challenge, particularly for components containing critical raw materials. Waste tantalum capacitors (TCs), widely used in consumer electronics to aerospace systems, represent an underexploited secondary resource, with less than 1% of Ta currently recovered at end-of-life [1], despite their classification as a critical raw material by the European Union. This work proposes a hydrometallurgical process for the valorization of waste TC, moving beyond conventional Ta-centric recovery strategies [2]. The process is designed to retain Ta in the solid phase, avoiding metallurgical reduction steps and enabling its direct reuse. Selective sulfuric-acid leaching dissolves Mn, Ni, Cu and Zn while preserving Ta and Ag in the solid residue. Mn is first recovered by selective precipitation, after which the remaining leachate is treated by sequential solvent extraction using CYANEX® 272, yielding high-purity Zn (93%), Cu, and Ni (98%) with overall recoveries exceeding 87%. A subsequent nitric-acid leaching step selectively dissolves Ag, which is recovered by chloride precipitation, leaving a Ta-rich solid with approximately 85% purity. Life-cycle assessment shows substantial reductions in environmental impact compared to primary metal production, with Ta and Ag recovery as the main contributors. A preliminary economic assessment further supports the process viability under realistic market conditions.

Acknowledgments: This work was financially supported by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). This work was further financially supported by Fundação para a Ciência e a Tecnologia, I.P. /MCTES through national funds: LSRE-LCM, UID/50020/2025 (DOI: 10.54499/UID/50020/2025); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); and CICECO-Aveiro Institute of Materials, UID/50011/2025 & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020). N.S. acknowledges the European Research Council (ERC) for the starting grant ERC–2023–StG–101116461. Ana M. Ferreira and F. Braga acknowledge FCT for the researcher contract CEECIND/00361/2022 (DOI: 10.54499/2022.00361.CEECIND/CP1720/CT0020) and the Ph.D. grant 2023.01749.BD (DOI:10.54499/2023.01749.BD), respectively. Ana C. Dias also acknowledges funding by national funds through FCT – Fundação para a Ciência e a Tecnologia I.P., under the project CESAM – Centro de Estudos do Ambiente e do Mar, references UID/50017/2025 (doi.org/10.54499/UID/50017/2025) and LA/P/0094/2020 (doi.org/10.54499/LA/P/0094/2020). Maria C. Hespanhol thanks Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq: 305649/2021-3; 407799/2022-2) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG: RED-00161-23, APQ-01134-23).

[1] M. Agrawal, R. Singh, M. Ranitović, Z. Kamberovic, C. Ekberg, K.K. Singh, *Sustain. Mater. Technol*. **2021**, 29, e00323.
[2] F. Braga, M.C. Hespanhol, A.M. Ferreira, A.C.R. Dias, H. Passos, N. Schaeffer, J.A.P. Coutinho. **2026**. (*submitted*)

Py-GC-MS-based methodology for the environmental assessment of PHB in agricultural soils.

Marina Alcaraz Dólera[a], Margarita Ros[a], José Antonio Pascual[a], Rosa Peñalver[b], Natalia Campillo[b], Natalia Arroyo[b], Pilar Viñas[b]

[a] *CSIC-Centro de Edafología y Biología Aplicada del Segura, Department of Soil and Water Conservation, Campus de Espinardo, P.O. Box 164, 30100 Murcia, Spain*
[b] *Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare-Nostrum", University of Murcia, E-30100, Murcia, Spain*

E-mail: marina.alcarazd@um.es

The development and application of biodegradable biopolymers as an alternative to persistent conventional plastics is crucial to mitigate plastic pollution in agricultural soils. Poly(3-hydroxybutyrate) (PHB), a type of biopolymer produced by microorganisms belonging to the polyhydroxyalkanoate (PHA), is emerging as a promising alternative for applications such as agricultural mulch [1]. However, the lack of specific analytical methods to detect and quantify PHB in soils limits the assessment of its environmental fate, especially at the microplastic scale, where fragmented particles can accumulate and require specific techniques for their identification and quantification.

This work presents the development of a methodology for quantifying PHB microplastics in agricultural soils by pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS). This analytical approach requires optimizing strategies for density separation and digestion of the sample's organic matter, enabling the isolation of the biopolymer from the soil matrix. Quantification is based on the detection of crotonic acid (*m/z* 86), a characteristic degradation product of PHB, enabling selective identification and reliable quantification. To evaluate the environmental persistence of PHB in agricultural soils, its degradation was monitored over time in several soil samples with different physicochemical properties, enabling the assessment of its behaviour under different environmental conditions.

Overall, the proposed methodology provides a robust and reliable analytical tool for monitoring micro-PHB in agricultural soils and generates essential evidence to support the evaluation of biodegradable plastics as sustainable alternatives to conventional materials.

The authors thank the Spanish MCIN project PID2024-156671NB-I00, financed by MCIN/AEI/10.13039/501100011033/ FEDER, EU. This research has been developed within the PHAntastic project, funded by the European Union's Horizon Europe Programme under grant agreement No 101130073.

[1] M. Brtnicky, J. Holatko, T. Hammerschmiedt, A. Mustafa, E. Kamenikova, A. Kintl, M. Radziemska, T. Baltazar, O. Malicek, J. Kucerik, *Int. J. Environ. Sci. Technol.* 2024, 22, 8675–8690.

Circular enzymatic biobleaching: revalorization of high-polluted waste streams

Fredes, Yerko,[a] Santema, L. Lars[b], Fraaije, Marco[b], Romero, Oscar,[a,*] Guillén, Marina,[a*]

[a] Bioprocess Engineering and Applied Biocatalysis Group, Department of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.

E-mail: Yerko.Fredes@uab.cat

Conventional cotton bleaching is an energy-intensive process that relies heavily on industrial hydrogen peroxide (H_2O_2). Traditional H_2O_2 production is petroleum-dependent and poses significant logistical risks regarding the transport and storage of high-concentration solutions [1]. To address these challenges, in-situ H_2O_2 generation has emerged as a safer, more sustainable alternative.

This study evaluates a novel biocatalyst utilizing an engineered bacterial carbohydrate oxidase optimized for glucose oxidation (NagOX L251R) [2]. The enzyme was expressed in *Escherichia coli*fused with a Type 3 Carbohydrate Binding Module (CBM3) from *C. thermocellum*, allowing for one-step immobilization and purification process by high-affinity attachment to a low-cost cellulosic support (Perloza® MT100) [3]. This immobilization strategy eliminated residual catalase activity and achieved nearly three times the catalytic activity compared to standard Immobilized Metal Affinity Chromatography (IMAC) methods.

The resulting biocatalyst was applied to upcycle carbohydrate-polluted wastewater from cotton processing, generating 56.5 mM of H_2O_2 within two hours. This revalorized H_2O_2-rich effluent was subsequently used for cotton biobleaching. By incorporating the hydrogen peroxide activator Tetraacetylethylenediamine (TAED), bleaching was successfully performed under milder conditions (pH 7.0, 90°C) than industrial standards (pH 12, 110 ºC). The treated fabrics reached a whiteness index of 50.4–56.6 Berger degrees. Notably, this bio-based approach achieved industrial-grade results while superiorly preserving the mechanical strength and polymerization degree of the cotton fibers.

This work was supported by the Generalitat de Catalunya (2021 SGR 00143), the European Union's Horizon 2020 research and innovation program under project OXIPRO (Grant Agreement 101000607), and the DEMUBI project (PID2022-139725OA-I00), funded by MICIU/AEI/10.13039/501100011033 and FEDER. Additionally, the support of the Generalitat de Catalunya is acknowledged for the PIF pre-doctoral scholarship.

[1] F. Meng, X. Jia, F. Sun, B. Sun, and Z. Yang, "Systemic risk control in anthraquinone-based hydrogen peroxide synthesis: A technical review," *J. Loss Prev. Process Ind.*, vol. 97, Oct. 2025, doi: 10.1016/j.jlp.2025.105689.
[2] A. Boverio *et al.*, "Structural Elucidation and Engineering of a Bacterial Carbohydrate Oxidase," *Biochemistry*, vol. 62, no. 2, pp. 429–436, Jan. 2023, doi: 10.1021/acs.biochem.2c00307.
[3] M. Benito *et al.*, "Cloning, expression, and one-step purification/immobilization of two carbohydrate-binding module-tagged alcohol dehydrogenases," *J. Biol. Eng.*, vol. 16, no. 1, Dec. 2022, doi: 10.1186/s13036-022-00295-8.

Catalytic Diversification using Carbon Dioxide: Functional

DOZN™3.0 - A Quantitative Green Chemistry Evaluator for a Sustainable Future

MilliporeSigma (The life science business of Merck KGaA, Darmstadt, Germany) developed and launched DOZN™2.0 in 2017, a unique web-based greener alternative scoring matrix. This quantitative green chemistry evaluator is based on the 12 principles of green chemistry for customers to evaluate their relative greenness of their processes which provide a framework for learning about green chemistry and designing or improving materials, products, processes, and systems. DOZN™2.0 scores products based on metrics for each principle and aggregates the principle scores to derive a final aggregate score. Through the system it is possible to calculate a green score for each substance based on manufacturing inputs, GHS, and SDS data. DOZN™2.0 is flexible enough to encompass a diverse portfolio of products and it has been verified and validated by a third party to ensure best practices are applied. Based on customer feedback, an upgraded version of the tool, DOZN™3.0, launched in December 2024. Through DOZN™3.0, customers now have access to calculate the green scores of their processes and products. DOZN™3.0 keeps data privacy top of mind - allowing customers to score their processes/products in a safe and secure manner. Come learn how to make your science greener using this free, web-based tool provides users with more data so that they are properly equipped to improve their sustainability.

Sustainable Biocatalytic Production of Bio-Based Diethyl Succinate in Ionic Liquids

Susana Nieto,[a] Salma Chafiq[a], Francisco J. Ruiz,[a] René Cabezas[b], Rocío Villa[a], Pedro Lozano[a]

[a] *Departamento de Bioquimica y Biologia Molecular B e Inmunologia, Facultad de Quimica, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain.*

[b] *Departamento de Química Ambiental, Facultad de Ciencias, Universidad Católica de la Santísima Concepción, Concepción 4090541, Chile.*

E-mail: susanani@um.es

The interest of succinic acid (SA) as building-block for different industries (e.g., chemical, food, pharmaceutical) has prompted the search of new sustainable sources that replace non-renewable biomass.[1] Microbial fermentation is an appealing strategy to obtain bio-based SA, but the further downstream is a serious drawback. The use of ionic systems carefully selected may enable a smart strategy for SA solubilization and extraction, enabling the *in situ* esterification to obtain diethyl succinate (DES)[2], which can be separated from the reaction medium more easily.

This work explores the strength and sustainability of a carefully selected ionic liquid (IL) to enable the efficient biocatalytic synthesis of DES. The influence of key operational parameters (*e.g.,* substrate molar ratio, temperature, and IL content) has been systematically evaluated.

Under optimized conditions, conversions up to 86 ± 3% in 8 h reaction time have been achieved, leading to productivities as high as 8.31 ± 0.29 $\mu mol \cdot h^{-1} \cdot mg_{N435}^{-1}$. However, both DES and monoethyl succinate (MES) were produced, resulting in a moderate selectivity towards DES (41 ± 5%). Alternatively, the use of eutectic mixtures was investigated in order to improve these results. In this context, the ability of SA to form a reactive eutectic mixture (rEM) was demonstrated, yielding a liquid medium that acts simultaneously as solvent and substrate. After the addition of ethanol, 65 % conversion and 49 % yield were obtained, with a maximum productivity of 3.6 ± 0.5 $\mu mol \cdot h^{-1} \cdot mg_{N435}^{-1}$. These results confirm the superiority of the IL over the rEM.

To complete the study, the sustainability of both strategies has been determined by means of a green metrics analysis with special attention to the reaction efficiency and waste generation.[3]

Acknowledgments: This work has been partially supported by MICIU-AEI-FEDER 10.13039/501100011033 (PID2024-159264OB-C21/C22, and CPP2023-010883) grants.

[1] N. Nghiem, S. Kleff, S. Schwegmann, *Fermentation*. **2017**, *3*, 26–26.
[2] Zurob E, Quijada-Maldonado E, Castro-Muñoz R, Romero J, Plaza A, Cabezas R. Sep Purif Technol. **2025**. *354*, 129199
[3] S. Nieto, F. Martínez-Mora, I. Lozano, F. Ruiz, R. Villa, P. Lozano. *Catal. Tod*. **2023**, 114500.

Enhancing Laccase-Driven Poly(vinyl alcohol) Depolymerization Using Polyol-Based Biosolvents

Mariana I. S. Aguiar,[a] Marco Prazeres,[a] Daniela L. Espínola,[a] Maria Inês C. Santos,[a] João A. P. Coutinho,[a] Ana P. M. Tavares,[a] Frederik R. Wurm,[b] Andreia F. Sousa,[a] Ana M. Ferreira,[a*]

[a]Chemistry Department, University of Aveiro, Aveiro, Portugal, CICECO - Aveiro Institute of Materials.
[b]Department of Molecules & Materials, University of Twente, P.O. Box 217, 7500 AE, Enschede, Netherlands, MESA+ Institute.

E-mail: ana.conceicao@ua.pt

Polymer based liquid formulations, PLFs, are widely used in detergents coatings and personal care products and represent an emerging environmental concern due to the release of persistent water soluble polymers into aquatic systems. Poly(vinyl alcohol), PVA, is extensively employed in these formulations due to its film forming ability and chemical stability. Yet, this same stability limits its biodegradability and promotes environmental persistence. Although microbial degradation of PVA has been reported it typically relies on pyrroloquinoline quinone dependent dehydrogenases which restrict practical applicability whereas cofactor independent oxidoreductases such as laccases offer a more sustainable but still limited alternative.

This study aims to explore the oxidative depolymerization of PVA catalyzed by laccase from *Trametes versicolor* in biobased polyol based non-conventional media under mild conditions. Polyols differing in carbon chain length and hydroxyl group number were assessed as modulators of enzymatic activity with glycerol and xylitol showing improved catalytic performance compared to traditional buffer at pH 4.5. Additionally, glycerol promoted detectable PVA molecular weight reduction relative to buffer systems. A Design of Experiments, DoE, strategy was implemented to systematically evaluate the combined influence of laccase concentration and glycerol content in the presence of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid), ABTS, or 2,2,6,6-tetramethylpiperidin-1-oxyl, TEMPO. Response surface modelling enabled the identification of experimental regions associated with improved PVA transformation although complete depolymerization was not achieved.

These findings indicate that polyol based biosolvent environments modulate laccase activity and promote measurable polymer transformation under mild conditions highlighting their potential as sustainable non-conventional biocatalytic media for mitigating polymer persistence in PLFs.

Acknowledgements: This work was developed within the scope of the project CICECO–Aveiro Institute of Materials, UID/50011 & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work is funded by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project GREEN-PATH (Ref. 2023.15169.PEX, DOI 10.54499/2023.15169.PEX). MISA acknowledges FCT for the Ph.D. grant PRT/BD/154714/2023. AMF, APT and AFS acknowledge FCT for the research contracts CEECIND/00361/2022 (DOI 10.54499/2022.00361.CEECIND/CP1720/CT0020), CEECIND/01867/2020 and CEECINSTLA/00002/2022, respectively.

.

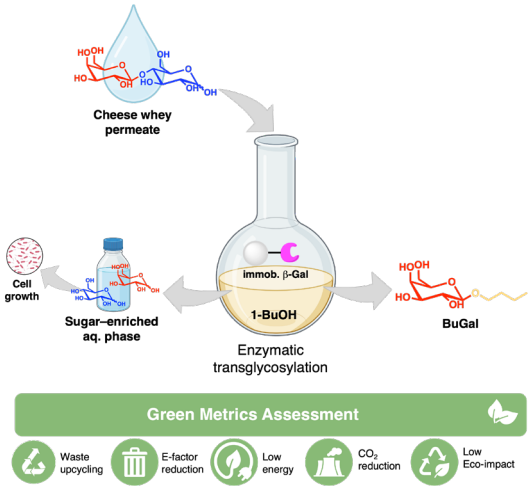
Redesign of cheese whey permeate upcycling: a biocatalytic approach guided by green metrics

Marina Simona Robescu,[a]* Lorenza Cassano,[a] Lorenzo Pasotti,[b] Michela Casanova,[b] Debora Dallera,[b] Paolo Magni,[b] Andrés Rafael Alcántara,[c] and Daniela Ubiali[a]

[a]Viale Taramelli 12, I-27100, Pavia, Italy, Department of Drug Sciences, University of Pavia
[b]Via Ferrata 5, I-27100, Pavia, Italy, Department of Electrical, Computer and Biomedical Engineering, University of Pavia
[c]Plaza de Ramon y Cajal s/n, Madrid, Spain, Department of Chemistry in Pharmaceutical Sciences, Complutense University of Madrid

E-mail: marinasimona.robescu@unipv.it

Valorizing industrial side-streams through biocatalysis can contribute to the transition toward circular manufacturing by implementing sustainable and effective waste-to-value processes. In this work [1], cheese whey permeate, an abundant effluent of the dairy industry, was upcycled into the hydrophilic headgroup 1-butyl β-D-galactopyranoside of sugar fatty acid ester surfactants via enzymatic transglycosylation. This biotransformation was systematically redesigned by using a comprehensive green metrics-guided approach to enhance process sustainability, while ensuring operational simplicity and scalability. By moving from a homogeneous ternary reaction medium to a biphasic system and replacing flash chromatography with a streamlined downstream process involving liquid-liquid extraction and a recyclable hydrophobic resin, the process was successfully scaled-up to 1.5 L yielding the product on gram scale. Process redesign resulted in a 8-fold reduction of E(nvironmental)-factor, about 60-fold improvement of solvent eco-impact, and 27-fold decrease in global warming potential (GWP). Moreover, the redesigned process enabled closed-loop material flows facilitating the direct recovery and recycling of materials (1-BuOH and the hydrophobic resin) within the same reaction unit. Finally, the recovered sugar-enriched aqueous stream from the enzymatic transglycosylation was reused as a nutrient-rich growth medium for microbial cultivation, establishing a highly integrated biomanufacturing framework.



[1] L. Cassano, L. Pasotti, M. Casanova, D. Dallera, P. Magni, A.R. Alcántara, D. Ubiali, M.S. Robescu *under review*.

Sustainable biocatalytic processes in green solvents for the production of bioactive compounds

Martina Bigliardi,[a] Caroline E. Paul,[b] M. L. Contente[a]*

[a] *University of Milan, Department of Food, Nutrition and Environmental Sciences, Celoria 2, Italy*

[b] *Delft University of Technology, Department of Biotechnology, Van der Maasweg 9, HZ Delft, The Netherlands*

E-mail: martina.bigliardi@unimi.it

A sustainable enzymatic platform for the synthesis of *N*-acylethanolamines (NAEs), bioactive fatty acid amides with anti-inflammatory and neuroprotective properties, was establish for the first time.

An efficient, scalable and eco-friendly route to bioactive lipid-based therapeutics was developed using oleaginous yeasts grown on whey permeate. The extracted triacylglycerls were quantitatively converted into ethyl esters in a rotating-bed reactor employing immobilized libase B from *Candida antarctica* (CaL B). This step was followed by aminolysis in eucalyptol, a green medium-boiling-point solvent, affording a defined mixture of fatty amides enriched in oleyl- and palmitoyl-ethanolamide (≥95% yield), without the need for purification steps.

Additionally, a one-pot multi-enzymatic cascade was developed for the synthesis of chiral aromatic epoxides from biomass-derived phenolic acids. A phenolic acid decarboxylase (*Bp*FDC) enables the in situ formation of non-commercially available vinyl phenols, which are are subsequently converted by a styrene monooxygenase (*Gc*StyA). The use of a nicotinamide cofactor biomimetic avoided the need for costly NADH regeneration systems. This cascade afforded chiral epoxides within 2 hours, with up to 95% conversion and excellent (S)-selectivity, thus providing a sustainable route to valuable chiral intermediates.

[1] L. Martínez-Montero, D. Tischler, P. Süss, A. Schallmey, M. C. R. Franssen, F. Hollmann,. C. E. Paul. *Catal. Sci. Technol*. **2021**, *11*, 5077.

[2] P. G. Quintana, G. G. Liñares, S. N. Chanquia, R. M. Gorojod, M. L. Kotler, A. Baldessari, *European Eur. J. Org. Chem*., **2016**, *3*, 518−528.

Synthesis and Solubilization Potential of Glycerol-Derived Solvents: A Sustainable Approach to Green Chemistry

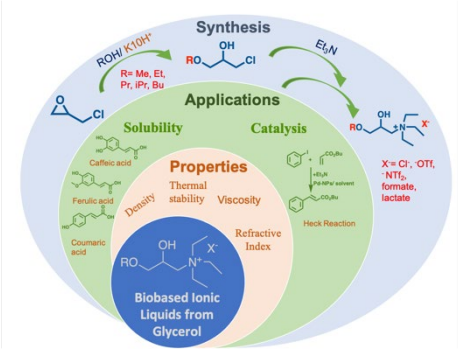
Elísabet Pires Alejandro Leal-Duaso, Sara Gracia-Barberán, Jorge Cambronero-Arregui, Alberto Clemente, María Lanau, and José A. Mayoral

[a] *Instituto de Síntesis Química y Catálisis Homogénea. CSIC-University of Zaragoza, Faculty of Science, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain.*

E-mail: epires@unizar.es

The principles of Green Chemistry emphasize the use of renewable feedstocks and the design of safer chemicals to minimize the environmental and health impacts of industrial processes.[1] Solvents represent a significant portion of chemical waste, with an annual consumption of approximately 28 million tons. In this context, glycerol has emerged as a key renewable platform molecule for green solvents development, due to its abundance as a byproduct of the biodiesel and oleochemical industries. [2]

This work focuses on the development of a versatile portfolio of glycerol-derived solvents—including ethers, deep eutectic solvents (DES), and ionic liquids (ILs)—as sustainable alternatives to conventional petrochemical media.



The synthesis of these solvents has been optimized to ensure scalability and efficiency. Glycerol ethers (mono- and diethers) are produced via the reaction of glycerol-derived platform molecules, such as epichlorohydrin, with various alcohols (ROH) using bases like KOH or $K10H^+$. These processes have been successfully scaled to hectogram levels. Furthermore, a new family of bio-based ionic liquids ([N20x] series) has been synthesized, incorporating diverse anions such as chloride, triflate, lactate, and formate, achieving purities of up to 98%. Deep eutectic solvents were also prepared with 100% atom economy by combining hydrogen bond acceptors (HBA) and donors (HBD), such as choline chloride and glycerol derivatives.

The application of these solvents in solubilization processes was evaluated using hydroxycinnamic acids (caffeic, ferulic, and coumaric acids),[3,4] flavonoids, and non-steroidal anti-inflammatory drugs (NSAIDs). Results indicate that glycerol ethers often outperform traditional glycols (EG and PG) in terms of solubility, with the additional oxygen atom playing a crucial role. Notably, ionic liquids like [N201]Cl exhibited exceptional solubilizing power, surpassing values reported in the literature. To streamline the selection process, the COSMO-RS theoretical model was employed, demonstrating high accuracy in predicting solubility trends and providing a robust tool for preliminary solvent screening. These findings highlight the potential of glycerol-derived solvents as modular, low-toxicity, and high-performance media for a wide range of industrial applications.

[1] P. Anastas, N. Eghbali. *Chem. Soc. Rev*. **2010**, *39(1)*, 301–312
[2] García J.I, García H. Pires E., *Green Chem*. **2014**, 16(3), 1007-1033
[3] S. Gracia-Barberán, M. Lanau, A. Leal-Duaso, P. López Ram de Viu, A.M. Mainar, J. A. Mayoral, E. Pires, *ACS Sust. Chem & Eng*, **2025**, 13(23), 8556-8566
[4] S. Gracia, J. Barrio, A. Leal-Duaso, J. A. Mayoral, E. Pires. *RSC Sust*. **2025**, *3*, 5225–5240.

Cu-catalyzed stereodivergent decarboxylative amination of bicyclic carbamates: Access to cyclobutane-1,3-diamine synthons

Yue Ren[a,b], Wangyu Shi[a,b], Arjan W. Kleij[a,c*]

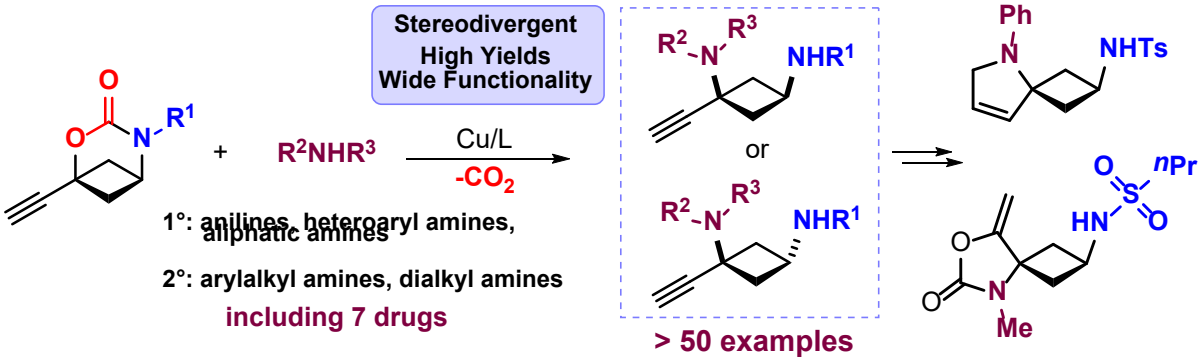
[a] *Institute of Chemical Research of Catalonia (ICIQ-Cerca), Av. Paisos Catalans 16, 43007 Tarragona (Spain)*

[b] *Departament de Química Física i Inorgánica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona (Spain)*

[c] *Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluis Companys 23, 08010 Barcelona (Spain)*

E-mail: yren@iciq.es

Cyclobutane fragments are considered significant to the design and synthesis of bioactive molecules, and in new drug discovery.[1] In recent years, a variety of functionalized cyclobutanes have been successfully obtained using bicyclobutane (bcb) as a starting point.[2] Due to limitations of the bcb structure and the requirement of a step-wise synthesis, streamlined access to a range of stereodefined cyclobutane-1,3-diamines has so far been elusive.[3] At present, the common synthetic methods towards aminated cyclobutanes require multiple steps using stoichiometric approaches while suffering from a lack of functional diversity and/or providing a single stereo-isomeric product. A catalytic procedure that provides access to diaminated scaffolds in a stereodivergent way using the same catalytic process remains unexplored. Here, we show that a Cu-mediated approach allows to convert 2-oxa-4-azabicyclo[3.1.1]heptan-3-one derivatives into trisubstituted cyclobutane-1,3-diamines in high yield and chemo-selectivity. Both *cis* and *trans* diastereomers could be selectively obtained by simple solvent control, and in typically high isolated yields of >80%.



[1] K. Majima, M. Yamano, *J. Org. Chem*. **2021**, *86*, 11464-11471.
[2] A. Maity, K. Balanna, C. G. Daniliuc, A. Studer, *Chem. Sci*. **2025**, *16*, 7264-7269.
[3] D Dmytro, S. Radchenko, S. O. Pavlenko, O. O. Grygorenko, D. M. Volochnyuk, S. V. Shishkina, O. V. Shishkin, I. V. Komarov, *J. Org. Chem*. **2010**, *75*, 5941–5952.

Closing the Loop: Flow Platform for the Sustainable Synthesis, Application and Electrochemical Recovery of Nickel Catalysts

Charlotte Willans,[a*] Laurence Wilson,[a] and Alice Martin[a]

[a] *University of York, Heslington, York, YO10 5DD*

E-mail: charlotte.willans@york.ac.uk

Transition metal-catalysed reactions remain a cornerstone of modern chemical synthesis in both academia and industry. However, the reliance on toxic, expensive, and unsustainably sourced metals presents a significant challenge.[1] While earth-abundant metals such as nickel offer a more sustainable alternative to PGMs, their inherent toxicity and environmental burden of their waste streams remain critical barriers to green manufacturing.[2]

This work presents a circular economy approach to homogeneous catalysis. We have developed an automated flow platform designed for the sequential synthesis of metal catalysts, execution of catalytic reactions, and subsequent electrochemical recovery of the metal.[3,4] This integrated approach addresses core principles of Green Chemistry by reducing chemical waste and improving the environmental profiles of metal processes.

A significant bottleneck for such automated systems is the accurate, real-time analysis of reactions. Current methods to quantify metals in solution, such as ICP-OES/MS, are limited by the necessity of offline sample preparation, preventing simple in-line integration. To address this, we have developed a novel method for monitoring metal recovery: quantitative Colorimetric Analysis of Metals (qCAM) (Fig. 1). Using a simple digital camera for quantitative analysis, qCAM allows for rapid assessment of reaction solutions with a sensitivity down to the sub-ppm level. This aligns with the contamination limits implemented in the pharmaceutical sector, offering a low-cost, high-efficiency tool for maintaining sustainable standards in automated chemical production.[5]

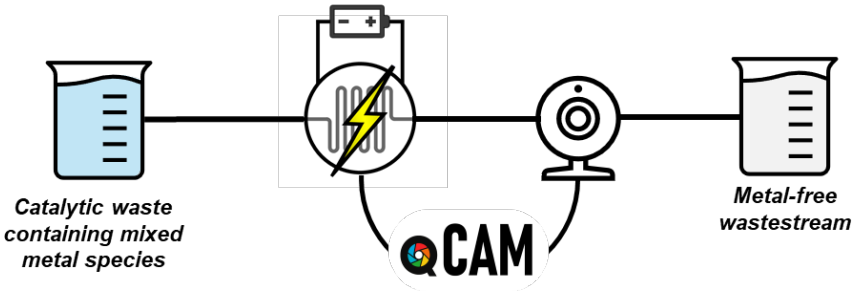


Figure 1. Colorimetric analysis of catalytic waste streams following electrochemical metal recovery.

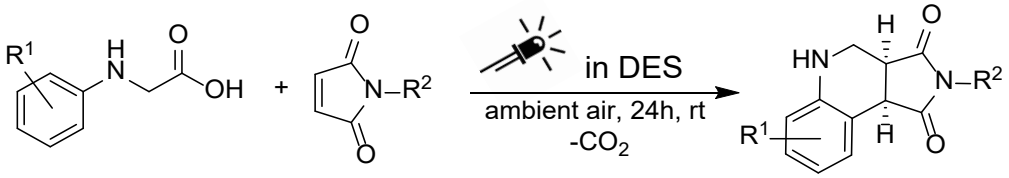
[1] C. C. C. Johansson Seechurn et al., *Angew. Chem. Int. Ed*. **2012**, *51*, 5062-5085.
[2] V. P. Ananikov, *ACS Catal*. **2015**, *5*, 1964-1971.
[3] D. R. Husbands et al., *Chem. Commun*. **2024**, *60*, 8876-8879.
[4] C. Schotten et al., *Catal. Sci. Technol*. **2022**, 12, 4266-4272.
[5] European Medical Agency, ICH guideline Q3D (R2) on elemental impurities, The Netherlands, 2022.

Visible Light-Induced Catalyst-Free Decarboxylative Povarov-Type Reaction of *N*-Aryl Glycines with Maleimides in Deep Eutectic Solvents

Jose Antonio Ñíguez Elena,[a] Diego Alonso Velasco,[a,*] and Rafael Chinchilla Cruz[a,*]

[a]*Organic Chemistry Department and Organic Synthesis Institute (ISO), Apdo. 99, 03080 Alicante (Spain)*

E-mail: jose.niguez@ua.es



Scheme 1.

Photoredox reactions, particularly those induced by visible light, have considerably expanded the utility and scope of radical chemistry in organic synthesis in recent years.[1] However, these reactions are usually conducted using Volatile Organic Compounds (VOCs) as reaction media, which pose inherent environmental risks. To avoid these drawbacks, different alternative solvents have emerged as a convenient alternative to VOCs in organic transformations, specially Deep Eutectic Solvents (DES), owing to their low volatility, ease of preparation, and biodegradability.[2]

Despite these advantages, reported examples of visible-light-promoted synthetic transformations in DES remain scarce.[3] In this communication, we present the synthesis of polycyclic tetrahydroquinoline derivatives in DES via a visible-light (blue LED)-induced, catalyst-free Povarov-type cyclization in ambient air, based on the decarboxylation of *N*-aryl glycines and subsequent cyclization of the formed α-aminoalkyl radical with maleimides (Scheme 1).

[1] a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322-5363; b) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035-10074; c) J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nat. Rev. Chem.* **2017**, *1*, 0052; d) L. Marzo, S. K. Pagire, O. Reiser, B. Koenig, *Angew. Chem., Int. Ed.* **2018**, *57*, 10034-10072; e) X. Zhang, K. P. Rakesh, L. Ravindar, H.-L. Qin, *Green Chem.* **2018**, *20*, 4790-4833.

[2] a) D. A. Alonso, A. Baeza, R. Chinchilla, G. Guillena, I. M. Pastor, D. J. Ramón, *Eur. J. Org. Chem.* **2016**, *2016*, 612-632; b) F. M. Perna, P. Vitale, V. Capriati, *Curr. Opin. Green Sustainable Chem.* **2020**, *21*, 27-33.

[3] R. Mattioli, D. Di Risola, R. Federico, A. Ciogli, F. Gasparrini, C. Villani, M. Fontana, A. Maggiore, M. d'Erme, L. Mosca, A. Francioso, *Molecules* **2022**, *27*, 2348; b) M. D. Nolan, A. Mezzetta, L. Guazzelli, E. M. Scanlan, *Green Chem.* **2022**, *24*, 1456-1462; c) S.-J. Burlingham, A. Torregrosa-Chinillach, D. A. Alonso, R. Chinchilla, *Tetrahedron Green Chem.* **2023**, *2*, 100030; d) D. Procopio, X. Marset, G. Guillena, M. L. Di Gioia, D. J. Ramon, *Adv. Synth. Catal.* **2024**, *366*, 870-876; e) P. G. Kargar, M. Hosseini, *Inorg. Chem. Commun.* **2026**, *186*, 116156.

Sustainable approaches to sulfur containing polymers through the exploitation of carbon disulfide as a sulfur-rich feedstock

Christopher J. Whiteoak,[a,*] Santiago Gullón Moreno,[a] Carlos Díez-Poza,[a] Hermann Pinson,[a] Cristina García Nievas,[a] and Marta E. G. Mosquera[a,*]

[a] Universidad de Alcalá, SOSCATCOM Research Group, Department of Organic and Inorganic Chemistry, Facultad de Farmacia and Instituto de Investigación Química Andrés M. del Río (IQAR), Campus Universitario, Carretera Madrid-Barcelona, Km 33,100, 28805 Alcalá de Henares, Madrid, Spain.

E-mail: christopher.whiteoak@uah.es

The incorporation of sulfur atoms into polymer main chains often results in materials with enhanced properties in many aspects, including improved mechanical, optical, and thermal properties.[1] Beyond these advantages, the possibility to produce sulfur-based polymers through sustainable means is further pushing significant growth in this field.[2] One way of introducing sulfur atoms into polymer chains is to use carbon disulfide (CS_2) in place of carbon dioxide (CO_2) in already established polymerization processes which use this greenhouse gas. One example of a well-studied polymerization reaction that employs CO_2 is the ring-opening co-polymerization (ROCOP) of cyclic ethers (eg. epoxides and oxetanes) and CO_2.[3] In this contribution we will present our most recent results using both epoxides and oxetanes for the analogous ROCOP with CS_2, catalyzed by a gallium aminotrisphenolate complex, a reaction that is far less studied and manifests a higher level of complexity in the polymer products. Beyond this, over the last few years, the polyaddition of *bis*-cyclic carbonates and diamines (forming non-isocyanate polyurethanes; NIPUs) has generated a lot of interest as the resulting polymers are seen as sustainable replacements for widely used polyurethanes.[4] Again, using the same gallium-based catalyst system we have optimized a route for the synthesis of cyclic dithiocarbonates which can then be used to prepare the sulfur containing analogues of these NIPUs, which present structural advantages as a result of the use of this sulfur-containing cyclic monomer. Again, this contribution will present our most recent results in this field.

Scheme 1. Overview of the polymer forming reactions highlighted in this contribution.

[1] T.-J. Yue, W.-M. Ren, X.-B. Lu, *Chem. Rev*. **2023**, *123*, 14038-14083.
[2] M. J. H. Worthington, R. L. Kucera, J. M. Chalker, *Green Chem*. **2017**, *19*, 2748-2761.
[3] J. Huang, J. C. Worch, A. P. Dove, O. Coulembier, *ChemSusChem*. **2020**, *13*, 469-487.
[4] R. Turnaturi, C. Zagni, V. Patamia, V. Barbera, G. Floresta, A. Rescifin, *Green Chem*. **2023**, *25*, 9574-9602.

A Sweet Flow: HMF Production and *in-situ* Valorization into Valuable Nitrile-containing Compounds via Telescopic Flow Chemistry.

Julián E Sánchez-Velandia[a*], Mattia Annatelli [a], Cristopher Tinajero[b], Marcileia Zannatta[b], Victor Sans[b], Fabio Aricò[c], Eduardo García-Verdugo[d]

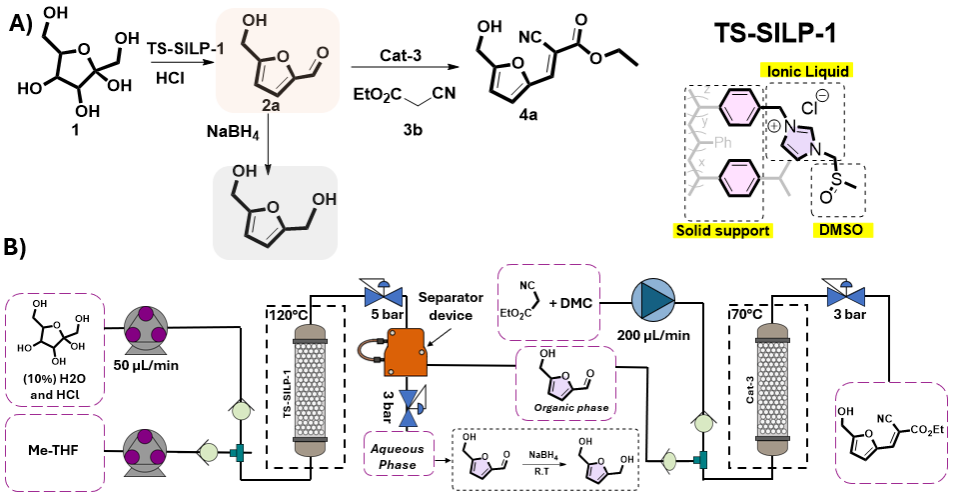
[a] *Supramolecular and Sustainable Research Group, Departamento de Química Inorgánica y Orgánica, Universidad Jaume I, Castellón, España*

[b] *Institute of Advanced Materials (INAM), Universitat Jaume I (UJI), Avenida de Vicent Sos Baynat, S/n, Castellón, España*

[c] *Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Venice, Italy*

E-mail: velandia@uji.es

Biomass have gained attention due to the possibility to replace fossil feedstocks for the production of biobased transportation fuels, heat, power, and biomaterials[1]. In this research, a biorefinery approach is reported for applying telescopic flow chemistry for the efficient synthesis of sugar-derived biomass compounds, specifically D-fructose, into valuable nitrile-containing compounds. This approach deals with the use of Task-Specific Solid Ionic Liquid Phases (TS-SILPs), designed at the molecular level to integrate both the stabilizing properties of ionic liquids and dimethyl sulfoxide within a solid phase solvent system. In this way, these polymeric materials facilitate the stabilization of the well-known 5-hydroxymethylfurfural and its key intermediates, thereby enhancing both its synthesis and downstream transformations. The solid-state nature of the TS-SILPs enables the development of a liquid–solid–liquid continuous flow configuration, which simplifies separation, allows for its continuous separation and reuse, and enables the synthesis and telescopic transformation of HMF into different derivative products. This methodology streamlines unit operations and aligns with principles of green chemistry, demonstrating the potential of designing multifunctional supported solvents as media to advance sustainable biomass valorization through integrated continuous processing.



Scheme 1. (A) General one process two steps synthesis of HMF derivatives by coupling multiphasic HMF synthesis with its telescopic valorization by Knoevenagel condensation and by reduction to BHMF of the organic and the aqueous phase, respectively. (B) Schematic representation of the biorefinery platform developed in this research.

Acknowledgements: This work was partially funded by the Generalitat Valenciana through project CIPROM/2023/57, by Grant PID2024-159264OB-C21 funded by MCIN/AEI/10.13039/501100011033 and by ERDF a way of making Europe, and by Universitat Jaume I under the PPITC25 programme (Action 5.1, reference 19I001.06).

[1] X. Zhang, K Wilson, A.F. Lee. *Chemical Reviews.* **2016**, *116*, 12328-12368.

Effect of chao- and kosmotropic natural deep eutectic solvents on the chitin separation and from h. Illucens pupae molt shells

Guillermo Alberto Portillo Perez,[a]* Maria Franco Marcos,[b] Mario Martinez Martinez Martinez,[b]

[a] *AgroFood Park 48, Aarhus N, 8200, Denmark, Department of Food Science, Aarhus University.*
[b] *Author affiliation: Avda. de Madrid, Palencia, Spain, Agricultural Engineering Department*

E-mail: gportillo@food.au.dk

Deep eutectic solvents (DES) have recently gained notoriety as a green medium for chitin isolation and purification, with different solvents demonstrating varying degrees of success in protein removal (chaotropic) [1]. Depending on their nature, some DES have also shown kosmotropic properties, effectively preventing protein denaturing [2]. While considerable research exists on the nature and effects chao- and kosmotropic ions [3], little research has been done to understand the contribution of such molecules when working in tandem in DES. Herein we explore the effect seven different combinations of hydrogen bond acceptor (HBA) and donor (HBD) moieties with both chao- and kosmotropic properties on the separation of chitin and protein from black soldier fly (Hermetia illuciens) molt shells from their pupae stage. DES-treated samples were analyzed in FTIR, showing lower amine/amide proportion in relation to the hemiacetal signal, when compared to the pure insect material (Fig. 1). However, this ratio was still larger than pure chitin. In contrast, N^2 content analysis resulted in much lower protein estimates, suggesting that not all protein was enzymatically available. DTG analysis revealed that, for samples treated with more chaotropic solvents, e.g., guanidine- urea mixtures, this protein loss was indeed related to protein removal. On the other hand, samples treated with kosmotropic DES presented three different degradation curves, related to chitin, protein-chitin, and protein. Confocal microscopy corroborated these results, showing protein intertwined with chitin fibers, especially in kosmotropic DES. Kosmotropic-heavy DES led to protein-chitin reassembly or even crosslinking [4], rather than separation, leading to underestimation of protein content from common analytical techniques.

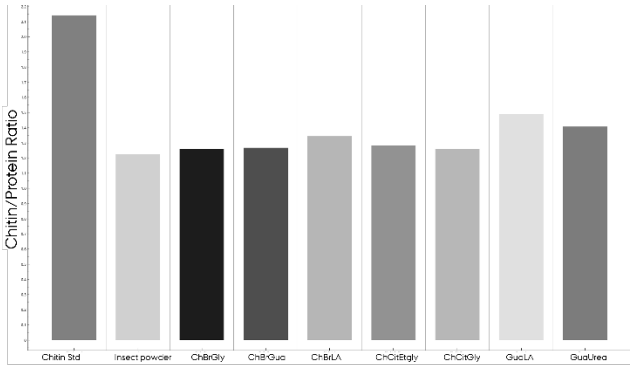


Fig 1. Chitin/Protein ratio based on FTIR spectra – Hemiacetal band area (1180-900 cm^{-1}) is divided by the protein Amine bands I and II (1680-1480 cm^{-1}).

[1] J. Wang, C. Teng et al. Green Chemistry 24, 552-564 (2022).
[2] A. Damjanović, M. Logarušić et al. Physical Chemistry Chemical Physics, (2024).
[3] K. P. Gregory, G. R. Elliott et al. Phys Chem Chem Phys 24, 12682-12718 (2022).
[4] J. A. Gerrard, P. K. Brown. International Congress Series 1245, 211-215 (2002).

Extraction and purification of Phlorotannins from *Sargassum muticum* using natural deep eutectic solvents

Minxing Zhang,[a] Lidia Montero,[a] Luana Cristina dos Santos,[a] Antera Martel,[b] Jose Antonio Mendiola,[a*] and Elena Ibáñez[a,*]

[a] *Laboratory of Foodomics, Institute of Food Science Research, CIAL, CSIC-UAM, Madrid, Spain*

[b]*Spanish Bank of Algae, FCPCT-ULPGC, Muelle de Taliarte s/n, 35214 Gran Canaria, Spain*

E-mail: j.mendiola@csic.es; elena.ibanez@csic.es

Brown alga *Sargassum muticum* is an invasive specie with rapid growth and wide distribution along European coastlines, increasingly recognized as a potential source of bioactive compounds [1]; among them phlorotannins, which are natural bioactive compounds found exclusively in brown algae. Phlorotannins are polymers composed of varying numbers of phloroglucinol units linked together, exhibiting a wide range of biological activities such as antioxidant, antibacterial, antitumor, and anti-inflammatory effects, and have been studied as potential therapeutic agents for treating cancer, neurodegenerative disorders, diabetes, and cardiovascular diseases [2]. Isolation of phlorotannins from brown seaweeds is commonly quite challenging, long and contaminant since it uses high amounts of toxic organic solvents [2]. Therefore, one of the main challenges nowadays is developing sustainable and green downstream processes for the recovery of these valuable compounds. A new suggested approach is using natural deep eutectic solvents (NADES) as green and promising extraction solvents, mainly due to their low toxicity, biodegradability, and reusability [3].

Guided by sustainability principles, in this work, two NADES were rationally selected through Hansen Solubility Parameters (HSP) theory to reduce reliance on conventional organic solvents. The designed NADES (proline:glycerol and proline:xylitol at 1:2 and 1:1 molar ratio, respectively) were successfully applied in ultrasonic-assisted extraction to extract phlorotannins from *Sargassum muticum* collected at three different locations. After NADES extraction, purification and NADES removal was performed using solid-phase extraction; for comparison purposes, conventional extraction was also carried out. Total phenolic content (TPC), total phlorotannin content (DMBA), antioxidant (ABTS and DPPH), and anticholinesterase (AChE and BChE) activities of all extracts were determined both before and after purification.

Results showed that among all extracts, those purified extracts obtained using proline and xylitol exhibited the best performance (comparable to those achieved using conventional extraction) not only containing the highest TPC and DMBA, but also demonstrating higher antioxidant activity than Trolox, as well as cholinesterase inhibitory activity comparable to galantamine with no significant difference. These findings position *Sargassum muticum* as a promising and sustainable bioresource for developing extracts with antioxidant and neuroprotective activities. To address the challenges posed by the complex structures and low concentration of phlorotannins, a green and efficient strategy combining NADES-based extraction with sustainable purification techniques is proposed. This approach not only enables the obtention of high-activity components for structural characterization but also paves the way for their eco-efficient industrial valorization, aligning perfectly with the principles of green chemistry and a circular bioeconomy.

[1] M. D. Catarino, et al, *Mar Drugs.* **2023**, *21*.
[2] L. Pereira and J. Cotas, *Mar Drugs.* **2023**, *21*.
[3] S. Amador, et al., *Mar Drugs.* **2025**, *23*.

Evaluation of different surfactants in the etherification of glycerol with tert-Butanol using microemulsions

Francisco Pérez, Vicente Montes, Felipa M. Bautista, and Rafael Estevez*
Departamento de Química Orgánica, Instituto Químico para la Energía y el Medioambiente (IQUEMA), Universidad de Córdoba, Campus de Excelencia Internacional Agroalimentario CeiA3, Edificio Marie Curie, E-14014, Córdoba, España.
E-mail: q82pehif@uco.es

Despite their dominance, fossil fuels cause severe environmental damage, driving the shift towards renewables like biodiesel [1]. However, biodiesel production generates 10 wt.% glycerol as a byproduct, making its valorization essential. Etherifying glycerol with tert-butanol produces h-GTBEs, valuable diesel additives that improve combustion and reduce emissions. Yet, this acid-catalyzed reaction is equilibrium-limited, as the water formed promotes hydrolysis and restricts high product yields [2].

The present work investigates the etherification reaction carried out within a confined reaction medium based on a water-in-oil microemulsion, where the reaction takes place inside the dispersed polar domains. This study builds upon previous research performed under optimized reaction conditions (84 °C and 7.5 wt% catalyst), using a formulation composed of 2.0 g of diesel as the continuous phase and 0.85 g of a polar phase consisting of tert-butanol, glycerol, and acetonitrile. In that prior study, 1.9 g of the surfactant Synperonic 91/6 was employed, achieving a glycerol conversion of 63% and a selectivity toward higher ethers of 51%. In present work, the influence of surfactant properties, specifically the hydrophilic-lipophilic balance (HLB) and dosage, on glycerol conversion (X_G) and selectivity towards high ethers ($S_{h\text{-}GTBE}$) was thoroughly evaluated. The results indicate that more hydrophilic surfactants, such as Tween 80 (HLB = 15), significantly enhance catalytic performance. The optimal balance was achieved with a Tween 80 dosage of 0.6 g, yielding a robust glycerol conversion of 61.84% and the highest observed selectivity towards h-GTBE (51.37%). Conversely, the use of highly lipophilic surfactants like Span 80 (HLB = 4.3) resulted in the poorest performance, with both conversion (37.58%) and selectivity (34.18%) dropping considerably. Interestingly, a higher surfactant dosage did not correlate with improved outcomes. For instance, increasing the Tween 80 mass from 0.6 g to 1.0 g, or employing an excessive amount of Brij 35 (3.8 g), led to a drastic decline in product selectivity. On the other hand, Span 20 (HLB = 8.6) emerged as a highly competitive alternative; at a lower dosage of 0.37 g, it provided an excellent conversion (54.94%) and selectivity (47.38%). This optimal mass-to-performance ratio makes Span 20 a highly attractive option from an economic and purification standpoint, avoiding the detrimental effects of excessive surfactant loading while maintaining high reaction efficiency.

Table 1. Results of the reaction with different surfactants based on the amount used and HLB. M. represents the mixture between Span 20 and Span 80; XG the glycerol conversion and Si the selectivity to h-GTBE.

Surfactant	Tween 80	Tween 80	Tween 80	Brij 35	Brij 35	Span 20	M. 75% Span 20	M. 50% Span 20	M. 25% Span 20	Span 80
Mass (g)	0.6	0.8	1	3.8	1.42	0.37	0.37	0.37	0.37	0.37
HLB	15	15	15	16. 9	16. 9	8.6	5.375	6.45	5.375	4.3
X_G (mol %)	61.84	52.44	62.58	57.64	40.44	54.94	53.43	52.27	42.28	37.58
$S_{h\text{-}GTBE}$ (mol %)	51.37	35.45	36.46	22.35	37.74	47.38	43.09	40.46	38.93	34.18

[1] T. Liu, P. Miao, Y. Shi, K.H.D. Tang, P.S. Yap, Sci Total Environ. 2022, 810, 152181
[2] A. Cornejo, I. Reyero, I. Campo, G. Arzamendi, L.M. Gandía, Catalysts 2023, 13, 1386
Acknowledgements. Research granted by Project PID2022-142275OB-I00 (MCIU/AEI/10.13039/501100011033 y FEDER, UE).

Sustainable Valorization of Insect Biomass: Optimized Oil Recovery Using Green Solvents

L. C. Branco,* C. Esteves, K. Zalewska, J. Lopes, A. Forte, A. F. M. Santos, S. Freitas, M. J. Nunes

LAQV-REQUIMTE, Chemistry Department, NOVA School of Science and Technology, NOVA University of Lisbon, 2829-516 Caparica, Portugal

E-mail: l.branco@fct.unl.pt

Addressing global food and energy insecurity requires sustainable sources, with edible insects emerging as a promising solution [1-3]. Research and industrial interest in insect farming are rapidly growing, and several companies in Europe are actively developing this sector. A new bioindustrial ecosystem is emerging, integrating academic and industrial efforts to valorize insect biomass, particularly through the recovery of proteins and lipids using environmentally friendly technologies [4].

In this study, the extraction of oils from Tenebrio molitor larvae flour was optimized using multiple green approaches. Solid–liquid extraction was performed with task-specific ionic liquids and natural deep eutectic solvents, offering high selectivity and reduced environmental impact. Supercritical CO_2 ($scCO_2$) extraction was also implemented as a solvent-free method, enabling mild, tunable, and efficient recovery of neutral lipids. Tailored eutectic systems were additionally applied to enhance lipid solubilization via hydrogen-bond interactions, achieving yields comparable to $scCO_2$ and approaching the theoretical lipid content of the flour.

Extracted oils were purified using zeolite-based adsorbents to remove pigments, oxidation by-products, and polar impurities. This strategy preserved the triacylglycerol fraction, improving clarity, stability, and functional quality. Analytical characterization was performed using Nuclear Magnetic Resonance (NMR), Gas Chromatography-Mass Spectrometry (GC–MS), and Liquid Chromatography-Tandem Mass Spectrometry (LC–MS/MS), confirming high extraction efficiency and lipid integrity.

The optimized extraction and purification protocols were extended to Acheta domesticus and Hermetia illucens flours, demonstrating process versatility. The recovered oils and proteins exhibit strong potential for food and cosmetic applications, providing essential fatty acids and bioactive compounds. This work supports the development of sustainable insect biorefineries and contributes to achieving the United Nations Sustainable Development Goal 2: Zero Hunger.

Acknowledgements: This work was supported by the InsectERA – Novo sector bioindustrial Project, nºC644917393000000032, co-financed by PRR - Recovery and Resilience Plan of the European Union (Next Generation EU). The authors also thank the support from FCT/MCTES (UIDB/50006/2020, LA/P/0008/2020 and UIDP/50006/2020 of the Associate Laboratory for Green Chemistry – LAQV).

1.FAO, IFAD, UNICEF, WFP and WHO. *https://www.fao.org/state-of-food-security nutrition/2021/en/* (accessed on 25 February 2026).
2. Chi-Wen Lin et al. *Int. J. Biol. Macromolecules* **2026**, 339, 150017.
3. K. Mohan et al. *Biomass and Bioenergy* **2026**, 205, 108498.
3. InsectERA Project – Official Site Available Online: *https://www.insectera.pt* (accessed on 25 February 2026).

Green in Motion: Biocatalysis–Reactor Synergy in Sustainable Manufacturing

Green in Motion: Biocatalysis–Reactor Synergy in Sustainable Manufacturing

Martina Letizia Contente[a*]

[a]*Department of Food, Environmental and Nutritional Sciences (DeFENS), University of Milan, Via Celoria 2, 20133 Milan, Italy.*

E-mail: martina.contente@unimi.it

Biocatalysis is rapidly establishing itself as a cornerstone of sustainable chemical manufacturing, offering eco-friendly routes to pharmaceuticals, food ingredients, cosmetics, and fine chemicals. [1] Modern strategies emphasize process intensification, where enzyme immobilization and advanced reactor engineering work hand in hand to boost efficiency and scalability.

Continuous-flow biocatalysis exemplifies this shift, enabling higher productivity while minimizing solvent use, waste generation, and energy consumption. Immobilized enzymes are central to this progress: they not only allow catalyst recovery and reuse but also enhance stability under challenging industrial conditions, extending their functional lifetime and reducing costs. [2,3]

Innovative reactor designs, such as rotating bed reactors (RBRs), further advance sustainability by improving mass transfer and catalytic performance. These systems have already demonstrated success in valorizing renewable feedstocks—transforming agro-industrial by-products into bioactive molecules and aroma compounds with significant economic and environmental value.[4]

Together, these developments highlight how biocatalysis is evolving into a robust, scalable, and

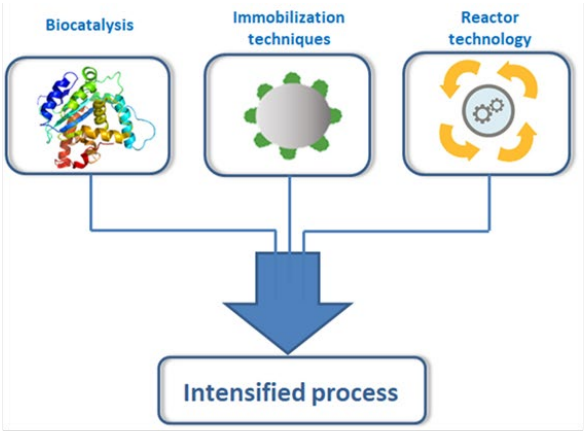


Figure 1: Merging biocatalysis, protein immobilization and reactor technology for intensified enzymatic processes

truly green technology, paving the way for a more sustainable future in chemical production.

[1]A. Sheldon, D. Brady *ChemSusChem* **2019**, *12*, 2859-2881
[2]M.Crotti, M.S. Robescu, J.M. Bolivar, D. Ubiali, L. Wilson *et al. Front. Catal.* **2023**, *3*, 2023
[3]S. Donzella, M.L. Contente *J. Flow Chem*. **2024**, *14*, 85-96
[4]M. Bigliardi, S. Donzella, D.I. Dăescu *et al. ACS Sustainable Chem. Eng.* **2025**, *13*, 18214-18222

3D printed biocatalytic flow reactors

Anca Pordea,[a,*] Valentina Cuzzucoli Crucitti,[a] William Pritchard,[a] Jordan Hill,[a] Bruno Vuillod,[a] Eduards Krumins,[a] Simon J. Attwood,[a] Derek J. Irvine,[a] Ricky D. Wildman[a,*]

[a]University Park, Nottingham, UK, Faculty of Engineering, University of Nottingham

E-mail: anca.pordea@nottingham.ac.uk

Biocatalysis in continuous flow is a key development area for sustainable chemical manufacturing, giving access to green and intensified processes. For these processes to be applicable, modern reactor technology must offer flexibility, control and reproducibility. Immobilisation of enzymes on a solid support helps retaining them in the reactor, but hinders contact between enzyme and substrate. 3D printing has the potential to transform flow reactor technology, through precise control of topologies and rapid prototyping, potentially leading to highly optimised designs with increased flow rate and accessibility of the enzymatic catalysts.

Polymer hydrogel networks incorporating enzymatic catalysts are fabricated via high-resolution 3D printing to serve as biocatalytic reactor cores. Using Projection Micro-Stereolithography (PμSL), we demonstrate the production of enzymatically active hydrogel structures featuring channel dimensions down to 10 μm.[1] We use polymeric resins that are soluble in water and can crosslink under UV during the 3D printing process, forming an insoluble hydrogel. The enzyme is added to the resin and is physically entrapped within the micro-/nano- structures of the gel. An overall reduction in reaction rate can be observed during the enzymatic reaction, an effect which we hypothesise is mainly due to mass transfer limitations within the gel. Strategies for enhancing yield and reactor productivity will be presented, aimed at mitigating mass-transport limitations through control of hydrogel porosity and of the geometrical architectures of the printed reactor cores.

[1] S. J. Attwood, D. Leech, Y. He, A. K. Croft, R. J. M. Hague, D. J. Irvine, R. D. Wildman, A. Pordea, *Chem. Eng. Sci.* **2025**, *305*, 121156.

Pickering Emulsion-Templated Ultra-Porous Films from Biopolymers as Supports for Enzyme Immobilization

Dang W. [a], Heise K. [a]

[a] Institute of Nanoscale and Biobased Materials, TU Bergakademie Freiberg, Germany

E-mail: wenqian.dang@esm.tu-freiberg.de

Pickering emulsions (PEs) have attracted much attention due to their high stability. These emulsions exhibit unique advantages in film fabrication, particularly because of the adjustable porosity. Here, we prepared hydrophilic, ultra-porous films from two biopolymers, sodium alginate and chitosan, using cellulose nanocrystals (CNC) as stabilizers for oil-in-water PEs. Our tailored PE formulation allows for precise control over the resulting pore architectures. By tuning CNC concentration and oil volume fraction, pore structure can be adjusted predictably. To counter the loss of robustness at high porosity, ionic cross-linking is optimized in two different strategies by varying parameters such as crosslinker concentration and cross-linking time. FTIR indicates characteristic functional groups upon cross-linking, and SEM reveals a regular, open porous network. The PE-based films show improved wet integrity compared with the non-crosslinked ones. Beyond structural control, these films offer a rationale for prospective enzyme immobilization: the interconnected porosity is expected to provide high specific surface area and short diffusion pathways beneficial for enzyme loading and mass transfer, while the functional groups on the film surface, such as hydroxyl, carboxyl or amino groups, provide potential interaction/coupling sites via adsorption, ionic binding, or covalent attachment after suitable activation. Overall, our PE-templated films represent a versatile platform for future functional films integrating enzymes and other catalytic components.

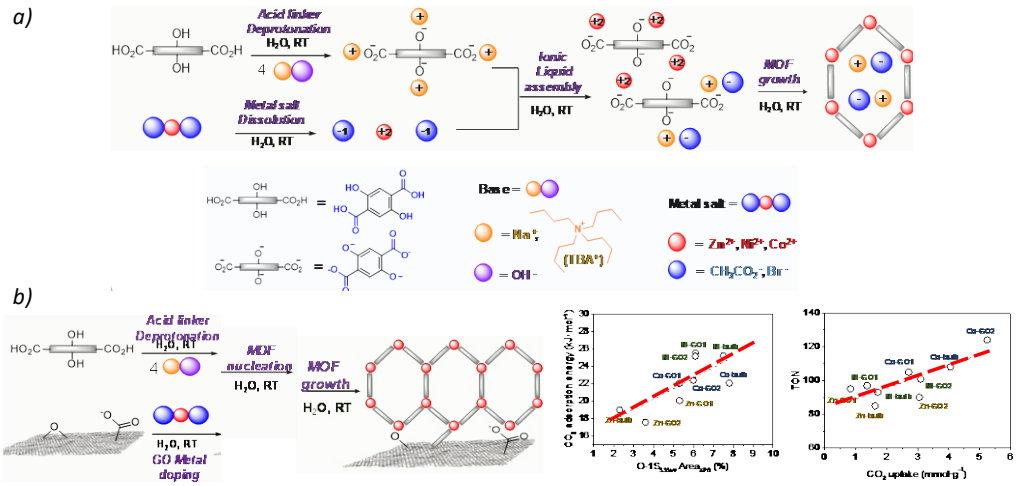
GREEN METAL-ORGANIC FRAMEWORKS FOR CO2 FIXATION

F. G. Cirujano[a], E. García-Verdugo[a], M. Merchán[b], M. M. Velázquez[b], N. Martín[a]

[a]*Departamento de Química Inorgánica y Orgánica, Universitat Jaume I. Av. Vicent Sos Baynat, s/n, 12006. Castelló de la Plana, Castelló. España.* [b]*Departamento de Química Física, Universidad de Salamanca, Plaza de los caídos, s/n, 37008 Salamanca, Spain*

E-mail: cirujano@uji.es

On the one hand, we present a green method to incorporate ionic liquids, e.g., alkylammonium bromide, into metal-organic frameworks (MOFs) by the linker deprotonation with organic (ammonium-type) bases in the presence of metal bromides at RT aqueous conditions (see Scheme 1a).[1] On the other hand, similar MOFs have been growth in aqueous suspensions of graphene oxide, allowing for an improvement in the CO2 adsorption and conversion, both at the ionic liquid-MOF or graphene oxide-MOF interface conditions (see Scheme 1b).[2]



Scheme 1. Ionic liquid (a) or Graphene oxide (b) incorporation to MOFs under green conditions.

[1] N. Martín, M. Maireles, J. S. Velandia, B. Altava, F. G Cirujano, E. García-Verdugo, *Nano Research* **2025**, 18, 94907069.

[2] F. G. Cirujano, N. Martín, E. López-Maya, M. G. Álvarez, M. J. Sánchez, E. G.Verdugo, M. D. Merchán, M. M. Velázquez, *ACS Appl. Mater. Interf.* **2025**, DOI: 10.1021/acsami.4c19708

Redefining Sustainable Synthesis: Mechanochemistry as a Driver for Advanced Coordination Chemistry and Green Catalysis

Javier F. Reynes,[a] Lucía Álvarez-Miguel,[b] Frederick Winkelmann,[c] Michael Felderhoff*,[c] Marta Elena G. Mosquera*,[b] Christopher J. Whiteoak*,[b] and Felipe García*[d]

[a] *Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Avenida Julián Clavería 8, 33006, Oviedo, Asturias, Spain.*

[b] *Departamento de Química Orgánica y Química Inorgánica, Facultad de Farmacia e Instituto de Investigación Química Andrés M. del Río (IQAR), Universidad de Alcalá, Campus Universitario, Ctra. Madrid-Barcelona Km. 33,600, Alcalá de Henares, 28871, Madrid, Spain.*

[c] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*

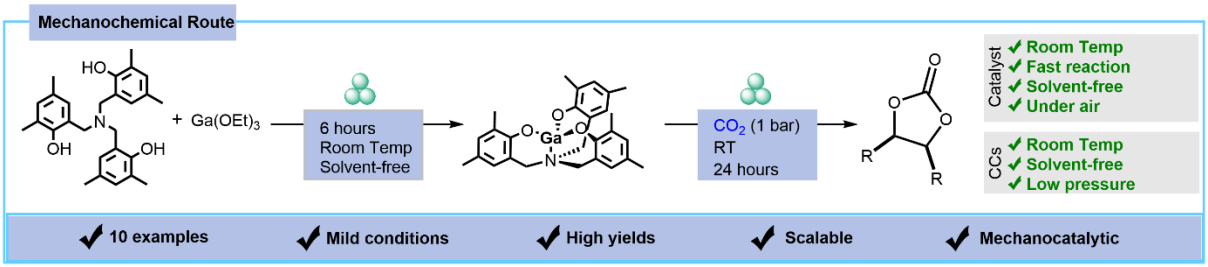
[d] *School of Chemistry, Monash University, Clayton, Victoria 3800, Australia*

E-mail: fernandezreyjavier@uniovi.es

Mechanochemistry has emerged as a powerful and sustainable alternative to conventional solution-based synthesis, enabling chemical transformations under solvent-free or low-solvent conditions with reduced energy input and waste generation.[1] In parallel, coordination chemistry involving main-group elements offers attractive catalytic platforms relying on earth-abundant and low-toxicity metals.[2][3]

In this contribution, we present our recent work on the mechanocatalytic conversion of epoxides into cyclic carbonates using CO_2 as a renewable C1 feedstock under mild conditions. This approach combines mechanochemical activation with main-group catalysis, affording high conversions and selectivity while showing improved performance compared to conventional solution-based methods based on the green chemistry metrics.[3]

In addition to these results, this contribution will highlight the latest advances in coordination chemistry supporting these sustainable processes, including the development of new coordination complexes and ongoing studies of their structure–reactivity relationships under mechanochemical conditions.[4]



Scheme 1. Schematic representation of the proposed mechanochemical route

[1] J. F. Reynes, V. Isoni, F. García, *Angew. Chem.* **2023**, *135*, 44

[2] S. Aldridge, C. Jones, *Chem. Soc. Rev.*, **2016**, *45*, 763–764.

[3] F. Leon, C. Li, J. F. Reynes, V. K. Sigh, L. Xiao, H. C. Ong, G. Hum, H. Sun, F. García, *Faraday Discuss.*, **2023**, *241*, 63-78

[4] J. F. Reynes, L. Álvarez-Miguel, F. Winkelmann, M. Felderhoff, M.E.G. Mosquera, C.J. Whiteoak, F. Garcia, *Angew. Chem.* **2025**, e202502584

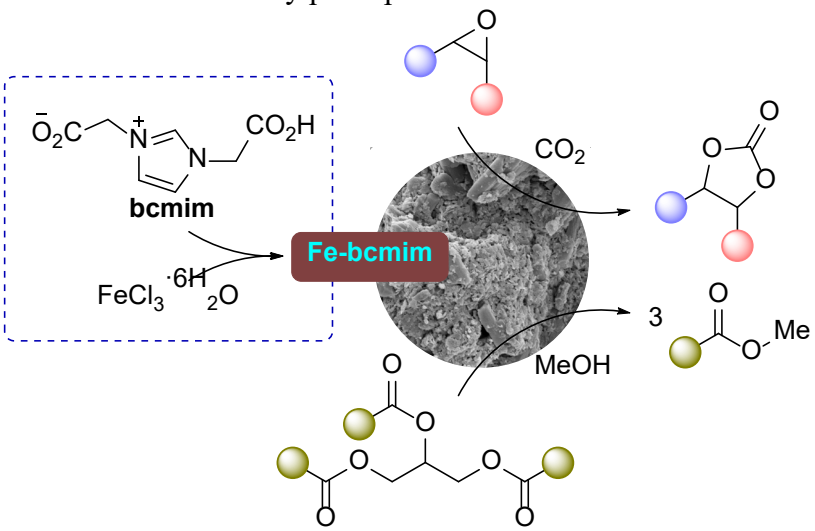
An Iron-Based MOF as a Versatile Catalyst for CO_2 Valorization and Renewable Feedstok Transformation

Anna Nacher-Luis,[a] Tatiana Martí,[a,b] Yanira Pérez-Almarcha,[a] Gabriela Guillena,[a,*] Diego J. Ramón,[a,*] Celia Guillem,[b] and Isidro M. Pastor[a,*]

[a] *Institute of Organic Chemistry, University of Alicante, crta San Vicente del Raspeig s/n, 03690, San Vicente del Raspeig, Alicante, Spain.*
[b] *Kongsberg Discovery Spain, Partida Atalayes 20, 03570, Villajoyosa, Alicante, Spain.*

E-mail: ipastor@ua.es

Carbon dioxide is a major contributor to global climate change, prompting the development of strategies for its transformation into value-added products in accordance with the principles of circular chemistry [1]. In this work, we report a straightforward and environmentally friendly synthetic route for the preparation of an iron-based metal-organic framework (Fe-bcmim) constructed from 1,3-bis(carboxymethyl)imidazole as organic linker, and iron(III) chloride as metal source. The catalytic performance of this material was evaluated in esterification reaction of carboxylic acids with methanol and ethanol, as well as in the transesterification of various vegetable oils to produce fatty acid methyl esters (FAMEs) [2]. The reactions proceeded efficiently, highlighting the potential of Fe-bcmim as a sustainable catalyst for biodiesel production from renewable feedstocks. Furthermore, the catalytic activity of Fe-bcmim was investigated in the cycloaddition of CO_2 to epoxides [3], under solvent-free conditions, affording cyclic carbonates in good to excellent yields. This protocol not only provides an effective route for carbon dioxide valorization but also avoids the use of organic solvents, thereby enhancing the overall sustainability of the process. Overall, the results demonstrate that Fe-bcmim is a versatile and efficient catalyst for transformations involving renewable substrates, making it a promising candidate for the advancement of sustainable catalytic systems aligned with circular economy principles.



Scheme 1. Synthesis of Fe-based MOF and catalytic applications.

[1] T. Keijer, V. Bakker, J. C. Slootweg, *Nat. Chem.* **2019**, *11*, 190-195.
[2] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411-2502.
[3] B. R. James, J. A. Boissonnault, A. G. Wong-Foy, A. J. Matzger, M. S. Sandford, *RSC Adv.* **2018**, *8*, 2132-2137.

Catalytic higher ether synthesis and characterization: elevating Power-to-liquids higher alcohol products to a drop-in e-fuel

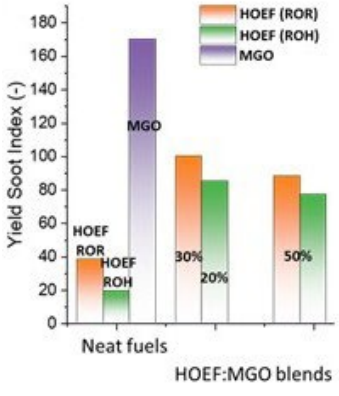
Daniel De Baker, [a] **Frans Kremer,** [b] **Alberto Rodríguez-Gómez,** [a] **Bastian Hesselmann,** [c] **Andreas J. Vorholt,** [c] **Gonzalo Prieto** [a,*]

[a] *ITQ Instituto de Tecnología Química (UPV-CSIC), Valencia 46022, Spain*
[b] *OWI Science for Fuels gGmbH, Aachen 52134, Germany*
[c] *Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34–36, 45470 Mülheim an der Ruhr, Germany*

E-mail: prieto@itq.upv.es

Hard to electrify transport sectors like waterborne transport need high-density, greener, ideally carbon-neutral, condensed e-fuels that are compatible with the current infrastructure and fleet of internal combustion engines. Some of these e-fuels can be synthesized from e-syngas in the context of Power-to-Liquids (PtL) technologies, including methanol (and its dehydrated counterpart, DME) as well as Fischer-Tropsch (FT) diesel. However, many lack current fleet compatibility, aren't liquid at ambient conditions and/or show low energy density [1]. To tackle these insufficiencies, the production and characterization of higher oxygenate e-fuels (HOEFs), i.e. based in higher aliphatic alcohols and ethers, is addressed in this study.

The Horizon Europe E-TANDEM project bases the production of these e-fuels on the tandem coupling of FT chain-growth and reductive olefin hydroformylation (RHF) catalytic processes in a single slurry-phase reactor. This integration gives way to synthetic, aliphatic (C_{5+}) e-alcohols that can be further dehydrated in a later reactor to less hygroscopic and higher energy-density e-ethers. In this study, synthetic alcohol dehydration has been studied with solid acid catalysts: WO_x/ZrO_2 mixed oxide that exhibits conjugate Lewis-Bronsted acid sites, and phosphonic organic resins that show exclusively Bronsted acidity. Although the former could perform at higher temperatures without degrading and required no pre-treatment, slow kinetics and higher selectivity towards intramolecular dehydration side-reactions to olefin products shifted the focus towards the resins as main catalysts. The latter delivered full conversion at 110 hours under reflux, 85% selectivity towards ethers and high yield of up to 60% with a relevant FT/RHF surrogate C_{6+} alcohol mixture under optimized reactor conditions.



The aromatic-free nature and the oxygen chemical function in the new HOEF molecular backbone (which promotes complete oxidation upon combustion) contributed to a remarkable reduction of soot compared to fossil fuels, as determined by normalized Yield Soot Indexing. Even when blending with fossil marine gas oil (MGO) a significant decrease in soot is achieved (Figure 1)

Figure 1. Yield soot index of fossil marine gas oil (MGO) and blends thereof with this study's HOEFs

Additional properties such as a high volumetric energy density (30.5 MJ/L), high material compatibility, and an exceptionally high cetane number (>100) which positions the e-ether mixture not only as a promising e-fuel but also as an effective cetane-booster additive, further justify alcohol dehydration as the final upgrading step.

[1] L. Latorre Valverde, Master's Thesis, UPV, Valencia, **2024**

Exploring the role of zeolite structure and acidity on Cu-based catalysts for dimethyl ether steam reforming

Juanjo López-Martín[a,b,*], Pedro J. Megía[a], Arturo J. Vizcaíno[a], José A. Calles[a,b], Alicia Carrero[a,b]

[a] *Chemical and Environmental Engineering Group. Universidad Rey Juan Carlos, c/Tulipán s/n 28933 Móstoles, Spain*

[b] *Instituto de Investigación de Tecnologías para la Sostenibilidad, Universidad Rey Juan Carlos, c/Tulipán s/n, 28933 Móstoles, Spain*

E-mail: juanjose.lopezm@urjc.es

In the transition towards a more sustainable energy system, hydrogen has emerged as a key energy vector [1]. However, the challenges associated with the storage and transport of hydrogen have increased interest in hydrogen carrier molecules. Among these, dimethyl ether (DME) is particularly attractive due to its properties, high H/C ratio and its suitability for hydrogen production via steam reforming. This reaction is endothermic and requires bifunctional catalysts with both acid and metallic sites to promote DME hydrolysis and methanol steam reforming, respectively. Therefore, this work studies DME steam reforming on copper catalysts supported on different zeolites [2].

The experimental results shown in Figure 1 evidence a positive effect of temperature on hydrogen yield, except for Cu/ZSM-5, sample because exothermic methanol and dimethyl ether to gasoline and hydrocarbons reactions is also taking place when HZSM-5 zeolite is used as support. It is noticeable that the highest hydrogen yields achieved with catalyst supported on USY zeolite (Cu/USY), having lower acid sites (0.16 mmol NH_3/g) but larger pore diameter and pore volume. On the contrary, the catalyst supported on ferrierite zeolite, 10Cu/FER, offers worse hydrogen yield, because of the higher acidity (1.25 mmol NH_3/g) and narrower pores of ferrierite zeolite.

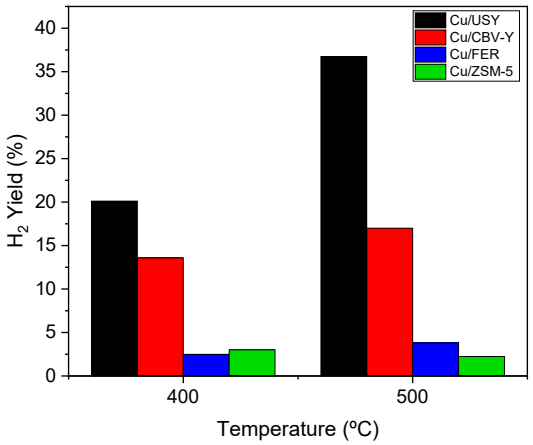


Figure 2 - H_2 yield from DME steam reforming over Cu catalysts supported on different zeolites. Reaction conditions: Steam-to-carbon ratio S/C = 2.5. Weight hourly space velocity (WHSV) = 5.2 h^{-1}. Time = 120 min

[1] P.J. Megía, A.J. Vizcaíno, J.A. Calles, A. Carrero, *Energy Fuels*. **2021**, *35*, 16403-16415.
[2] A.G. Gayubo, J. Vicente, Ereña J., L, Oar-Arteta, Azkoiti M.J., M. Olazar, J. Bilbao. *Applied Catalysis* A: General, **2014**, 483, 76.

Hollow Rotating Disk Electrode (h-RDE): Bridging Conventional RDE and GDE Testing for Gas-Fed Electrocatalysis

Florencio Santos,[a,*] Ghita Khatiri,[a] Gonzalo Escobar [a], Eduardo Laborda [b], Joaquín González [b], Francisco Palazón [a], Antonio J. Fernández[c]

[a] *Grupo de Materiales Avanzados para la Producción y Almacenamiento de Energía, Universidad Politécnica de Cartagena, Campus de Alfonso XIII, 30203 Cartagena, Spain*
[b] *Departamento de Química Física, Facultad de Química, Regional Campus of International Excellence ''Campus Mare Nostrum", Universidad de Murcia, 30100 Murcia, Spain*
[c] *Departamento de Química Física y Termodinámica Aplicada, Instituto Químico para la Energía y el Medioambiente, Universidad de Córdoba, E-14014 Córdoba, Spain*

E-mail florencio.santos@upct.es

Gas-dependent electrochemical reactions like Oxygen Reduction Reaction (ORR) in fuel cells and metal-air batteries require realistic triple-phase boundary (gas-electrolyte-catalyst) conditions unachievable by conventional RDE (electrolyte saturation). We present a hollow rotating disk electrode (h-RDE) combining RDE controlled hydrodynamics with direct gas feed akin to gas diffusion electrodes (GDE). The h-RDE platform enables realistic benchmarking of ORR/OER catalysts for fuel cells and Zn-air batteries. On the other hand, this new h-RDE setup enables the study of others systems like de anthraquinone AO process for the production of H_2O_2 as well as full MEA assembly for fuel cells systems.

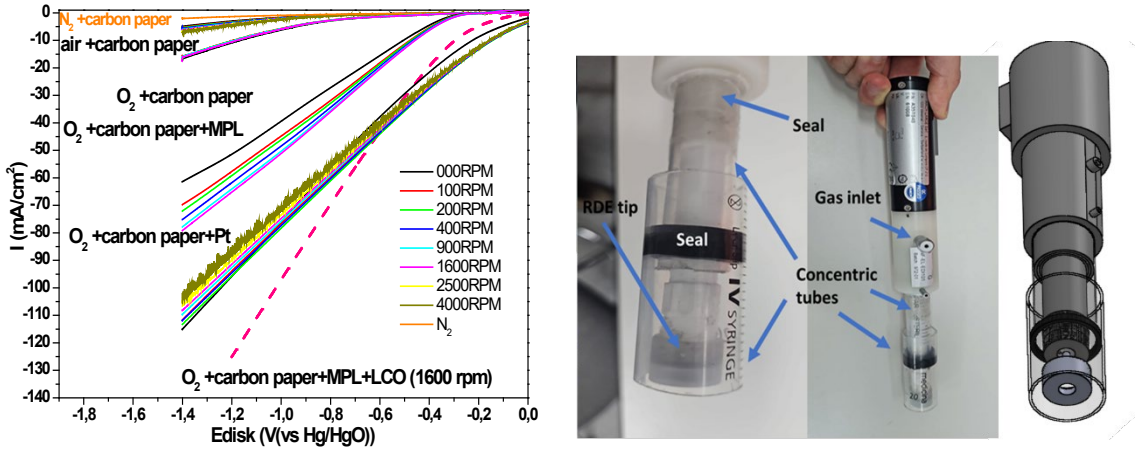


Figure 1: Left , ORR polarization curves at different rotation rates recorded in N_2 saturated 0.1 M KOH with different substrates and catalysts fed at the backside of the substrate using the hollow rotating electrode Right, images of the h-RDE show two concentric tubes rotating in unison with the central shaft. Together with the solution, they form a sealed chamber under slight overpressure. Tiny holes are drilled in the RDE tip to allow gas to reach the backside of the GDL under these pressurized conditions

[1] Santos, Florencio, Sebastian Lorca, Juan F. Gonzalez-Martinez, Antonio Urbina, Miguel A. Alvarez-Sanchez, José M. González-Domínguez, Enrique García-Bordejé, et al. "Metal-free Nanostructured-carbon Inks for a Sustainable Fabrication of Zinc/Air Batteries: From ORR Activity to a Simple Prototype." *Applied Research*, no. August (2023): 1–10. https://doi.org/10.1002/appl.202300023.

Xylose and glucose recovery from sunflower stalks by microwave-based pretreatment

Raquel García Barranco,[a,b]* Alfonso M. Vidal,[a,b] María del Mar Contreras,[a,b] Juan Miguel Romero-García,[a,b] Susmozas Ana,[c] and Encarnación Ruiz[a,b]

[a]Departamento de Ingeniería Química, Ambiental y de los Materiales. Universidad de Jaén, Campus Las Lagunillas, 23071, Jaén, Spain.
[b]Instituto de Investigación en Biorrefinerías (I3B). Universidad de Jaén, Campus Las Lagunillas, 23071, Jaén, Spain.
[c]Investigaciones Energéticas, Medioambientales Tecnológicas, CIEMAT. Avda. Complutense 40, 28040, Madrid, Spain.

E-mail: rgbarran@ujaen.es

Sunflower stalks are an abundant agricultural residue with significant potential as lignocellulosic feedstock for sustainable biorefinery applications. However, their recalcitrant structure and high lignin content limit the efficient recovery of fermentable sugars, representing a major bottleneck for valorization [1]. Microwave-assisted pretreatment has emerged as a promising alternative to conventional heating due to its rapid and homogeneous energy transfer, reduced processing times, and improved disruption of the lignocellulosic matrix, which can enhance mass transfer and increase pretreatment efficiency. Therefore, this study aimed to maximize xylose release through sulfuric acid pretreatment using microwaves and to improve the subsequent enzymatic hydrolysis of the solid fraction for glucose production. The biomass was first extracted and then treated with different sulfuric acid concentrations (up to 200 mg acid/g biomass), temperatures (up to 200 ºC), and times (up to 15 min), and the effects on hemicellulose solubilization and sugar yields were evaluated.

The pretreatment enabled a xylose concentration of about 13 g/L and notably enhanced glucose yield during enzymatic hydrolysis compared to untreated biomass. These findings highlight the potential of acid pretreatment under microwave irradiation as an effective strategy for the integral valorization of sunflower stalks, contributing to the development of economically viable and sustainable lignocellulosic biorefineries.

Acknowledgments: This publication was created as part of the grant PID2023-147594OB-C32 funded by MICIU/AEI/10.13039/501100011033, FEDER/EU

.[1] A. M. Preciado-Saldaña, J. Ruiz-Canizales, M. A. Villegas-Ochoa, J. A. Domínguez-Avila, G. A. González-Aguilar, *Rev. Iberoam. Tecnol. Postcosecha* **2022**, 23, 2.

Bioengineering Lysozyme-Loaded Alginate/Chitosan Films for Therapeutic Applications

Maria H Ribeiro,[a*] Carolina Simões,[a,b] Mariana Tibúrcio[a], Gonçalo Cunha[a], Natália Osório[b], Lidia Pinheiro[a]

[a] *Research Institute for Medicines, Faculty of Pharmacy, Universidade de Lisboa, Av.Gama Pinto, Lisboa, Portugal*; [b]*Escola Superior de Tecnologia do Barreiro, Instituto Politécnico de Setúbal*

Email: mhribeiro@ff.ulisboa.pt

The development of advanced biomaterials for therapeutic applications has gained significant attention in recent years, particularly in the context of bioactive protein delivery systems. In this study, lysozyme was investigated as a potential biopharmaceutical by incorporating it into alginate/chitosan films with distinct formulations. These structures were fabricated using both manual casting and 3D bioprinting techniques, followed by a comprehensive evaluation of their bioactive properties to assess their suitability for therapeutic applications.

The analyses focused on four key properties: enzymatic activity, antioxidant activity, anti-inflammatory activity, and antimicrobial activity. In addition, release assays, pH measurements, and rheological characterization were performed, with particular emphasis on viscosity analysis of the different formulations.

The results demonstrated that chitosan and/or alginate formulations, varying in molecular weight, degree of deacetylation, and magnetization, exhibited distinct behaviors. All samples presented an acidic pH (approximately 2.93), which favored chitosan solubility. Rheological analysis revealed that chitosan exhibited pseudoplastic and thixotropic behavior. As expected, samples without lysozyme showed increasing viscosity with increasing molecular weight. However, upon lysozyme incorporation, the medium molecular weight formulation became more viscous than the high molecular weight formulation, most likely due to specific physicochemical interactions between the polymer matrix and lysozyme.

In the release assays, low molecular weight films showed greater release during the initial days, whereas after 24 hours, high molecular weight films exhibited a more sustained release profile over time. Notably, only the high molecular weight films demonstrated antimicrobial activity. Regarding enzymatic activity, free lysozyme exhibited the highest activity, as expected, followed by low and medium molecular weight films. In the antioxidant activity assay, films containing trolox, low molecular weight films, and spherical structures showed the highest antioxidant capacity. Anti-inflammatory activity was more pronounced in magnetized films and in films with a degree of deacetylation ≥85%.

Overall, these findings demonstrate that the efficacy of these biomaterials strongly depends on their composition and structural characteristics, highlighting the importance of optimizing formulations according to the envisioned therapeutic application.

Choline-Based Ionic Liquids as Selective Cytotoxic Agents Against Cervical Cancer Cells

José Javier Delgado-Marín, Imane Moulefera, Jesús García-León, Ignacio Carnerero-Hinojosa, Mercedes G. Montalbán, Gloria Víllora*

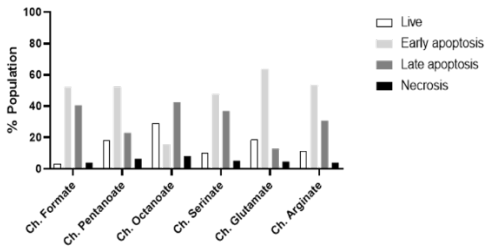
Chemical Engineering Department, Faculty of Chemistry, CEIR Campus Mare Nostrum (CMN), University of Murcia, 30071 Murcia, Spain.
E-mail: josejavier.delgado@um.es

Ionic liquids (ILs) have gained significant attention as advanced functional materials due to their negligible vapor pressure, high thermal and chemical stability, wide liquid temperature range, and tunable physicochemical properties. Among them, choline-based ILs have emerged as particularly attractive candidates for environmentally benign and biomedical applications, owing to their reported low toxicity, biocompatibility, and biodegradability. These features make them promising alternatives to conventional solvents in sensitive fields such as protein stabilization, vaccine preservation, and biomedical formulations [1]. In this work, six choline-based ILs were investigated. Their biological impact was evaluated through cytotoxicity studies on healthy (Ea.hy926) and cervical cancer (HeLa) cells. Table 1 summarizes the overall low toxicity of the choline-based ILs and their selective activity toward cervical cancer cells. These ILs induce apoptotic cell death in cancer cells (Figure 1) while exhibiting reduced effects on non-tumoral cells, thereby demonstrating their potential as a promising therapeutic approach for the treatment of cervical cancer. Based on the results of this study, we assessed the suitability of choline-based ILs for safe biomedical applications, including protein and vaccine preservation, as well as strategies against cervical cancer.

Table 1. IC_{50} cytotoxicity results of the studied ILs.

IL	IC_{50} (mM)	
	EA.hy926	HeLa
Choline formate	132.150±8.556	96.040±9.990
Choline pentanoate	31.253±1.915	18.123±1.269
Choline octanoate	5.133±0.422	4.299±0.378
Choline serinate	68.413±6.828	108.150±10.776
Choline glutamate	92.767±8.738	144.033±14.498
Choline arginate	37.725±3.741	23.473±4.753

Figure 1. Apoptosis-necrosis assay results.



Funding: This work is part of the following research projects: Ref. PID2023-150761OB-C21 funded by MICIU/AEI/10.13039/501100011033 and by FEDER, UE and Ref. 22129-PI-22 funded by the research support program of the Seneca Foundation of Science and Technology of Murcia, Spain. J.J. Delgado-Marín and J. León-García acknowledge support from the Juan de la Cierva contract (Ref. JDC2023-052774-I) and FPI contract (Ref. PID2023-150761OB-C21), respectively, funded by MICIU/AEI /10.13039/501100011033 and the FSE+.

[1] Khavani, M., Mehranfar, A., & Vahid, H, *J. Biomol. Struct. Dyn.* **2023**, 41(10), 4383-4397.

Highly active Metathesis Catalysts for Industrial Applications

Tamás Gazdag[a]*, Ágota Bucsai[a], Mária Bakos[a], Henrik Gulyás[a], Csaba Hegedüs[a], Hasan Mehdi[a], Krisztián Lőrincz[a], Jenő Varga[a], Levente Ondi[a]

[a] *XiMo Hungary Kft., Berlini út 47-49, 1045 Budapest, Hungary.*

E-mail: tamas.gazdag@ximo-inc.com

Olefin metathesis represents a highly sustainable, atom-efficient approach for C=C bond formation in pharmaceuticals, agrochemicals, polymers, and fragrance and flavor (F&F) applications. Compared to traditional methods, such as Wittig and cross-coupling reactions, which require stochiometric reagents and generate significant waste, this reaction minimizes byproduct formation and provides a more resource-efficient alternative. [1] To be industrially viable, metathesis catalysts must exhibit high selectivity and activity, enabling minimal catalyst loadings—typically well below 100 ppm (0.01 mol%)—to reduce both costs and environmental impact. However, achieving these performance criteria remains a major challenge.

Stereoselective synthesis plays a crucial role in the production of pheromones and fragrance compounds.[2] MAP-type Mo- and W-based Schrock alkylidenes were the first catalysts to facilitate the formation of cis C=C double bonds,[2] while the first Ru-based Z-selective catalyst was introduced by Grubbs.[3] Later, Hoveyda's discovery of Z-selective Ru-dithiolate complexes provided a significant advancement, achieving high Z-selectivity in the metathesis of terminal olefins while exhibiting stereoretention in the metathesis of Z- or E-configured internal olefins.[4] More recently, a critical missing piece of the puzzle was addressed with the introduction of a new family of highly efficient E-selective catalysts, capable of operating at loadings below 100 ppm.[5]

A key challenge in sustainable chemistry is the efficient utilization of renewable feedstocks.[6] The ethenolysis of internal double bonds derived from biomass or other renewable sources has long been hindered by catalyst limitations. However, recent advancements in Mo/W- and Ru-based complexes have enabled their successful application on an industrial scale, promoting the valorization of bio-based raw materials.

In this presentation, we present industrially relevant catalysts from the aforementioned groups to provide guidance on selecting the most suitable catalyst for specific olefin transformations. By optimizing catalyst selection, we aim to support the transition toward more environmentally friendly and resource-efficient chemical manufacturing.

[1] Abera T. A., *Journal of Chemistry*, **2021**, 3590613,
[2] Ibrahem I., Yu M., Schrock R. R., Hoveyda A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844–3845; Flook M. M., Jiang A. J., Schrock R. R., Muller P., Hoveyda A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962–7963.;
[3] Endo K., Grubbs R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8525–8527; Keitz B. K., Endo K., Herbert M. B., Patel P. R, Grubbs R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693–699.
[4] Koh M. J., Khan R. K. M, Torker S., Yu M., Mikus M. S., A. H. Hoveyda *Nature* **2015**, *517*, 181–186; Johns A. M., Ahmed T. S., Jackson B. W., Grubbs R. H., Pederson R. L. *Org. Lett.* **2016**, *18*, 772–775;
[5] Benedikter M. J., Ziegler F., Groos J., Hauser P. M., Schowner R., Buchmeiser M. R. *Coord. Chem. Rev.* **2020**, *415*, 213315, Buchmeiser M. R., Sen S., Schowner R. EP3134422, US10072036; H. Mehdi, WO2025003443
[6] Toth F., Ondi L., Frater G. WO2015155593;

Electrocatalytic Access to Quinoline Sulfones under Sustainable Conditions in Deep Eutectic Solvents

Darío Adsuar,[a] Xavier Marset,[a,b,*] Néstor Guijarro,[b,*] Diego J. Ramón,[a,*]

[a] Apdo. 99, 03080, Alicante, Spain, Institute of Organic Synthesis and Department of Organic Chemistry, University of Alicante.

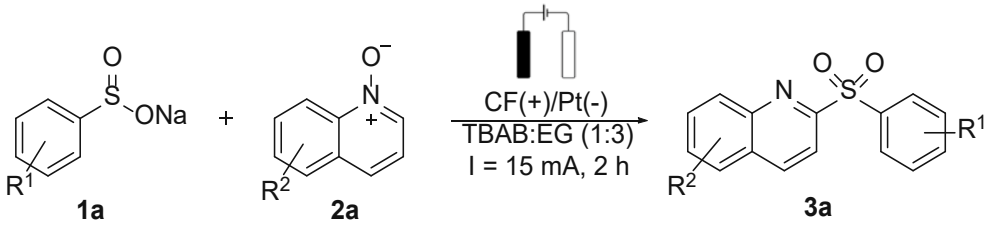
[b] Apdo. 99, 03080, Alicante, Spain, Institute of Electrochemistry, University of Alicante.

E-mail: dario.adsuar@ua.es

Solvents are a key component in chemical transformations, exerting a strong influence not only on reaction efficiency but also on the overall environmental impact of synthetic processes. Despite this, organic synthesis still relies heavily on volatile organic compounds (VOCs), whose toxicity, volatility, and associated health and environmental hazards raise significant sustainability concerns.[1] This situation underscores the need for alternative solvent systems that meet Green Chemistry principles and the Sustainable Development Goals (SDGs).

Deep Eutectic Solvents (DESs) have recently gained significant attention as eco-friendly reaction media. Made from affordable, biodegradable, and low-toxicity components, DESs offer a sustainable alternative to traditional organic solvents.[2] At the same time, organic electrosynthesis has emerged as an effective green method, using electricity to replace stoichiometric oxidants or reductants. This approach helps reduce waste and enhances the sustainability of redox transformations.

In this work, we present an electrocatalyzed deoxygenative sulfonylation of quinoline N-oxides using a DES that acts at the same time as the reaction medium and the supporting electrolyte (Scheme 1). [3] The method achieves high conversions and excellent selectivity across a wide range of substrates. A thorough sustainability assessment based on green chemistry metrics shows a significant improvement compared to similar protocols that use VOC-based systems.[4] Overall, these results emphasize the potential of Deep Eutectic Solvents to support more sustainable and innovative methods in organic electrosynthesis.



Scheme 1. General electrocatalyzed C_2-deoxygenative sulfonylation performed in deep eutectic solvents.

[1] Rumchev, K.; Brown, H.; Spickett, J. Rev. *Environ. Health.* **2007**, 22, 39-55.
[2] Ramón, D.J.; Guillena, G. Deep Eutectic Solvents: Synthesis, Properties and Applications. *Wiley-VCH*, Weinheim, **2019**.
[3] Adsuar, D.; Marset, X.; Ramón, D. J.; Guijarro, N, *ChemSusChem.* **2025**, 18, e*202501779*.
[4] Bardow, A.; Perez-Ramírez, J.; Sala, S.; Vaccaro, L. *Green Chem*. **2024**, 26, 11016–11018.

Chemical Valorization of Lindane Residues

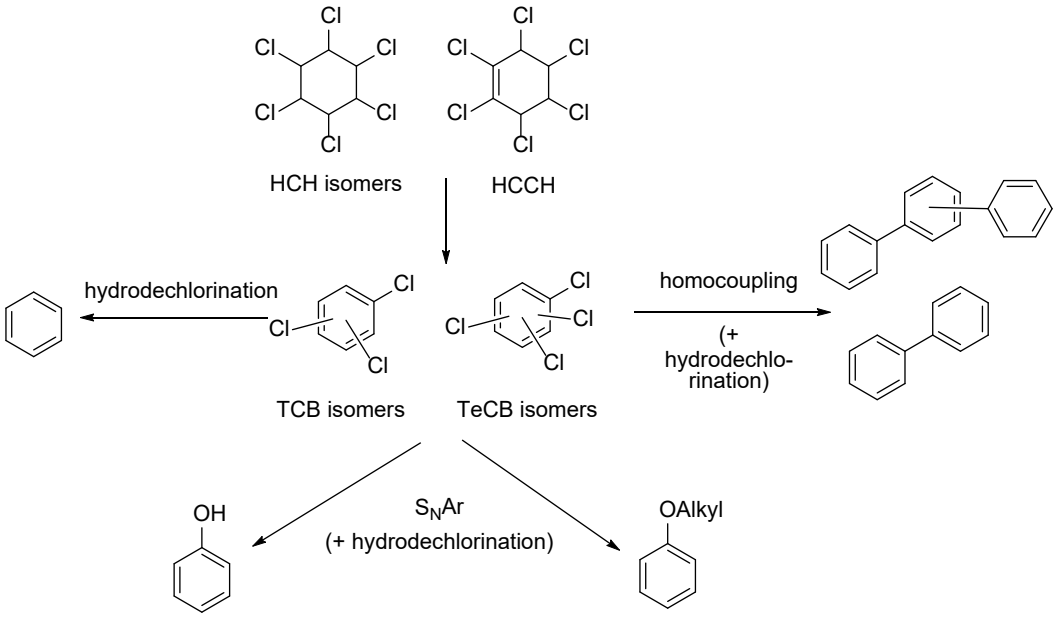
José M. Fraile,* Raquel Lumbreras, Clara I. Herrerías

Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

E-mail: jmfraile@unizar.es

Lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane, γ-HCH) was one of the most extensively used pesticides in the 20th century. Its synthesis, through a non-selective pathway, produced a huge amount of hazardous residues consisting mainly in the rest of the HCH isomers and hexachloroxyclohexenes (HCCH), which were confined in landfills and stockpiles along the world, creating a dangerous legacy [1]. Whereas the contaminated areas around the old lindane factories require remediation methods, the large amounts of residues concentrated in the stockpiles should be, ideally, transformed and valorized [2]. The basic dehydrochlorination to trichlorobenzenes (TCB) and tetrachlorobenzenes (TeCB) is probably the simplest method and the closest one to practical application.

In this communication we will show our work dealing with the combination of dehydrochlorination with three different types of reactions on the resulting mixture of polychlorinated benzenes [3]: *i*) Pd-catalyzed hydrodechlorination to benzene, *ii*) Pd-catalyzed homocoupling to polyphenylenes, and *iii*) non-catalyzed aromatic nucleophilic substitution to phenol and alkyl phenyl ethers. The potential as valorization methods in a circular economy strategy will be shown.



Scheme 1. Routes for chemical valorization of lindane residues.

[1] J. Vijgen, B. Fokke, G. van de Coterlet, K. Amstaetter, J. Sancho, C. Bensaïah, R. Weber, *Emerg. Contam.* **2022**, *8*, 97-112.
[2] A. Leal-Duaso, L. Salvatella, J.M. Fraile, *J. Environ. Manage.* **2025**, *375*, 124262.
[3] A. Leal-Duaso, J.M. Fraile, *Crit. Rev. Environ. Sci. Technol.* **2025**, *55*, 1628-1656.

Earth abundant catalysts for the sustainable production and upcycling of biobased polyesters with advanced properties

C. Rentero,[1] A. Medel,[1,2] E. Mula,[1] H. Amorín,[2] M. Algueró,[2] V. Sessini,[1]* and Marta E. G. Mosquera[1]*

[a] 1 Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación en Química "Andrés M. del Río" (IQAR), Universidad de Alcalá, Campus Universitario, 28871, Alcalá de Henares, Madrid, Spain.
[b] Instituto de Ciencia de Materiales (ICMM), CSIC, Cantoblanco, 28049, Madrid, Spain.

E-mail: martaeg.mosquera@uah.es

Nowadays the production of sustainable polymers with advanced properties is an open challenge. Within sustainable polymers, biobased polyesters have a prominent place. As such not only can be produced from renewable resources, also, those with chirality, such as poly-L-lactic acid (PLLA) or polyhydroxybutyrate (PHB) could present piezoelectric properties. Piezoelectric materials can be applied to build piezoelectric energy harvesters (PEHs) as promising independent renewable power sources for low-power electronic devices [1].

PLA and other polyesters can be produced from the catalytic Ring-Opening Polymerization (ROP) of the corresponding cyclic ester. Metallic complexes exhibit a great ability to exert a high control over the ROP process to give polymers with high molecular weight and adequate polydispersities [2]. Alkali metals and aluminium stand out among others, due to their abundance and low toxicity. Recently, in our group, we have developed different aluminum and alkali metal complexes with phenoxide ligands that bear different substituents in the aromatic rings to assess their influence on the catalytic activity and on the microestructure of the final polymer These compounds are very active in catalytic ROP processes of rac-lactide, L-lactide and ε-caprolactone and also in the ROP of a monomer quite reluctant to polymerize such as β -butyrolactone.

In this communication, the application of three catalytic systems based on sodium, potassium and aluminium is described for the ROP of different cyclic esters with the aim to obtain bioplastics and hybrid composites with advanced properties. Moreover, a potential closed-loop system is proposed employing potassium and sodium complexes, chemically upcycling PLA into value-added products [4].

Acknowledgements: This work was supported by the grant PID2021-122708OB-C33 and PID2024-159685OB-100 funded by the MICIU/AEI/10.13039/501100011033.

[1] (a) A. Leonés V. Sessini, M. E. G. Mosquera *et al.*, *Chem. Eng. J.*, **2025**, p. 169025.
[2] (a) M. Fernandez-Millán, M. E. G. Mosquera *et al Organometallics*, **2020**, *39*, 2278-2286. (b) C. Rentero V. Sessini, M. E. G. Mosquera *et al. Polymers*, **2022**, *14*, 2982,
[3] (a) E. Mula, V. Sessini, S. M. Guillaume, M. E. G. Mosquera, *et al, Macromol. Rapid Commun*., **2024**, 2400091. (b) A. Leonés, V. Sessini, M. E. G. Mosquera *et al. Polymers*, **2025**, *17*, 2605.
[4] C. Rentero, V. Sessini, M. E. G. Mosquera *et al Polymer*, **2025**, *320*, 128066.

Synthesis of C4 α-hydroxyesters from C2-biomass derived glycolaldehyde with Sn-β

Virginia de Blas Sánchez,[a,b] Ana Orozco Saumell,[a] Stevie Hallen Lima,[a] Manuel López Granados,[c,*] and Jose Iglesias[a, b, *]

[a] Chemical & Environmental Engineering Group, Universidad Rey Juan Carlos.
[b] Instituto Investigación de Tecnologías para la Sostenibilidad, Universidad Rey Juan Carlos.
[c] Energy and Sustainable Chemistry Group. Institute of Catalysis and Petrochemistry, CSIC.

E-mail: virginia.deblas@urjc.es

Methyl vinyl glycolate (MVG) is a highly functionalized 4-carbon α-hydroxyester useful to produce a wide variety of different chemicals, including functional biobased polyesters. Its production has been accomplished from glycolaldehyde, but side products such as methyl 4-methoxy-2-hydroxybutanoate (MMHB) or methyl lactate (ML), which are produced under the same conditions, hinder downstream purification. Our contribution presents the selective production of MVG from glycolaldehyde dimethyl acetal (GADMA) in the presence of shape-selective Sn-β zeolites prepared by a post-synthetic metalation procedure [1]. Catalytic tests conducted in batch reactors at different temperatures using GADMA as substrate and a mixture of methanol:water as solvent in the presence of Sn-β zeolite revealed the high influence of the reaction temperature on the selectivity of the overall transformation. Catalyst characterization was conducted by ^{27}Al-, ^{29}Si-, ^{119}Sn- MAS NMR, pyridine DRIFT, among other techniques.

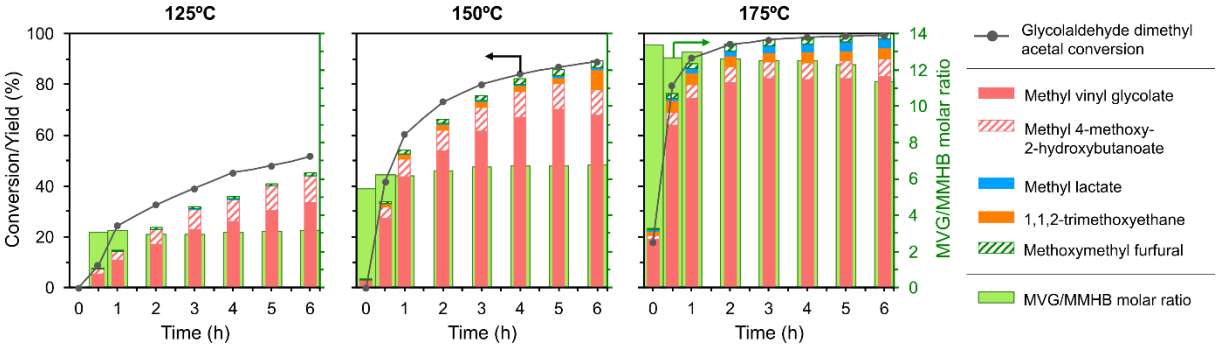


Figure 1. Effect of temperature in the conversion of GADMA into MVG by Sn-β zeolite.

Among the different Sn-zeolites that have been studied (MFI, BEA, MOR and FAU), Sn-β has been identified as the best system due to its narrow pore size. **Fig. 1** depicts its catalytic performance in the production of MVG at different temperatures. In all cases, MVG was the main product, albeit in different quantities. As the temperature increases, so does the MVG/MMHB molar ratio. MVG production involves glycolaldehyde evolving from GADMA hydrolysis to undergo self-condensation, selectively producing vinyl glyoxal (a C4 product) as key intermediate. Its transformation can then undergo 1,2-hydride shift towards MVG or 1,4-addition of methanol to produce MMHB. The formation of ML might be related to the formation of hexoses as intermediates, resulting in a competitive pathway. The use of Sn-β in combination with high temperature allows selective transforming GADMA into MVG, thus opening new opportunities in the synthesis of new biomass-derived functional polyesters.

This work is funded by projects PID2021-122736OB-C44, PID2024-155604OB-C41 and -C43 by Agencia Estatal de Investigación. VdBS thanks CM government for the predoctoral contract PIPF-2023/BIO-31144.

[1] J.M. Jimenez-Martin, et al., *ACS Sust Chem Eng.* **2022**, *10*, 8885-8896.

Eutectozymes: a novel platform based on solid eutectic matrices for advanced biocatalysis

Manuel Eduardo Martínez Cartagena[a] , Aitor Ontoria[a], Francisca Benítez[b], Elixabette Rezabal[b], Maria Soledad Orellano[a], Marcelo Calderón[a],[c], Christian Huck-Iriart[d], Agustin Picco[e], Matias Luis Picchio[a,c], A. Beloqui[a,c]

[a] POLYMAT, Dpto. de Química Aplicada, Facultad de Química, Universidad del País Vasco UPV/EHU, Donostia-San Sebastián, España
[b] Donostia International Physics Center (DIPC), UPV/EHU, Donostia-San Sebastián, España
[c] IKERBASQUE, Basque Foundation for Science, Bilbao, España
[d] ALBA Synchrotron Light Source, Barcelona, España
[e] INIFTA (UNLP–CONICET), La Plata, Argentina
E-mail: ana.beloquie@ehu.eus

Enzymatic immobilization on polymer supports represents an effective strategy to improve stability, reusability, and catalytic efficiency under demanding industrial conditions [1]. Eutectogels — soft materials formed by eutectic solvents (DES) and polymeric or supramolecular networks — offer a non-toxic, economical, and versatile alternative to hydrogels and ionogels [2]. This work presents, for the first time, the development of "eutectozymes," that is, natural hydrophobic eutectogels (HES) loaded with enzymes, designed as high-stability, high-activity heterogeneous microreactors [3].

Figure 1. Schematic representation of the synthesis procedure of the eutectogels and eutectozymes. Details described in [3].

Natural eutectic mixtures of menthol:eucalyptol and menthol:oleic acid were used as a hydrophobic matrix, combined with 1,3:2,4-dibenzylidene-D-sorbitol (DBS) and interpenetrated networks of PEGDA-co-EGPEA, through gentle biocatalytic polymerization (HRP/H_2O_2) (Figure 1) [3]. The model enzyme glucose oxidase (GOx) was incorporated to form eutectozymes. They were characterized using NMR, SAXS/WAXS, SEM, FTIR, and rheological tests, also evaluating kinetic parameters, thermal stability, pH, solvents, and applications in dye degradation and antimicrobial activity. The eutectogels showed lamellar organization at the nanoscale and hydrophilic microcavities (~50–200 µm) that acted as microreactors. Euc@GOx exhibited high substrate affinity ($^{app}K_m$= 1.2 mM) and great stability: more than 70% residual activity after 30 minutes at 70 °C, extreme pH levels (3–9), or pure organic solvents. It was possible to degrade 90–95% of recalcitrant dyes (AG25, MB, Rho) in ≤10 hours under mild conditions, and potent antimicrobial activity against MRSA was demonstrated.
In conclusion, eutectozymes constitute a new, soft, robust, and versatile platform for heterogeneous biocatalysis, combining eutectic stabilization with polymer networks and functional microcavities. Their high catalytic efficiency, robustness, and multifunctionality position them as promising materials in sustainable biotechnology, bioelectronics, and environmental technologies.

Acknowledgement. Fundación Ramón Areces (CIVP22S18625), Agencia Española de Investigación (PID2022-142128NB-I00), Marie Skłodowska-Curie (IONBIKE 2.0, 101129945), Gobierno Vasco (IT1766-22), UPV/EHU y ALBA Synchrotron.

[1] J. Meyer et al., *Eng. Life Sci.*, **2022**, 22, 165.
[2] M. L. Picchio et al., *ACS Sustain. Chem. Eng.*, **2022**, 10, 8135.
[3] M.E. Martinez-Cartagena et al., Adv. Mat., 2025, e17014

Coimmoblization of enzymes with different stabilities. How to re-use of the most stable immobilzed enzyme after the inactivation of the least stable enzyme using the glutaraldehyde chemistry.

Pedro Abellanas-Perez[1], Diandra de Andrades [1,2], Diego Carballares[1], Maria de Lourdes T. d M. Polizeli [2] & Roberto Fernández-Lafuente[1]

1 Departamento de Biocatálisis. ICP-CSIC, C/Marie Curie 2, Campus UAM-CSIC Cantoblanco, 28049 Madrid.

2 Department of Biology, Faculty of Philosophy, Sciences and Letters of Ribeirão Preto, University of São Paulo, Ribeirão Preto 14040-901, SP, Brazil.

Email: m.a.p@icp.csic.es

The combination of aminated supports (cationic ion exchangers) and the glutaraldehyde chemistry (chemical cross linker) allow obtaining two different heterofunctional supports. The artificial lipase Eversa Transform 2.0 was used as a model of a stable enzyme, and β-galactosidase from *Aspergillus oryzae* as an unstable one. Covalent attachment of the most stable enzyme was achieved by either immobilizing it via ion exchange to the support and its further modification with 1% glutaraldehyde or pre-activating the amino support with 10% glutaraldehyde and after immobilizing the enzyme. When pre-activating amino supports with 10% glutaraldehyde (two molecules of glutaraldehyde per amino group in the support were introduced) and reducing the support to eliminate its chemical reactivity, it was utilized to immobilize the β-galactosidase by physical adsorption. The enzyme was not released from the support under conditions compatible with the enzymes stabilities. However, if the support was modified with 1% glutaraldehyde (only one molecule of glutaraldehyde per amino group), the enzyme could be easily released by just using moderate high ionic strength [1]. This permitted to use this last strategy to coimmobilize the two enzymes with the possibility of releasing the β-galactosidase after its inactivation. First, Eversa Transform 2.0 was immobilized via ionic exchange to MANAE and later was modified with 1% glutaraldehyde to get enzyme-support covalent bonds. The biocatalyst was reduced with sodium borohydride and the β-galactosidase was coimmobilized with the lipase, in this instance via reversible ionic exchange. This combibiocatalyst was incubated at 55ºC and pH 8, conditions where the β- galactosidase lost its activity while Eversa retained its activity intact. Next, the combibiocatalyst was incubated at high ionic strength to release the inactivated β-galactosidase from the support. After, a new batch of fresh β-galactosidase was coimmobilized on the Eversa Transform, 2.0 biocatalyst and the combi-biocatalyst was inactivated again. This cycle was repeated three times with identical results [2].

[1] de Andrades D., et al. (2024) International Journal of Biological Macromolecules, 263, art. no. 130403, DOI: 10.1016/j.ijbiomac.2024.130403
[2] Carballares D., et al. (2024) ACS Sustainable Chemistry and Engineering, 12, 6564 - 6572, DOI: 10.1021/acssuschemeng.3c08231

Engineering of rubber degrading enzymes

Anca Pordea,[a,*] Amulyasai Bakshi,[a] Simone Morra,[a] Marko Hanževački,[b] and Aziana Abu Hassan[a,c]

[a]University Park, Nottingham, UK, Faculty of Engineering, University of Nottingham
[b]Cantock's Close, Clifton, Bristol, UK, School of Chemistry, University of Bristol
[c]148 Jalan Ampang, 50450 Kuala Lumpur, Malaysia, Malaysian Rubber Board

E-mail: anca.pordea@nottingham.ac.uk

Rubber waste is challenging to decompose and the majority ends up in landfill as a result. The enzymatic degradation of diene rubbers is an attractive option to revalorise them once they reach end of life. Latex clearing proteins (Lcps) degrade polyisoprene rubber, by cleaving the double bonds within the rubber chains, to produce oligoisoprenoids (Figure 1). Despite recent understanding of the structure and mechanism of Lcps, degradation rates remain limited and optimisation is required before the process can become economically viable.

Enzymatic rubber degradation depends on its physical morphology. Higher yields are obtained with natural rubber latex, which is an emulsion of hydrophobic rubber chains in a hydrophilic environment, than with synthetic rubbers suspended in buffer. The formation of stable polymer emulsions with hydrophobic solvents improves yields, but the presence of organic solvents destabilises the enzyme.[1]

Our aim is to engineer Lcps in the presence of hydrophobic environments, to facilitate improved contact between enzyme and rubber and thus improve reaction rates. Using computational approaches to find mutagenesis locations,[2] followed by site saturation library screening, we identified Lcp variants with increased efficiency in the presence of 10% (v/v) organic solvent, delivering up to 1.5-fold increased yield compared to WT LcpK30. Current efforts focus on increasing the screening throughput using a fluorometric assay.

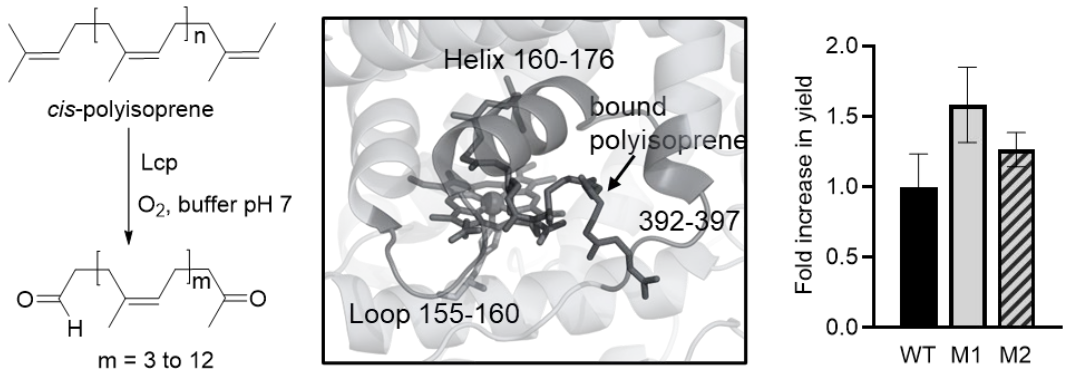


Figure 1. Left: Lcp-catalysed oligoisoprenoid formation. Middle: proposed interactions between Lcp and hydrophobic substrate. Right: yield increase for mutants (M1, M2) compared to wild-type (WT) from natural rubber degradation in 10% tetradecane

[1] V. K. B. Adjedje, E. Schell, Y.L. Wolf, A. Laub, M. J. Weissenborn, W. H. Binder, *Green Chem.* **2021**, *23*, 9433-9438.
[2] A. Abu Hassan, M. Hanževački, A. Pordea, *PLoS One.* **2024**, *19*, e0302398.

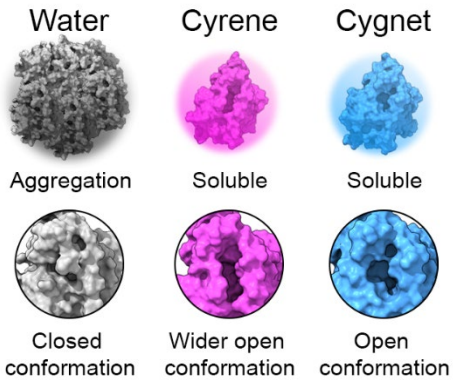
Levoglucosenone-derived solvents prevent aggregation and tune substrate accessibility of immobilized CALB

Mangiagalli Marco,*[a] Diletta Ami, [a] Laura Legnani, [a] Alessia Anna Arzuffi, [a] Giovanni Grazioso, [b] Alessandro Pellis, [c] Antonino Natalello [a]

[a] *Department of Biotechnology and Biosciences, University of Milano-Bicocca, Milano (Italy)*
[b] *Department of Pharmaceutical Sciences, University of Milan, Milano (Italy)*
[c] *Department of Chemistry and Industrial Chemistry, University of Genova, Genoa (Italy)*

E-mail: marco.mangiagalli@unimib.it

The transition towards sustainable biocatalysis requires the replacement of traditional petroleum-based solvents with bio-derived alternatives. Cyrene and Cygnet 2.0, which are high-boiling solvents derived from levoglucosenone, are particularly promising candidates for use in the CALB-catalyzed synthesis of aliphatic polyesters. Despite their similar chemical structures, these solvents exhibit distinct differences in their catalytic performance: Cygnet 2.0 produces polymers with a higher molecular weight than Cyrene [1].
Here, we investigated the effects of these levoglucosenone-derived solvents on the activity and structure of free and immobilized CALB, by combining Fourier transform infrared micro-spectroscopy with molecular dynamics (MD) simulations. Our results show that both Cyrene and Cygnet 2.0 effectively prevent CALB aggregation and enhance thermal stability. MD simulations further suggested that both solvents maintained CALB in a stable conformation, even at elevated temperatures, although Cyrene stabilized a wider open conformation compared to Cygnet 2.0. However, these subtle conformational differences alone may not fully explain the lower catalytic efficiency of CYR. Our findings suggest that solvent interactions with the substrate or nascent polymer, which can potentially create steric hindrance, modulate substrate accessibility.



Overall, this work provides new insights into the diverse mechanisms of organic bio-based solvents, which are valuable for the design of novel biocatalytic processes and selection of appropriate reaction media for lipase-catalyzed reactions.

[1] R. Milescu, A. Zhenova, M. Vastano, R. Gammons, S. Lin, C. H. Lau, J. H. Clark, C. R. McElroy, A. Pellis, ChemSusChem 2021, 14(16), 3367-3381.

Designing Designer Solvents: Optimizing Protein Stability in Deep Eutectic Solvents through a Combined Experimental and Computational Approach

Anja Damjanović,[a] Ana Jurinjak Tušek,[a*] Lidija-Marija Tumir,[b*] Esteban Cea-Klapp,[c*] Nicolás F. Gajardo-Parra,[c*] Selin Kara,[d,e] Ivana Radojčić Redovniković,[a] Marina Cvjetko Bubalo[a*]

[a] *Faculty of Food Technology and Biotechnology, University of Zagreb, Croatia*
[b] *Ruđer Bošković Institute, Zagreb, Croatia*
[c] *Pontificia Universidad Católica de Chile, Santiago, Chile*
[d] *Callinstr. 5, 30167 Hannover, Germany, Leibniz University Hannover*
[e] *Gustav Wieds Vej 10, 8000 Aarhus, Denmark, Aarhus University*

Email: adamjanovic@pbf.hr

Liquid protein formulations are essential in biomedical and biotechnological applications, yet preserving protein stability in solution under environmental stress remains challenging. Deep eutectic solvents (DESs), particularly those based on natural metabolites, represent promising and sustainable alternatives to conventional stabilizing media. However, their broader implementation requires deeper insight into protein–solvent interactions.

In this work, bioinspired osmolyte-based DESs were systematically explored as protective media for the model enzyme lysozyme. A diverse library of systems composed of naturally derived components was prepared and evaluated under thermal and freeze–thaw stress conditions. Enzyme performance, structural integrity, and aggregation behavior were assessed using activity assays and spectroscopic techniques, alongside biocompatibility testing [1].

Selected DES systems showed strong stabilization effects, preserving enzymatic activity even at high protein concentrations. Solvent composition and water content critically influenced the balance between structural stabilization and functional activity. A comprehensive meta-analysis integrating experimental results with COSMOtherm-derived molecular descriptors identified key stabilization drivers [2]. Guided by these insights, new sarcosine-based DES systems were rationally designed and demonstrated superior performance. Finally, molecular dynamics simulations confirmed that the addition of sarcosine- based DES contributes to the stabilization of the protein's structural conformation. This study establishes a framework that integrates experimental screening with computational modeling to decode protein–solvent interactions and enable the targeted development of sustainable, protein-stabilizing DES formulations.

---

[1] *A. Damjanović, M. Logarušić, L.-M. Tumir, T. Andreou, M. Cvjetko Bubalo, I. Radojčić Redovniković*, *Phys. Chem. Chem. Phys.* 2024, 26, 21040–21051. doi:10.1039/D4CP02275K

[2] *A. Damjanović, M. Logarušić, A. Jurinjak Tušek, M. Radović, N. Ukalović, T. Weitner, T. Andreou, M. Cvjetko Bubalo, I. Radojčić Redovniković, J. Mol. Liq. 2025, 436, 128259. doi:10.1016/j.molliq.2025.12825*

POSTERS

SCPR Sustainable Chemical PRocesses

SBCD Sustainable (Bio)Catalytic and Down-stream processes

COCT CO_2 Capture and/or Transformation

SMSP Smart Materials for Sustainable chemical Processes

BIBR BIomass and BioResources

PDCC Plastic Depolymerization and Circular Chemistry

GEHB Green Energies (Hydrogen, Biofuels, etc.)

BMPC Bio-based Materials, Pharmaceuticals, Cosmetics

NRMB Novel non-conventional Reaction Media for Biocatalysis

ESST Enzymes Stability and STabilization

NMDE New enzymes: Metagenomic and Directed Evolution

Extraction of platinum and palladium with carvacrol-based deep eutectic solvents

Sahar Gholami,[a] Pablo López-Porfiri,[a] María Pérez-Page,[a] Jesús Esteban,[b,a*]
[a] *Department of Chemical Engineering, School of Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom*
[b] *Department of Chemical and Materials Engineering, Faculty of Chemical Sciences, Complutense University of Madrid, Madrid 28040, Spain*
E-mail: jeesteba@ucm.es; jesus.estebanserrano@manchester.ac.uk

Pt and Pd are platinum group metals of crucial relevance essential in diverse technologies yet limited in natural supply [1,2]. As such, recovery from secondary resources is sought after in the most efficient and sustainable way possible, for which hydro and solvometallurgy approaches offer milder operating conditions than pyrometallurgy and less kinetically constrains than biometallurgy. Here we present two novel hydrophobic deep eutectic solvents (DESs) based on the natural compound carvacrol and their use in the selective liquid-liquid extraction (LLX) of Pt(IV) and Pd(II) from simulated leachates. Tri-n-octylphosphine oxide:carvacrol (TOCA) and lidocaine:carvacrol (LICA) were thoroughly characterised (thermal stability, density, and viscosity), with COSMO-RS [3] predictions, DSC, and FT-IR measurements confirming the strong hydrogen-bonding interaction and non-ideal behavior between the constituents of the mixtures. Extraction efficiency and selectivity in Pt and Pd separation were optimized under varying conditions (DES type and composition, and aqueous HCl concentration in the aqueous phase). TOCA demonstrated excellent selectivity towards Pt(IV) extraction with x_{TOPO} = 0.40, achieving 79.23% Pt and 18.74% Pd extraction efficiencies from 2 mol L^{-1} HCl and a separation factor of 19.21. Conversely, LICA with x_{Lid} = 0.50 selectively extracted Pd(II) near quantitatively from 0.25 mol L^{-1} HCl, with only 26.43% Pt extraction. In terms of the governing phenomena during LLX, FT-IR and UV-visible spectroscopies together with pH measurements pointed at a neutral ion-pair association mechanism with proton co-extraction. Efficient back-extraction of metals using EDTA as chelating agent for the Pt(IV) for TOCA and acidified thiourea for Pd(II) in LICA systems enabled DES stripping for recyclability. TOCA maintained performance over five cycles, while LICA showed lidocaine leaching, hence requiring rebalancing composition to retain selectivity. These findings underscore the remarkable potential of carvacrol-based DESs as efficient media to close the loop of greener Pt and Pd recovery from leachates.

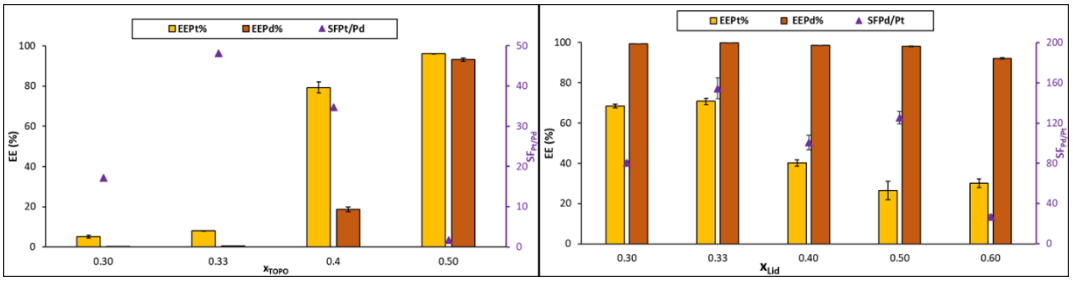


Fig. 6. Effect of HBA:HBD molar ratio on extraction efficiency and selectivity for Pt(IV) and Pd(II) using (a) TOCA and (b) LICA

[1] Z. Yuan, H. Liu, W. F. Yong, Q. She and J. Esteban, *Green Chem.* **2022**, 24, 1895–1929.
[2] S. Gholami, M. Perez-Page, C. D'Agostino, J. Esteban. *Chem. Eng. J.*, 2025, 159497.
[3] A. Klamt, A. *J. Phys. Chem.* **1995**, *99*(7), 2224– 2235.

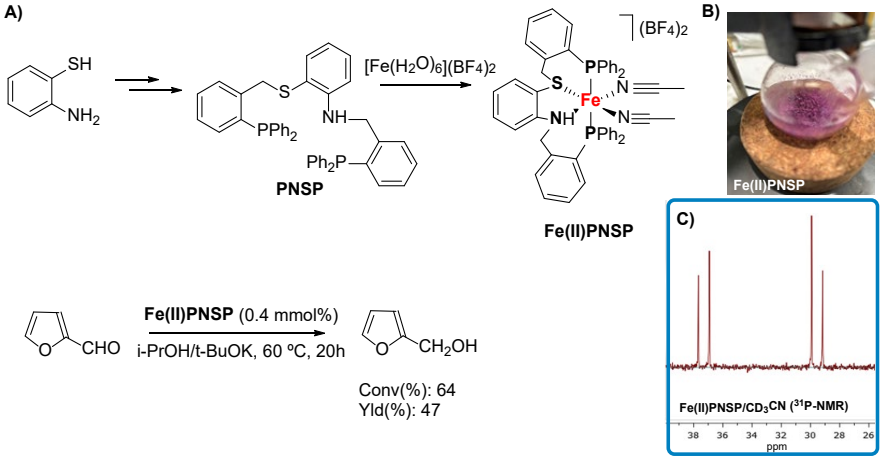
Transfer hydrogenation of furfural to furfuryl alcohol catalyzed by a Fe(II) complex with a tetradentate PNSP ligand

María José Sabater[a,b]*, **Iñaki Misa**[a], **Marc Ferrando**[a], **Marta Feliz**[a]*

[a] *Instituto de Tecnología Química (ITQ), Consejo Superior de Investigaciones Científicas-Universitat Politècnica de València, 46022, Valencia (Spain)*
[b] *Department of Pharmacy, School of Health Sciences, Universidad Cardenal Herrera-CEU, CEU Universities, Alfara del Patriarca,Valencia (Spain)*

E-mail: mjsabate@itq.upv.es

Iron represents a sustainable alternative to noble metals due to its abundance, low cost, and low toxicity. Therefore, the use of iron catalysts may constitute a significant advance in this research field [1-3]. In this context, this work has focused on the development of an efficient iron(II) based catalyst (**Fe(II)PNSP**) coordinated with a lineal heteroleptic tetradentate phosphane ligand PNSP,[4] which was synthesized in 3 steps, for the transformation of furfuraldehyde into furfuryl alcohol using isopropanol as hydrogen donor. Complex **Fe(II)PNSP** was exhaustively characterized (Scheme 1).



Scheme 1. A) Schematic synthesis of **Fe(II)PNSP** (top) and catalyzed transfer hydrogenation of furfural into furfuryl alcohol (bottom). B) Image of pure **Fe(II)PNSP** as a deep purple solid. C) ^{31}P-NMR spectrum of **Fe(II)PNSP** in CD_3CN.

The catalytic reaction was carried out by adding $[Fe(H_2O)_6](BF_4)_2$ 6 (0.7 mg; 0.002 mmol) and **PNSP** (1.4 mg; 0.002 mmol) into a Schlenk-tube under argon atmosphere under magnetic stirring to give **Fe(II)PNSP**, which is indicated by a change of the colorless solution into deep purple (Scheme 1). Then 1 mL dry isopropanol were added and the solution was stirred for 2 min at 60 ºC. Furfural (0.5 mmol) was added and the reaction was monitored by ^{1}H-NMR. After 20 h reaction, 64% conversion was obtained along with a furfuryl alcohol yield of 47%, hence confirming that **Fe(II)PNSP** is a sustainable and promising alternative to noble metal-based catalysts.

[1] M-C Fu, R. Shang, Z. Huang, Y. Fu, *Synlett*, **2014**, *25*, 2748-2752.
[2] G. Wienhöfer, F.A. Westerhaus, K. Junge, M. Beller, *J. Organomet. Chem*., **2013**, 744, 156-159.
[3] E. P. Bailey, T. J. Donohoe, M. D. Smith, *ACS Catal*, **2026**, DOI: 10.1021/acscatal.5c07305
[4] J. Liu, A. Zhang, H. Song, Q. Tong, C-H Tung,W. Wang, *Chin. Chem. Lett*., **2018**, *29*(6), 949-953.

Environmentally friendly improvement of an API intermediate standard process for more sustainable chemical processes at industrial scale

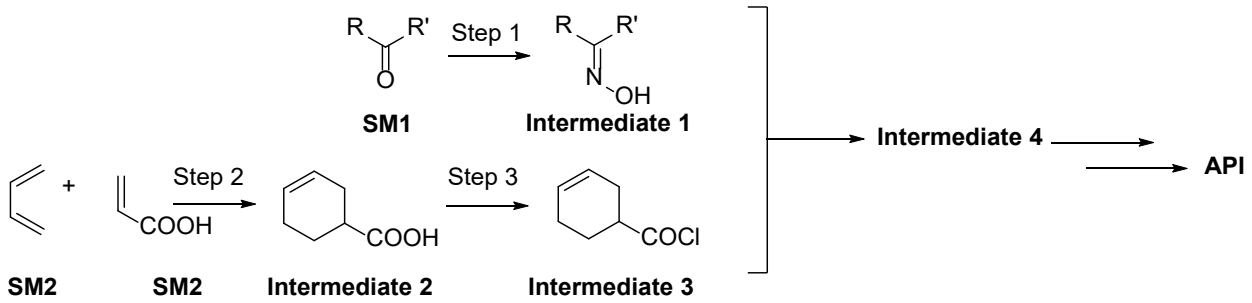
René I. Rodríguez Curiel,[a,*] María José González-Soria,[a,*] Ginés Martínez Valera[a,*]

[a] *Olon-Derivados Químicos, Camino de Pliego No.150, 30820 Alcantarilla – Murcia, Spain)*

E-mail: R.Rodriguez.Derivados@olonspa.it

In recent years, the urgency to develop greener and more environmentally sustainable chemistry, while reducing emissions and waste, has grown significantly. In this context, Olon has a strong commitment to a progressive and significant reduction of its environmental footprint. One of the key strategies to reach this goal is the improvement of standard manufacturing processes at the plant.

Within this framework, the synthesis of API Intermediate 4 was selected for process optimization. All synthetic steps were thoroughly reviewed with the objective of enhancing efficiency, decreasing waste generation, and improving the overall sustainability of the route:



Scheme 1. Synthetic scheme of Intermediate 4.

Step 1. Methyl ethyl ketone was replaced with Ethyl acetate, considered a less toxic and more environmentally friendly solvent. This modification also enabled the reduction of crystallization steps from two to one, while preserving the final product purity.

Step 2. Importantly, the use of methylene chloride was completely eliminated. Optimized reaction conditions[1] were implemented, resulting in a significant decrease in reaction time from 7 days to 15 h, and contributing to a safer, more sustainable process.

Step 3. Further refinement of the reaction parameters was performed, leading to an additional reduction in the overall reaction time of 22 h.

Overall, these modifications resulted in lower waste generation, reduced energy consumption, and an increase in process yield. Consequently, the manufacturing route has become more efficient, safer, and considerably more sustainable.

[1] D. Sun, F. Sato, Y. Yamada, S. Sato, *Bull.Chem.Soc.Jpn.* **2013**, *86*, 276-282.

Biobased and Functional Ionic Liquids as Green Catalysts in the Oxidation of Electron-Deficient Alkenes

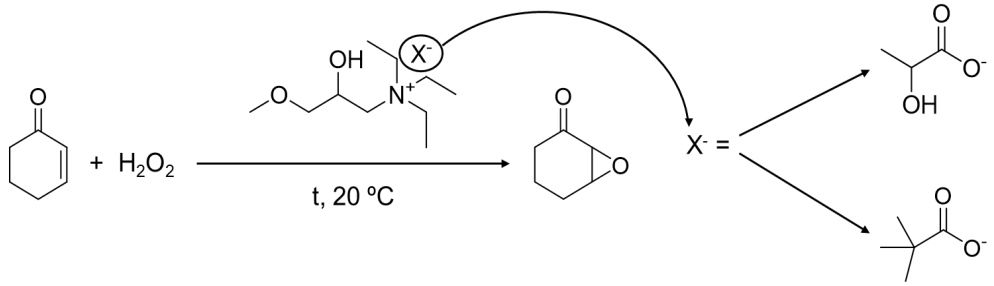
Jorge Cambronero-Arregui,[a] Bruno Enguita,[a] Alejandro Leal-Duaso[a,*] and José A. Mayoral[a,*]

[a] *Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-University of Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain*

E-mail: jcambronero@unizar.es

Green Chemistry promotes the design of processes that minimize both their environmental impact and the consumption of non-renewable resources. Among its principles are the valorization of renewable raw materials and the development of alternative safer solvents to replace conventional ones that often are toxic, volatile, and flammable.[1] In this context, glycerol represents a renewable feedstock from which different biobased solvents, both molecular and ionic can be obtained, offering tunable properties and low toxicity.[2,3] Another key green principle is catalysis, which enhances efficiency and selectivity while minimizing waste generation and energy consumption. Within this framework, oxidation reactions, and particularly the epoxidation of alkenes, are key transformations in organic synthesis that can benefit from the use of sustainable catalysts.[4]

In this work, the dual role of biobased functional ionic liquids derived from glycerol has been studied as reaction media and catalysts in the epoxidation of electron-deficient alkenes. The catalytic activity of the ionic liquids was evaluated through the model epoxidation reaction of cyclohex-2-enone, and a substrate screening was carried out to analyze the influence of alkene structure and ionic liquid properties on the reactivity and products selectivity. In addition, a heterogenization test of the catalytic system was performed by supporting the ionic liquid on a basic solid, resulting in improved activation of less reactive substrates. These results highlight the potential of biobased ionic liquids as sustainable alternatives in base-catalyzed oxidation reactions.



Scheme 1. Epoxidation reaction of cyclohex-2-enone in the presence of hydrogen peroxide catalysed by functional glycerol-derived ionic liquids.

Acknowledgments: We thank the financial support from Agencia Española de Investigación (PID2021-125762NB-I00) and Gobierno de Aragón (group 23_37R)

[1] P. Anastas, N. Eghbali. *Chem. Soc. Rev.* **2010**, *39*(1), 301–312.
[2] J. I. García, H. García-Marín, E. Pires. *Green Chem.* **2014**, *16*(3), 1007–1033.
[3] S. Gracia-Barberán, J. Del Barrio, A. Leal-Duaso, J. A. Mayoral, E. Pires. *RSC Sustain.* **2025**, *3*, 5225–5240.
[4] M. E. Ali, M. M. Rahman, S. M. Sarkar, S. B. A. Hamid, S. B. A. *J. Nanomater.* **2014**, *2014*(1), 192038.

Zirconium–Imidazolium Xerogels as Sustainable Catalysts for Biodiesel-Oriented Transesterification

Yanira Pérez-Almarcha,[a] Anna Nacher-Luis,[a] Mario Martos,[b] Irene Bosque,[a,*] and Isidro M. Pastor[a,*]

[a] *University of Alicante: C/ Sant Vicent del Raspeig, s/n, Alicante, Spain.*
[b] *University of Gothenburg: Medicinaregatan 7B, Gothenburg 41390, Sweden*

E-mail: yanira.perez@ua.es

The development of environmentally friendly catalytic systems for biodiesel production is a key challenge in the transition toward sustainable energy technologies, particularly for the efficient conversion of oils and fats into fatty acid methyl esters (FAMEs). In this work, a zirconium imidazolium-based Metal Organic Gel was synthesized via a simple aqueous gelation process and converted into a Metal Organic Xerogel (MOX), which was evaluated as a heterogeneous solid acid catalyst for esterification and transesterification reactions relevant to biodiesel synthesis.[1] The catalytic performance of the xerogel was investigated using free fatty acids, model esters, and vegetable oil feedstocks under mild to moderately elevated conditions, and its efficiency was assessed through conversion, isolated yields, recyclability, and green chemistry metrics. The Zr-based MOX exhibited high catalytic activity and selectivity in the transesterification of triglycerides, achieving high isolated yields of FAMEs from olive oil, with physicochemical properties consistent with biodiesel standards. Compared to conventional homogeneous acid catalysts, the xerogel enabled simplified workup, catalyst recovery by filtration, reduced waste generation, and improved environmental performance. These results demonstrate that zirconium imidazolium xerogels constitute a robust and sustainable catalytic platform for biodiesel-related transformations, highlighting their potential as green alternatives for renewable fuel production and biomass valorization.[2]

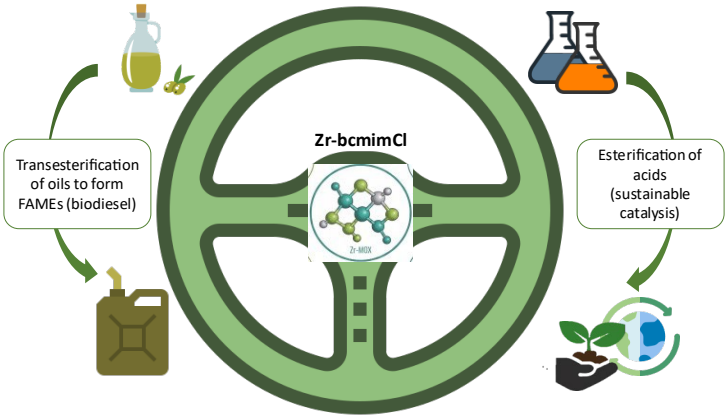


Figure 1. Sustainable catalysis using Zr-bcmimCl.

[1] Y. Pérez-Almarcha, M. Martos, A. Nacher-Luis, I. Bosque, I. Pastor, *Chem. Asian J.* **2025**, *20*, *e00532.*
[2] Q. Zhang, J. Wang, S. Zhang, J. Ma, J. Cheng, Y. Zhang, *Bioeng.* **2022**, *9*, 700.

The Tsuji–Trost Reaction in Deep Eutectic Solvents: A Sustainable Approach.

Alejandro Armero,[a] Xavier Marset,[a,b] Gabriela Guillena[a] and Diego J. Ramón[a]*.

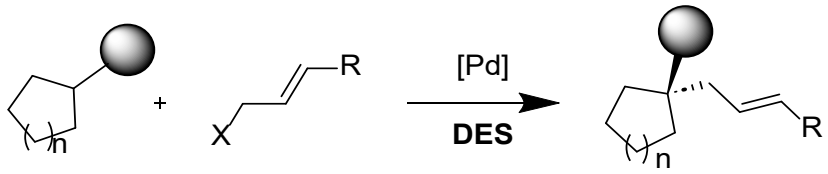
[a]*Departamento de Química Orgánica, University of Alicante.*
[b]*Instituto Universitario de Electroquímica, University of Alicante.*

Email: alejandro.armero@ua.es

The substitution of volatile organic compounds (VOCs) in chemical processes has emerged as a major objective in the shift toward more sustainable and environmentally responsible chemistry. VOCs are significant contributors to atmospheric pollution, present notable health hazards, and are typically obtained from non-renewable resources.[1]

In response to these issues, DES have gained attention as flexible and eco-friendly alternatives to conventional organic solvents. Their low vapor pressure, non-flammable nature, biodegradability, and straightforward preparation from inexpensive and readily accessible components make them particularly attractive.[2] Moreover, DES possess adjustable physicochemical properties that can be fine-tuned for specific applications, positioning them as promising substitutes for traditional VOC-based solvents. Their implementation can substantially lower the environmental impact of chemical reactions by decreasing emissions, minimizing waste generation, and enhancing operational safety.

In this study, the Tsuji–Trost allylation[3] reaction was investigated in a range of DES (Scheme 1), using different palladium catalysts and ligands under both thermal conditions and mechanochemical activation via ball milling. A wide variety of allylic substrates, including esters and carbonates, were evaluated, demonstrating the broad scope and high tolerance toward diverse functional groups. Key reaction parameters were carefully optimized to obtain high yields under mild and sustainable conditions. The application of DES not only ensured effective catalytic performance but also simplified handling and improved safety. Overall, these results emphasize the practical relevance of DES in palladium-catalyzed allylic substitution reactions and support their role in advancing greener approaches in contemporary organic synthesis.



Scheme 1. Tsuji-Trost Allylation in Deep Eutectic Solvents.

[1] Zhou, X.; Zhou, X.; Wang, C. Zhou, H.; *Chemosphere* **2023**, *313*, 137489 (+9).

[2] Ramón, D. J.; Guillena, G.; Deep Eutectic Solvents: Synthesis, Properties and Applications. *Wiley-VCH*, Weinheim, **2019**.

[3] Fan, L.; Wang, S.; Gong, L.; *Org. Lett.* **2019**, *21*, 6720-6725.

Redox Performance of Green-Synthesized Mixed-Metal Azolates

Agata Karkosik,[a] Aitana Ferrer-Sanchis,[a] Eduardo García-Verdugo Cepeda,[a] Nuria Martín García,[a] Belén Altava Benito,[a] Francisco García Cirujano[a,*]

[a]*Department of Inorganic and Organic Chemistry, Universitat Jaume I, Av. Vicent Sos Baynat, s/n, 12006, Castelló de la Plana, Castelló, Spain*

E-mail: karkosik@uji.es

Metal-organic frameworks (MOFs), specifically zeolitic imidazolate frameworks (ZIFs), composed of zinc (II) ions and 2-methylimidazole linker (see ZIF-8 structure in Fig. 1a), exhibit exceptional chemical and thermal stability[1] and the possibility of tuning the inorganic cornerstone by incorporating a second transition metal: X = Ni, Fe, Cu, Co, and Mn into the $(ZnX)N_4$ secondary building unit. Herein, we investigate how varying metal compositions influence the structural, electronic, and catalytic properties of ZIF-8-$Zn_{0.9}X_{0.1}$, enhancing its redox activity.

The double-mixed-metal ZIF-8-$Zn_{0.9}X_{0.1}$ materials were directly synthesized at room temperature by adding an aqueous solution of metal (Zn:X 9:1 molar ratio) acetates to 2-MeIm solution - formed upon TEA assisted deprotonation. Physicochemical characterization of the family of materials was conducted using XRD, XPS, TGA, FTIR, and UV-Vis spectroscopy. The thorough characterization enabled the determination of crystalline structure, atomic composition, and (optical) energy bandgap, offering insights into the materials' geometric and electronic structure. Finally, the redox activity was evaluated in TBHP-assisted oxidation of alkenes and alcohols with Mn-doped ZIF-8 showing the highest activity.

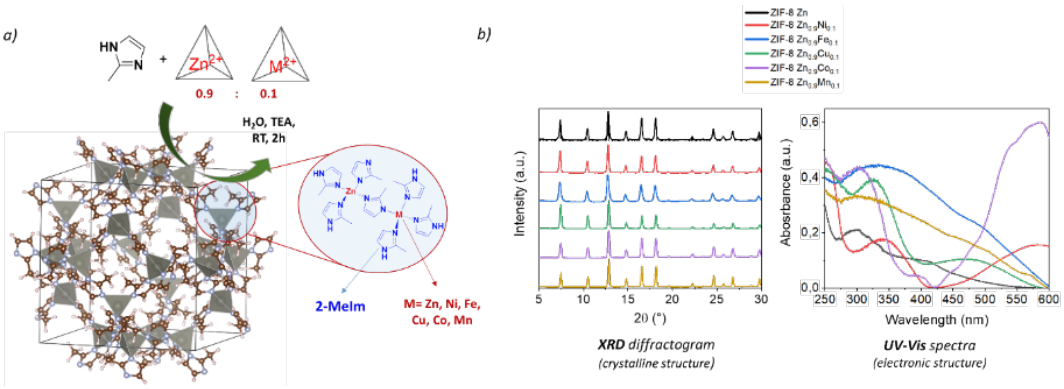


Figure 1. (a) Synthesis of mixed-metal ZIF-8-ZnX; X = Ni, Fe, Cu, Co, Mn; (b) Structural (XRD) and optical (UV-Vis) characterization of the obtained ZIFs.

Acknowledgement: This study was supported by the Ramón y Cajal program (RYC2020-028681-I and RYC2021-033167-I) funded by MCIN/AEI/10.13039/501100011033 and by the European Social Fund (ESF) "Investing in your future", as well as by the European Union Next Generation EU/PRTR. Additional funding was provided by MICINN-FEDER-AEI (10.13039/501100011033) through projects PID2021-124695OB-C22 and PID2022-142897OA-I00, and by MCIN/AEI/10.13039/501100011033 and the European Union Next Generation EU-PRTR. The Generalitat Valenciana is acknowledged for the SEJGENT and PROMETEO projects (CISEJI/2023/78 and CIPROM/2023/57). Universitat Jaume I is acknowledged for project UJI-2023-03.

[1] K. S. Park, Z. Ni, A. P. Côté, et al., *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186–10191.
[2] F. G. Cirujano, E. López-Maya, N. Almora-Barrios, et al., *Inorg. Chem.* **2020**, *59*, 18168–18173.

Phase Change Material incorporated in Alkali Activated Material for sustainable cementitious application in thermo regulation improvement

Sávio Alcântara[a], Luca Spiridigliozzi[a,e,*], Marcos Lanzón[b,*], Gianfranco Dell'Agli[a], Mauro Mitsuuchi Tashima[c], Giovanni Dotelli[d], Nicolas Bertoldo[d]

[a] Dipartimento di Ingegneria Civile e Meccanica, Università degli Studi di Cassino e del Lazio Meridionale, Via G. de Biasio, 43, 03043, Cassino (FR), Italy.
[b] Universidad Politécnica de Cartagena, Departamento de Arquitectura y Tecnología de Edificación, Cartagena, Spain.
[c] Universidad Politécnica de Cartagena, Departamento de Ingeniería Minera y Civil, Cartagena, Spain.
[d]Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy.
e Department of Engineering and Science, Universitas Mercatorum, Piazza Mattei 10, 00186 Roma (RM), Italy
E-mail: ernandessavio.negreirosalcantara@studentmail.unicas.it

The use of Alkali Activated Materials (AAMs) is currently considered as a potential alternative for substituting conventional cementitious materials; their mechanical properties show a promising capacity of acting as new materials for the civil construction sector, with a significant lower carbon footprint involved in the synthesis process compared to the Ordinary Portland Cement [1]. In another segment, studies using phase change materials (PCMs) indicate a capacity of latent heat storage and release while alternating phase, typically solid and liquid [2]; allowing their application also in thermo isolating systems, improving energy consumption in heating and cooling systems.

Within that perspective, in this study we synthesize and characterize AAMs with incorporation of PCM, aiming to produce innovative materials with thermal isolating capacity for improvement of energy efficiency when applied in buildings. In alignment with principles of green chemistry and sustainable construction, when working with AAMs, it is possible to recycle industrial by-products of aluminosilicates as raw materials, as for example, ground granulated furnace slag and rice husk ash [3]; also, the synthesis of the AAM/PCM matrices are developed with low energy consumption, using an alkali solvent as activating solution.

The incorporation of organic PCM in AAMs has been studied by some of the authors, by synthesizing an AAM/PCM matrix that indicated the efficiency for the expected application [4]. Our study now proposes to alternate the initial typology of binders and PCM (all from industrial waste origin), aiming to observe what would be obtained as the final product in terms of mechanical properties, incorporation capacity, matrix stabilization and thermic storage/release capacity, addressing also the life cycle assessment (LCA) of recycling the raw materials used.

[1] P. Awoyera, A. Adesina, *Case Studies in Construction Materials*, **2019**, 11, e00268.
[2] A. De Garcia, L. F. Cabeza, *Energy and Buildings*, **2015**, 103, 414-419.
[3] J. L. Provis, *Cement and Concrete Research,* **2018**, 114, 40-48.
[4] Spiridigliozzi *et al.*, *Journal of Sustainable Cement-Based Materials*, currently under review.

Catalytic hidrogenation of chlorates in aqueous phase using Pt catalysts

Nadia Benmebirouk-Pareja,[a] Antonio Eduardo Palomares-Gimeno,[a,*] Paulina Gwóźdź,[b] Agnieszka Łącz,[b] Ewa Drożdż,[b,*]

[a] Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas (UPV-CSIC), Av. de los Naranjos, s/n, Valencia, Spain
[b] Faculty of Materials Science and Ceramics, AGH University of Krakow, al. A. Mickiewicza 30, 30-059, Krakow, Poland

Email: nbenpar@upv.edu.es

Water quality is essential for safe human consumption. Chlorate ions are emerging contaminants formed as by-products during water disinfection with oxidizing agents and pose significant health risks, prompting the World Health Organization (WHO) to establish a provisional limit of 0.7 mg/L in drinking water [1]. Catalytic hydrogenation is a sustainable strategy for chlorate removal, enabling the reduction of chlorate ions in water to harmless chloride, through the reaction:

$$ClO_3^- + 3H_2 \rightarrow Cl^- + 3H_2O$$

In this study, platinum-based catalysts supported on TiO_2, Al_2O_3, and Fe-modified oxide perovskite materials were evaluated under ambient temperature and atmospheric pressure. As shown in **Figure 1**, Pt catalysts supported on TiO_2 and perovskite materials exhibited higher catalytic activity than those supported on Al_2O_3, suggesting that the activity depends on the nature of the support. The increased conversion may be attributed to the photochemical properties of these materials, which can promote electron-hole pair generation and facilitate electron transport, thereby enhancing the reduction of ClO_3^- by adsorbed H_2 [2,3]. In particular, Pt catalysts supported on perovskite ($Sr_{0.8}Ca_{0.2}Ti_{0.9}Fe_{0.1}O_3$) exhibited the highest catalytic activity.

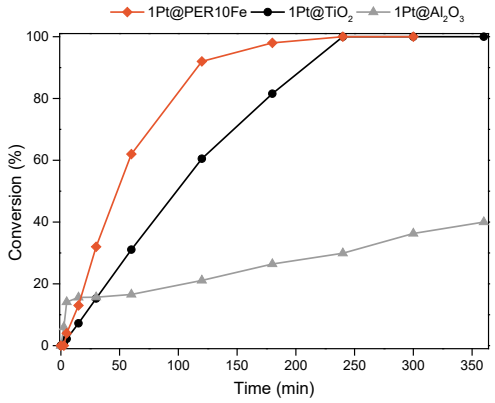


Figure 1. Activity of 1 wt% Pt catalysts on different supports.

[1] Guidelines for drinking-water quality: 4th edition incorporating the first and second addenda, World Health Organization, Geneva, **2022**.
[2] B. Bakbolat, C. Daulbayev, F. Sultanov, R. Beissenov, A. Umirzakov, A. Mereke, A. Bekbaev and I. Chuprakov, *Recent Developments of TiO_2-Based Photocatalysis in the Hydrogen Evolution and Photodegradation: A Review*, Nanomaterials**, 2020**, 10(9), 1790
[3] A. Baray-Calderón, J. L. Aleman-Ramirez, E. B. Díaz-Cruz, C. Martinez-Alonso, M. Fuentes-Pérez, H. Olvera-Vargas, D. K. Becerra-Paniagua, *Recent Advances in Perovskite-Based Heterojunction Photocatalysts: Synthesis, Properties, and Applications*, Korean Journal of Chemical Engineering**, 2025**, 42 (4), 803–826

METAL-FREE HFIP-PROMOTED SYNTHESIS OF BENZHYDRYL DERIVATIVES FROM STILBENES AS MASKED ELECTROPHILES UNDER OXIDATIVE CONDITIONS

Francisco J. Sierra-Molero,[a] Hernan Rico-Trilles,[a] Victoria Ruiz-Alfonso,[a] Alejandro Baeza,[a]* Diego A. Alonso[a]*

[a] Instituto de Síntesis Orgánica, and Dpto. de Química Orgánica
Universidad de Alicante
Apdo. 99, 03080 Alicante, Spain
Email: francisco.sierra@ua.es

The benzhydryl structural motif constitutes a privileged moiety that can be found in many biologically active molecules and drugs currently present in the market (Figure 1A). Thus, it is of great interest to develop new sustainable and affordable routes to produce these derivatives, specially from readily available starting materials such as olefins.

Classical methods for the synthesis of functionalized benzhydryls usually rely on nucleophilic substitution reactions onto benzhydryl structure derivatives bearing a good leaving group in the desired position, while more recent syntheses are based on metal catalyzed couplings.[1]

Here, through a metal-free umpolung strategy, we envisioned the use of stilbenes as electrophilic synthons for the synthesis of functionalized benzhydryl derivatives by reacting with different nucleophiles (Figure 1B). The overall reaction constitutes a one-pot procedure where, under oxidative conditions and promoted by HFIP,[2] four consecutive reactions take place sequentially to obtain the desired substituted benzhydryl derivative: epoxidation of the olefin, Meinwald rearrangement to the corresponding aldehyde, Baeyer-Villiger oxidation to generate a formate intermediate and final nucleophilic substitution.

This protocol allows the use of a wide variety of nitrogen-, oxygen-, sulfur-, and carbon-based nucleophiles, delivering the desired product in moderate yields. In addition, easily accessible starting materials are used, no isolation of any intermediate is needed, and no metal catalyst is used, which in combination with the step-economy of the procedure, favors the sustainability and affordability of the process.

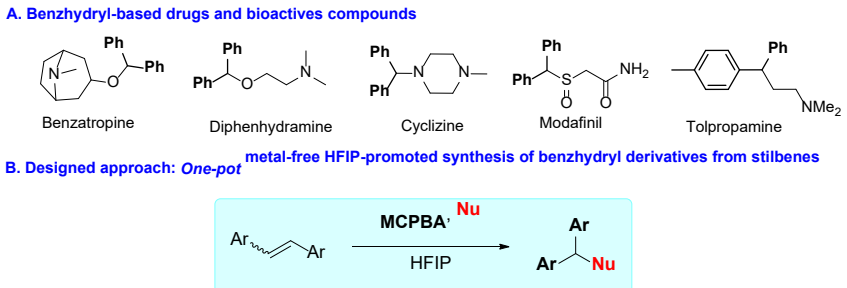


Figure 1

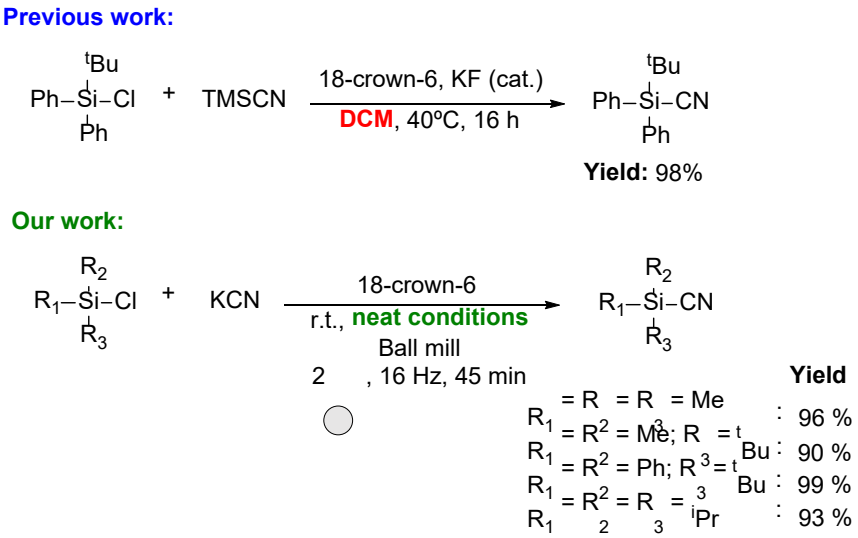
[1] D. Roy, G. Panda, *ACS Omega.* **2020**, *5*, 19-30.
[2] H. F. Motiwala, A. M. Armaly, J. G. Cacioppo, T.C. Coombs, K. R. K. Koehn, V. M. Norwood, J. Aubé, *Chem. Rev.* **2022**, *122*, 12544-12747.
[3] F. J. Sierra-Molero, A. Baeza, D. A. Alonso, *Eur. J. Org. Chem*. **2025**, *28*, e202500547.

Sustainable Synthesis of Cyanosilanes and Their Application in Asymmetric Organocatalyzed Cyanosilylation of Carbonyls

Luis Paredes Soler,[a] Jose Antonio Ñíguez Elena,[a] Rosa Mira Iniesta,[a] Daniel Montes Álvarez,[a] Juana María Pérez Galera,[b] Ignacio Fernández,[b] Juan López de Leon,[c] Claudia Araceli Contreras Celedón,[c] Francisco Méndez,[d] Diego José Ramón Dangla,[a*] Diego Alonso Velasco.[a*]

[a]*Institute of Organic Chemistry (ISO), University of Alicante.*
[b]*Department of Chemistry and Physics, University of Almería.*
[c]*Institute of Chemical-Biological Research, Universidad Michoacana de San Nicolás de Hidalgo.*
[d]*Department of Chemistry, Universidad Autónoma Metropolitana-Iztapalapa.*
E-mail: luis.paredes@ua.es

Alkylsilyl cyanides are valuable and versatile reagents in organic synthesis, being trimethylsilyl cyanide (TMSCN) the most commonly used due to its commercial availability. Nevertheless, modifying the steric and electronic properties of cyanosilanes through variation of the alkyl substituents can have a significant impact on their reactivity and synthetic utility. In this work, two efficient synthetic methodologies for the sustainable preparation of sterically demanding cyanosilanes, *tert*-butyldimethylsilyl cyanide (TBDMSCN) and *tert*-butyldiphenylsilyl cyanide (TBDPSCN), are described, providing access to less explored yet potentially valuable reagents.



In addition, the applicability of cyanosilanes in asymmetric synthesis was investigated through the organocatalyzed cyanosilylation of carbonyl compounds. Although the screening of new organocatalysts under sustainable conditions led only to moderate enantioselectivity, the reaction proved feasible using simple conditions. Finally, the optimized protocol was applied to a small substrate scope employing TMSCN, demonstrating the utility of cyanosilylation as a practical transformation for the functionalization of electrophiles.

[1] Kazuaki S. *Bull. Chem. Soc. Jpn.* **1987**, *60* (6), 2257–2258.
[2] Tan, D.; Friščić, T. *Eur. J. Org. Chem.* **2017**, *2018* (1), 18–33.
[3] Zhou, H.; Zhou, Y.; Bae, H. Y.; Leutzsch, M.; Li, Y.; De, C. K.; Cheng, G.-J.; List, B. *Nature* **2022**, *605* (7908), 84–89.

Selective Colorant Removal from Plastic Packaging via Bio-Based Solvent Extraction

Mariana I. S. Aguiar,[a] Marco Prazeres,[a] João Araújo Pereira Coutinho,[a] Ana Maria Ferreira,[a*]

[a]Chemistry Department, University of Aveiro, Aveiro, Portugal, CICECO - Aveiro Institute of Materials.

E-mail: ana.conceicao@ua.pt

Nearly 40% of global plastic waste originates from packaging materials, where additives such as colorants compromise recycling performance by deteriorating physicochemical properties and reducing the market value of secondary polymers [1]. The development of efficient and selective colorant removal strategies is therefore essential to enable high-quality recyclates and improve plastic waste management.

This work presents a solid–liquid extraction strategy for the selective removal of colorants from polyethylene (PE) and polyethylene terephthalate (PET), employing bio-based solvents under mild operating conditions (≤ 90 °C). High colorant removal efficiencies were achieved for both low-density polyethylene (LDPE) and PET packaging materials, reaching complete removal (100%) for selected polymer–solvent combinations in some of the bio-based solvents tested (e.g., γ-valerolactone). No changes in polymer chemical structure or thermal behavior were detected after treatment, as confirmed by Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). In the best-performing bio-based solvent, simple post-extraction filtration enabled complete separation of the extracted colorants from the solvent phase, allowing solvent reuse and recovery of isolated pigments without additional purification steps. Following additive removal, the treated materials are suitable for subsequent mechanical recycling.

Bio-based solvent extraction therefore provides a technically viable chemical process to selectively remove colorants while preserving polymer properties, enabling the upgrading of plastic packaging waste prior to recycling.

Acknowledgments: This work was developed within the scope of the project CICECO–Aveiro Institute of Materials, UID/50011 & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work is funded by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project GREEN-PATH (Ref. 2023.15169.PEX, DOI 10.54499/2023.15169.PEX). AMF acknowledge FCT for the research contract CEECIND/00361/2022 (DOI 10.54499/2022.00361.CEECIND/CP1720/CT0020).

[1] K. Houssini, J. Li and Q. Tan, Complexities of the global plastics supply chain revealed in a trade-linked material flow analysis, *Commun. Earth Environ.*, **2025**, 6, 257.

Thiazolidine-Grafted Zeolite Imidazolate Frameworks: A Cysteine-Derived Route to Improved Metal Loading and Tune the CO_2 Hydrogenation Efficiency

Mireia Mercé[1], Eduardo García-Verdugo[1], Francisco G. Cirujano[1,*] and Nuria Martín[1,*]

[1]Departamento de Química Inorgánica y Orgánica, Universitat Jaume I. Av. Vicent Sos Baynat, s/n, 12006. Castelló de la Plana, Castelló. España.

E-mail: mmerce@uji.es

Keywords: CO_2 conversion; adsorption; amino acids; catalysis; metal capture; metal organic frameworks.

The covalent functionalization of ZIFs with sulfur-containing ligands is an effective strategy for controlling active metal centers in heterogeneous catalysis. Herein, ZIF-8/90 materials functionalized with thiazolidine groups derived from L-cysteine were synthesized via post-synthetic condensation of aldehyde functionalities on the imidazolate linker. X-ray diffraction (XRD), N_2 physisorption, thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR) confirm successful functionalization. The introduction of S/N donor sites significantly enhances metal uptake, achieving up to threefold higher Pd loading compared to the non-functionalized ZIF. The cysteine-functionalized ZIF catalyst shows improved resistance to metal leaching and nanoparticle aggregation during CO_2 hydrogenation to formic acid at room temperature, preserving Pd nanoparticles of 1–3 nm after catalytic cycling.[1]

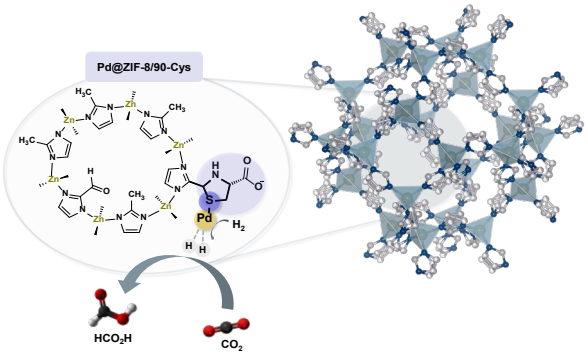


Figure 1: Pictorial representation of the CO_2 hydrogenation reaction to formic acid catalysed by Pd supported on a functionalized imidazolate zeolite (ZIF-8/90-Cys)

Acknowledgments: This study was supported by the "Ramon y Cajal" contract with code RYC2020-028681-I and RYC2021-033167-I funded by MCIN/AEI/10.13039/501100011033 and by "ESF investing in your future", "European Union NextGenerationEU/PRTR." This work was partially supported by MICINN-FEDER-AEI 10.13039/501100011033 (PID2022-142897OA-I00), MCIN/AEI/10.13039/501100011033 and by the European Union Next Generation EU-PRTR. Generalitat Valenciana is acknowledged for the SEJGENT and PROMETEO projects (CISEJI/2023/78 and CIPROM/2023/57). Universitat Jaume I is acknowledged for the project UJI-2023-03.

[1] Mercé, M., García-Verdugo, E., Cirujano, F. G., & Martín, N. (**2026**). Thiazolidine-Grafted Zeolite Imidazolate Frameworks: A Cysteine-Derived Route to Improved Metal Loading and Tune the CO_2 Hydrogenation Efficiency. *ChemSusChem*, *19*(1), e202502190.

Sustainable remediation of strobilurin fungicides–contaminated soil by persulfate oxidation combined with solarization

Isabel Garrido [a], Carmen María Martínez-Escudero [a], Virginia Hernández [a], Fulgencio Contreras [a], Pilar Hellín [a], Pilar Flores [a], José Fenoll [a,*]

[a] Research Group on Sustainability and Quality of Fruit and Vegetable Production. Instituto de Investigación y Desarrollo Agrario y Medio Ambiental. C/ Mayor s/n. La Alberca, 30150, Murcia, Spain.

E-mail: isabel.garrido3@carm.es

Strobilurins are a group of fungicides intensely applied to vegetable cultivation in Southeastern Spain. These compounds have activity against pathogenic fungi, inhibiting of mitochondrial respiration in complex III [1]. Important synthetic strobilurin fungicides include azoxystrobin, pyraclostrobin, kresoxim-methyl and trifloxystrobin. Residues of these compounds can be found in agricultural soil [2]. Since the occurrence of these pesticides in soils can cause an impact on the environment and, consequently, on human health, developing efficient and sustainable techniques to remove their residues from contaminated soil should be imperative. In this context, Advanced Oxidation Processes (AOPs) have been considered for removing environmental pollutants from soils [3]. The aim of this work was to identify an appropriate technology for the remediation of soils polluted with strobilurin fungicides, assessing the effectiveness of three AOPs (photo-Fenton process at neutral pH, TiO_2 photocatalysis and persulfate oxidation) to remove them in different agricultural soils. The study also monitored the main transformation products formed during strobilurin degradation. The most influential parameters of the tested AOPs (type of ligand/photocatalyst/oxidant agent, reagent loading and soil moisture content) were examined at laboratory scale. Optimal conditions were later applied at larger scale. Lab-field experiments were conducted introducing 3.0 kg of soil spiked with fungicides to reach 1.0 mg kg^{-1} (individual levels). After adding the corresponding reagents, samples were exposed to the combination of solarization and AOP technique during 30 days. Our results showed that the combined treatment solarization/persulfate oxidation was the most efficient approach for fungicides removal. Residue levels, agronomic and productive indicators in lettuces cultivated in soils exposed to combined persulfate remediation treatment were also assessed. This research underscores the potential of the combined persulfate oxidation and solarization as a sustainable and efficient, technology for soils contaminated with pesticides, offering a prominent solution for soil remediation at field scale.

The authors acknowledge financial support received from grant PID2022-143118OR-I00 funded by MICIU/AEI/ 10.13039/501100011033 and by ERDF/EU.

[1] C.M. Martínez-Escudero, I. Garrido, P. Flores, P. Hellín, F. Contreras, J. Fenoll, *Chem. Eng. J.* **2022,** *310*, 114781.
[2] Z Huan, Z. Xu, D. Lu, D. Xie, J. Luo, *Bull. Environ. Contam. Toxicol* **2013**, *91 (6)*, 734–738.
[3] E. Morillo, J. Villaverde, *Sci. Total Environ*. **2017**, *586*, 576–597.

Photocatalytic oxidation of cyantraniliprole in real wastewater using $TiO_2/Na_2S_2O_8$: Study of intermediate products by liquid chromatography mass spectrometry after dispersive liquid–liquid microextraction

Isabel Garrido [a], Carmen María Martínez-Escudero [a], Fulgencio Contreras [a], Pilar Hellín [a], Pilar Flores [a], Lixy Olinda León-Morán [b], Natalia Campillo [b], Marta Pastor-Belda [b], Natalia Arroyo-Manzanares [b], Pilar Viñas [b], José Fenoll [a,*]

[a] *Research Group on Sustainability and Quality of Fruit and Vegetable Production. Instituto de Investigación y Desarrollo Agrario y Medio Ambiental. C/ Mayor s/n. La Alberca, 30150, Murcia, Spain.*
[b] *Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, Regional Campus of International Excellence "Campus Mare Nostrum", E-30100 Murcia, Spain.*

E-mail: isabel.garrido3@carm.es

Cyantraniliprole is a second-generation anthranilic diamide insecticide [1]. Its extensive application in agricultural settings has led to its presence in surface waters and groundwater, being wastewater treatment plants (WWTP) one of the major routes in which this pollutant reaches the environment. Considering this, it should be compulsory the development of sensitive and selective analytical methods to determine cyantraniliprole and its transformation products (TPs). In this study, a methodology to monitor cyantraniliprole and its main TPs was developed. For this purpose, preliminary experiments were conducted to identify these analytes in water samples exposed to photocatalytic treatment ($TiO_2/Na_2S_2O_8$) using ultraviolet A irradiation with light emitting diode lamps (UVA-LED). The findings were then applied to the analysis of real WWTP effluents subjected to heterogeneous photocatalytic process under sunlight irradiation. Given the low expected levels of cyantraniliprole TPs in the samples, a liquid microextraction technique was chosen for sample clean-up and preconcentration. Liquid chromatography with mass spectrometry using triple quadrupole and time-of-flight analyzers was used to determine TPs. Two untargeted strategies were applied for TPs identification: suspect screening based on a home-made database created from TPs described in literature and non-target screening involving the extraction of molecular features, their prioritization according to photo-degradation behavior and structural elucidations. Eight TPs in water were tentatively identified under both suspect (six TPs) and non-target (two TPs) screening during the photocatalytic experiment using UVA-LED. Based on this identification, a possible photocatalytic degradation pathway of cyantraniliprole has been proposed. Regarding the solar experiment conducted with real WWTP effluents, cyantraniliprole concentration in samples ranged from 0.07 to 0.14 mg L^{-1}, while five TPs were found in all WWTP samples.

The authors acknowledge financial support received from grant PID2022-143118OR-I00 funded by MICIU/AEI/ 10.13039/501100011033 and by ERDF/EU and PID2024-156671NB-I00 funded by MCIN/AEI/10.13039/501100011033/ FEDER, EU..

[1] X. Zhang, X. Wang, Y. Liu, K. Fang, T. Liu, *Chemosphere* **2020**, *249*, 126479.

Sustainable Base Catalysis via Designed Metal Clusters: Towards Green Transformations

Belén Lerma-Berlanga[1,*], Lluís Martínez Belenguer[1], Yongkun Zheng[1] and Antonio Leyva-Pérez[1,*]

[1] *Instituto de Tecnología Química (ITQ), Consejo Superior de Investigaciones Científicas-Universitat Politècnica de València, 46022, Valencia, Spain*

E-mail: blerber@itq.upv.es

Transesterification and related base-catalyzed nucleophilic alcohol addition reactions are cornerstone transformations in sustainable chemistry, underpinning the production of biodiesel and high-value organic carbonates such as ethyl methyl carbonate (EMC), key compounds in strategic industrial sectors including lithium-ion batteries and sustainable fuels. Herein, we demonstrate the versatility of inorganic metal-based nanoclusters as catalytic platforms through two complementary strategies that exploit confinement, nanoscale organization, and chemical environment to control catalytic performance.

First, we report advances based on zeolite confinement and hierarchical architectures to stabilize alkaline oxide nanoclusters for the selective synthesis of EMC [1]. Commercial NaX zeolite already exhibits significant catalytic activity toward EMC formation and can be reused for up to ten consecutive cycles or implemented under continuous-flow conditions while maintaining stable performance. Importantly, the incorporation of alkaline and alkaline-earth salts and oxide clusters—particularly K_2O and MgO—within the zeolite framework markedly enhances catalytic activity, enabling EMC yields of up to 99%, surpassing the thermodynamic equilibrium without the need for reactive distillation, while maintaining good selectivity (up to 65%). This strategy is effective not only for NaX but also for NaY, H-USY, H-ZSM-5, and H-BETA zeolites, which otherwise display limited intrinsic activity. In parallel, we explore the catalytic potential of sustainable, ligand-free subnanometric $MgCO_3$ clusters organized as gel-like systems, synthesized via CO_2 sequestration in bioavailable ethanol [2]. These $MgCO_3$ nanoclusters are approximately four times more active than their calcium-based counterparts in dimethyl carbonate transesterification and exhibit turnover frequencies up to 40 times higher than bulk $MgCO_3$. The enhanced performance is attributed to the harder Lewis acidic character of Mg^{2+}, stabilized within the nanostructured carbonate network while remaining highly accessible to reactants. Overall, this work establishes complementary design principles for metal cluster-based base catalysis and opens new avenues for sustainable CO_2-derived catalytic systems.

[1] Y. Zheng, N. Solá–Ferrer, Ll. Martínez–Belenguer, B. Lerma–Berlanga, A. Leyva–Pérez, *J. Catal.* **2026**, 456, 116729.
[2] Ll. Martínez–Belenguer, K. Zítová, J. P. Cerón–Carrasco, B. Lerma–Berlanga, A. Leyva–Pérez, *Appl. Mater. Interf.* **2026**.

Valorization of Keratin for the Recovery of Platinum Group Metals

Rita M. Carvalho,[a,b,c] Matilde Dias,[a] Flávia N. Braga,[a,b] Filipe H. B. Sosa,[b] João A. P. Coutinho,[b,c] Helena Passos[a,*]

[a] *LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.*
[b] *CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.*
[c] *RYA - Purification Technologies, PCI - Creative Science Park, 3830-352 Ílhavo, Portugal.*

E-mail: hpassos@fe.up.pt

Platinum Group Metals (PGM) are scarce elements with unique properties essential in numerous industrial applications. Due to the increased global demand and the environmental burden of primary mining, the recovery of PGM from secondary sources, particularly spent automotive catalytic converters (SAAC), has emerged as a sustainable alternative. This approach contributes to resource conservation and significantly reduces environmental impacts associated with conventional extraction processes [1].
Keratin is a naturally occurring biopolymer present in several animal parts, including wool. Regardless of its structural form, keratin contains multiple functional groups, including thiol, amino, carboxyl, hydroxyl, and disulfide groups [2]. These functional groups are responsible for keratin´s high tensile strength, chemical resistance, and thermal stability, while also providing active sites for metal binding in aqueous solutions. In recent years, keratin-based materials have attracted increasing attention as low-cost, sustainable biosorbents for the removal and recovery of metal ions from aqueous solutions. Wool keratin has demonstrated effective adsorption of a broad range of metal ions, including Hg, Cu, Ag, Cd, Pb, Cr, and Al, even at low concentration [3]. However, studies focusing on the interaction between keratin and PGM remain limited,[4] particularly for wool keratin.
The present study aims to evaluate the adsorption capacity of wool keratin for the recovery of PGM from HCl concentrated solutions. Different pre-cleaning and chemical pre-treatment procedures were investigated and compared. Adsorption kinetics and thermodynamics were evaluated. Morphological and structural characterizations were performed to elucidate the adsorption mechanisms and the effect of pre-treatment on metal uptake performance. Preliminary results suggest selective adsorption of PGMs by wool keratin, with Pd being preferentially adsorbed compared to other PGMs.

This work was supported by FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). This work was further financially supported by FCT, I.P. /MCTES through national funds: LSRE-LCM, UID/50020/2025 (DOI: 10.54499/UID/50020/2025); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); and CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI: 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI: 10.54499/UIDP/50011/2020), LA/P/0006/2020 (DOI: 10.54499/LA/P/0006/2020). R. Carvalho acknowledges FCT for Ph.D. grant 2025.06718.BDANA.

[1] European Commission: Directorate-General for Internal Market, I. E. and Sme,. Study on the Critical Raw Materials for the EU 2023 - Final Report; Office of European Union, **2023**.
[2] Vashista, S. Arora, A. Sah, M. K., *Korean J. Chem. Eng.,* **2024**, 41, 1901-1921.
[3] Kar, P. Misra, M., *J. Chem. Technol. Biotechnol.*, **2024**, 79, 1313-1319.
[4] Nohabar, A. N. Braga, F. H.B. Sosa, F. Schaeffer, N. A. P. Coutinho, J. Passos, H., *Waste Manag.*, **2026**, 212, 115346.

Solvent–free propargylamine synthesis by Pd–impregnated Al–LDHs synthesized from aluminum slag

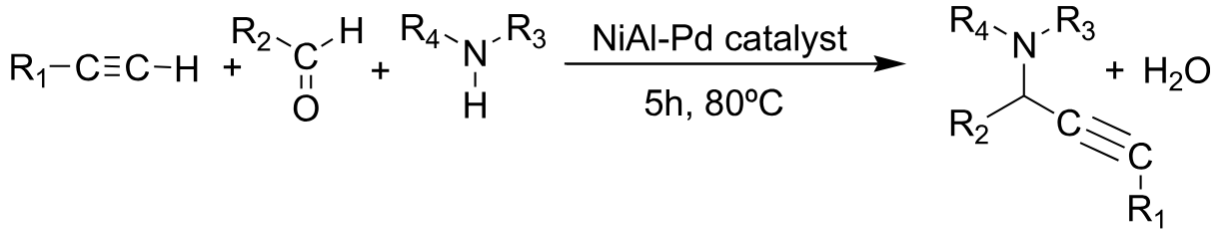
Alejandro Jiménez, [a]* Pablo Rodríguez,[a] Raquel Trujillano,[a] Raihamol E. Thampikannu,[b] Kannan Vellayan,[b] Miguel Ángel Vicente,[a]*

[a] GIR – QUESCAT, Dep. Química Inorgánica, Universidad de Salamanca, 37008 Salamanca, Spain
[b] Department of Chemistry, Government College Kattappana, Kattappana P.O., Kerala 685508, India

E–mail: mavicente@usal.es; alejm@usal.es

Propargylamines are high–value compounds in organic synthesis and pharmacology, serving as key precursors for alkaloids and various bioactive molecules [1]. Currently, their production through one–pot, solvent–free A3 coupling (aldehyde, amine, and alkyne) is favored due to its high atom economy and sustainability [2]. In this field, aluminum–based layered double hydroxides (LDHs) have proven to be excellent catalytic supports owing to their layered structure and ion–exchange capacity. The performance of these materials can be optimized by impregnating them with palladium and varying the divalent cations within their structure. An innovative aspect of this approach is the recovery of Al^{3+} from industrial waste, specifically aluminum salt cake, allowing for the synthesis of low–cost catalysts that promote circular chemistry processes [3].

This study evaluates various Al–based LDHs, synthesized by co–precipitation from aluminum slag and impregnated with Pd^{2+}, as heterogeneous catalysts for propargylamine synthesis (Scheme 1) [3]. The materials were characterized using techniques such as PXRD, FT–IR, and N_2 physisorption. The NiAl–Pd catalyst showed the highest efficiency in the coupling of benzaldehyde, morpholine, and phenylacetylene, reaching optimal yields under conditions of 80 ºC for 6 h with a 30 mg of catalyst dosage. The nature of the divalent cation directly influenced the activity of the palladium active sites. The system demonstrated good cyclic stability, maintaining an activity higher than 80 % after four reuse cycles. These results position LDHs derived from industrial wastes as a sustainable and effective alternative for producing pharmaceutical intermediates.



Scheme 1. General reaction for the synthesis of propargylamine derivates.

[1] R. Manujythi, T. Aneeja, G. Anilkumar, *RSC Adv.* **2021**, *11*, 19433–19449.
[2] M.J. Ndolomingo, N. Bingwa, R. Meijboom, *J. Mater. Sci.* **2020**, *55*, 6195–6241.
[3] R.E. Erattammottil, A. Jiménez, M.A. Vicente, V. Rives, K. Vellayan, *Mol. Catal.* **2024**, *569*, 114594.

Griffitite as heterogeneous catalyst in solvent–free synthesis of tetrasubstituted imidazoles

Miguel Ángel Vicente,[a] Alejandro Jiménez,[a] Pablo Rodríguez,[a] Raquel Trujillano,[a] Raihamol E. Thampikannu,[b] Alan M. Johnson,[b] Kannan Vellayan,[b]

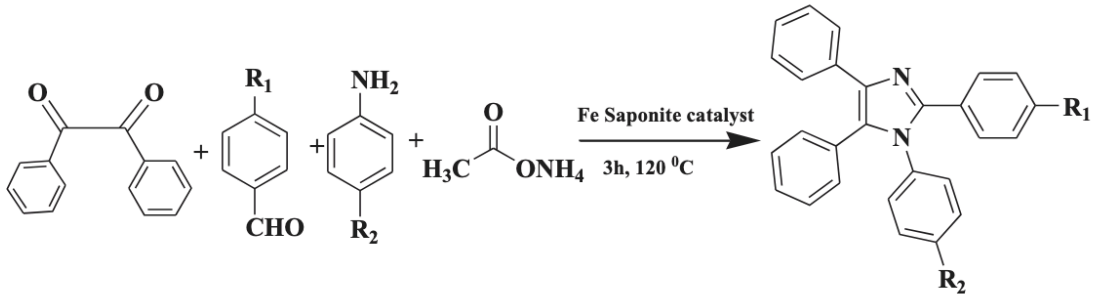
[a] *GIR – QUESCAT, Dep. Química Inorgánica, Universidad de Salamanca, 37008 Salamanca, Spain*

[b] *Department of Chemistry, Government College Kattappana, Kattappana P.O., Kerala 685508, India*

E–mail: alejm@usal.es

Imidazole–derived compounds are essential in fine chemistry, pharmaceuticals, and materials science, serving as building blocks for biocompounds like purines and vitamins. Their tetrasubstituted variants offer diverse biomedical effects, including antitumor and antiviral properties [1]. Currently, solvent–free imidazole synthesis is favored for its cost–effectiveness and sustainability. In this area, smectites such as montmorillonite and saponite act as efficient catalysts due to their porosity and adjustable acidity [2]. Saponite specifically allows for the incorporation of transition metals that improve performance through redox properties. In particular, Fe–rich saponite utilizes iron in octahedral positions to create a synergy between Lewis and Bronsted acidity [3].

This study evaluates solids derived from griffithite, an iron–rich saponite, as heterogeneous catalysts for substituted imidazole synthesis without solvents (scheme 1) [3]. The mineral was used in its natural state, purified, and calcined at 750 ºC. The calcined material achieved the highest yield at 86 %, compared to 78 % for the uncalcined sample. Optimal conditions were established at 120 ºC, 3 h, and 30 mg of catalyst. Results confirmed that electronegative groups in substrates like aldehydes and amines enhance reactivity. The catalyst remained effective over four reuse cycles, proving to be an eco–friendly option for sustainable synthesis.



Scheme 1. General reaction for the synthesis of tetrasubstituted imidazoles.

[1] S. Yadegarian, A. Davoodnia, A. Nakhaei, *Orient. J. Chem.* **2015**, *31*, 573–579.
[2] A. Ochirkhuyag, J. Temuujin, *Adv. Synth. Minerals,* **2024**, 14, 629.
[3] R.E. Erattammottil, A. Jiménez, M.A. Vicente, A.M. Johnson, K. Vellayan, *Appl. Clay Sci.* **2025**, *277*, 107956.

Electrochemical Hydrogenation of Nitriles for Sustainable Production of Value-added Amines

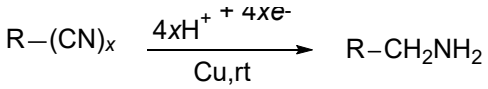
Gopika Gopakumar,[a] Jose Solera-Rojas,[a] Iván Muñoz-Capdevila,[b] Carmen Mejuto,[a] Eduardo García-Verdugo Cepeda,[b] Belén Altava Benito,[b] Francisco Fabregat-Santiago,[a,*] Elena Mas-Marzá,[a,*]

[a] Institute of Advanced Materials, Universitat Jaume I, Av.Vicent Sos Baynat, s/n, 12006, Castello de la Plana, Castello, Spain.
[b] Department of Inorganic and Organic Chemistry, Universitat Jaume I, Av.Vicent Sos Baynat, s/n, 12006, Castello de la Plana, Castello, Spain.

E-mail: gopakuma@uji.es

The transition towards a sustainable and circular chemical economy demands the development of greener alternatives to conventional high-pressure thermocatalytic hydrogenation processes. In this context, nitriles are particularly important substrates, as their hydrogenation leads to valuable amines widely used in pharmaceuticals, agrochemicals, polymers, and fine chemicals. However, nitriles also represent a challenging class of organic compounds to hydrogenate due to the exceptional stability of the carbon–nitrogen triple bond (C≡N), which demands efficient and selective catalytic strategies. [1]

This work explores the room-temperature electro-hydrogenation of aromatic and biomass-derived nitriles using Cu electrodes and water as the proton source. The relevance of this electrochemical strategy lies in the distinctive properties of copper surfaces, which can effectively mediate complex proton–electron transfer steps by providing a favorable balance between sufficient adsorption of organic substrates and the delaying of the competing hydrogen evolution reaction (HER) [2]. Such a balance is essential for activating the highly stable C≡N bond, enabling the production of value-added furan-based and other aromatic amines, which are key building blocks for several next-generation polymers and pharmaceutical products. [3] In conclusion, our approach highlights the potential of using electricity to upgrade renewable feedstocks into high-value chemical intermediates. At the same time, it opens new opportunities to exploit these systems as efficient liquid organic hydrogen carriers, contributing to more sustainable energy storage and utilization strategies.



Acknowledgements: This work has been funded by the Generalitat Valenciana under the PROMETEO 2024 programme (CIPRO/2023/57). GG acknowledge Generalitat Valenciana for the predoctoral contract.

[1] N. Guenani, J. Solera-Rojas, D. Carvajal, C. Mejuto, A. Mollar-Cuni, A. Guerrero, F. Fabregat-Santiago, J. A. Mata, E. Mas-Marzá, *Green Chem*. **2024**, *26*, 8768-8778.
[2] M. Zheng, J. Zhang, P. Wang, H. Jin, Y. Zheng, S.Z. Qiao, *Adv. Mater.* **2024**, *36*, 2307913-2307941.
[3] J. Solera-Rojas, C. Forés, G. Beltrán-Gargallo, F. Fabregat-Santiago, J. A. Mata, C. Mejuto, E. Mas-Marzá, *ACS Sustainable Chem. Eng.* **2025**, *13*, 8660–8670.

Glucose-to-Glucaric Acid via Selective Electrochemical Oxidation

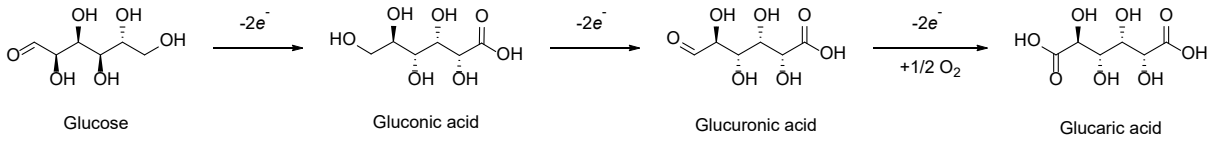
Rivin George,[a] Jose Solera-Rojas,[a] Carmen Mejuto,[a] Eduardo García-Verdugo Cepeda,[b] Francisco Fabregat-Santiago,[a] Belén Altava Benito,[b] Elena Mas-Marzá,[a*]

[a] Institute of Advanced Materials, Universitat Jaume I, Av.Vicent Sos Baynat, s/n, 12006, Castello de la Plana, Castello, Spain.
[b] Department of Inorganic and Organic Chemistry, Universitat Jaume I, Av.Vicent Sos Baynat, s/n, 12006, Castello de la Plana, Castello, Spain.

E-mail: rgeorge@uji.es

The simultaneous generation of green hydrogen and the electrochemical upgrading of biomass-derived molecules represents a highly efficient approach to sustainable chemical synthesis. In this context, the selective electrochemical oxidation of glucose (scheme 1) coupled with the cathodic hydrogen evolution reaction (HER), offers a promising and environmentally benign alternative to value-added products. Amongst its oxidation products, glucaric acid is a 'top valuable bio-refined product' because it is used widely in medicine and industry including, treating cancer, lowering cholesterol and producing nylon-66 [1]. However, achieving its selective formation remains challenging because deep oxidation often competes with undesired C–C bond cleavage.

This work focuses on the design and fabrication of electrocatalytic materials to drive this multi-step oxidation. To this end, various electrode preparation strategies are employed to achieve tailored surface properties and well-dispersed metal active sites. These engineered electrodes undergo comprehensive electrochemical characterization to evaluate their active surface area, charge transfer kinetics, and catalytic stability prior to bulk electrolysis.



Scheme 1. Electrochemical oxidation of glucose.

A critical aspect of this study is the optimization of both the reaction environment and catalyst composition to control product selectivity. While monometallic architectures, such as bare nickel, often yield poor selectivity in the tailored alkaline media [2], integration of rationally selected metals, from chemically reduced gold (Au) nanoparticles to various earth-abundant transition metals, aims to increase the selectivity past initial oxidation products such as gluconic acid, toward the fully oxidized glucaric acid. This approach provides a practical pathway for the co-production of valuable biomass-derived chemicals and clean hydrogen.

Acknowledgements: This work has been funded by the Generalitat Valenciana under the PROMETEO 2024 programme (CIPROM/2023/57). Rivin George acknowledges Generalitat Valenciana for the predoctoral contract.

[1] X. Wu, Z.-J. Zhao, X. Shi, L. Kang, P. Das, S. Wang, S. Chu, H. Wang, K. Davey, B. Zhang, S.-Z. Qiao, J. Gong, Z.-S. Wu, *Energy Environ. Sci*. **2024**, 17, 3042–3051.
[2] M. P. J. M. van der Ham, J. Creus, J. H. Bitter, M. T. M. Koper, P. P. Pescarmona, *Chem. Rev*. **2024**, 124, 11915–11961.

Support Influence on Cu Catalysts for δ-Valerolactone Production

Miguel Macías-Villasevil,[a,b] Beatriz García,[a] Ana Orozco-Saumell,[a] Manuel Lopez-Granados,[c] Rafael Mariscal,[c] Jose Iglesias,[a,b*] Alicia García,[a] Jovita Moreno.[a,b*]

[a] Chemical & Environmental Engineering Group. Universidad Rey Juan Carlos.
[b] Institute of Technologies for Sustainability. ITPS-URJC. Universidad Rey Juan Carlos.
[c] Sustainable Energy and Chemistry Group, Institute of Catalysis and Petrochemistry, CSIC.

E-mail: miguel.macias@urjc.es

δ-valerolactone (DVL) is a cyclic ester used in the production of biodegradable and biocompatible polyesters. Its production is limited by the high cost associated with the scarcity of fossil-derived C5 feedstocks. An alternative method involves producing DVL from 1,5-pentanediol (PDO), which can be obtained from furfural (FF). This work proposes the synthesis of DVL via catalytic transfer hydrogenation (CTH) by coupling PDO dehydrogenation with FF hydrogenation in one step [1]. This process uses copper catalysts supported on SiO_2, La_2O_3, ZrO_2 and CeO_2, prepared by incipient wetness impregnation. Following reduction at 500 °C in a 10% H_2/Ar atmosphere, catalytic tests were conducted in a batch reactor at 240 °C, using a mixture of 9.2 wt% FF and PDO (1:2 molar ratio), 0.25 g of catalyst, and 1,4-dioxane as solvent.

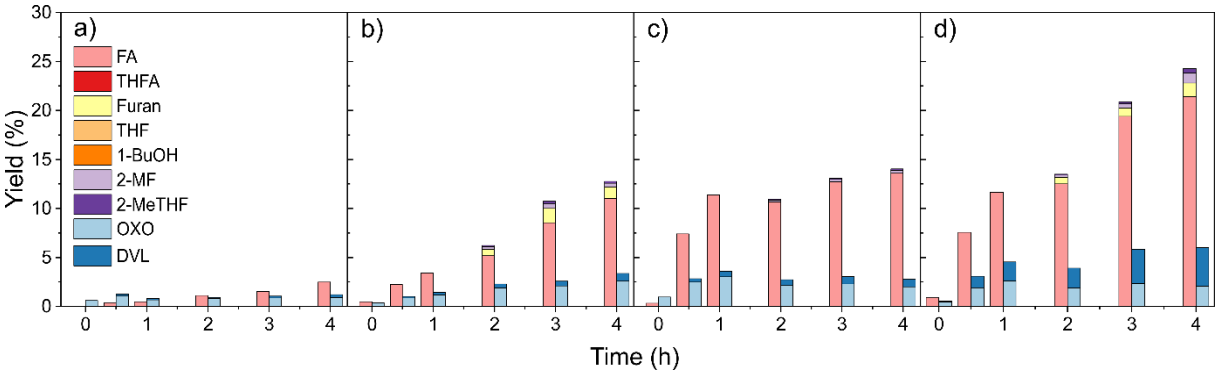


Figure 1. Catalytic tests with supported 10% Cu catalysts: a) SiO_2, b) La_2O_3, c) ZrO_2, d) CeO_2.

Figure 1 shows the catalytic performance of the Cu catalysts. FF conversion was found to be 52% for SiO_2, 66% for La_2O_3, 83% for ZrO_2 and 81% for CeO_2, with mass loss attributed to FF degradation at 240 °C. PDO conversion was approximately 80%. The best performance was observed with CeO_2, yielding 22% furfuryl alcohol (FA) and 4% DVL. This enhanced activity is attributed to more efficient Cu reduction, resulting in smaller Cu^0 particles and a stronger metal–support interaction [2]. The activation of the carbonyl of FF by Cu/ZrO_2 made the process more selective for obtaining FA and prevented decarbonylation at high temperatures. In contrast, La_2O_3 and SiO_2 produced the least selective results for the desired FF hydrogenation and PDO dehydrogenation products [3]. Nevertheless, these results confirm that DVL can be produced by CTH using biomass-derived raw materials. This research is part of project PID2021-122736OB-C44 and PID2024-155604OB-C41, both funded by 582 MCIN/AEI/10.13039/501100011033/FEDER, EU.

[1] H. Wang, et al. Liac *Sustain Energy Fuels*, 2021, *5*, 930–934.
[2] C.P. Jiménez-Gómez, et al, *Catalysis Today,* 2017, *279*, 327–338.
[3] C. Zhang, et al, Nanoscale, 2025, 17, 18229–18239.

Bioplastics in agricultural soils: limits of biodegradability and analytical challenges for a robust environmental assessment.

Marina Alcaraz Dólera[a], Rosa Penalver[b], José Antonio Pascual[a], Margarita Ros[a].

[a] *CSIC-Centro de Edafología y Biología Aplicada del Segura, Department of Soil and Water Conservation, Campus de Espinardo, P.O. Box 164, 30100 Murcia, Spain*
[b] *Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare-Nostrum", University of Murcia, E-30100, Murcia, Spain*

E-mail: marina.alcarazd@um.es

The use of bioplastics in agriculture is promoted as a green chemistry strategy to reduce the accumulation of conventional plastics in agricultural soils. However, the environmental safety of bioplastics under real-world agricultural conditions is still uncertain. This study examines the behavior of bioplastics in agricultural soils from three key perspectives: degradation mechanisms, analytical methodologies used to evaluate them, and biological responses of the soil-plant system. A bibliometric analysis and critical review of the available experimental evidence were conducted to inform this examination.

The most used analytical techniques, such as mass loss, microscopic observation, and surface spectroscopic changes, primarily show physical alterations or disintegration processes. These techniques do not provide a complete assessment of the fate of the carbon derived from the polymer. This methodological bias can lead to an overestimation of actual degradation rates and, consequently, of the environmental safety of these materials. Thus, biodegradable microplastics and other intermediate residues could persist in soil, particularly with intensive agricultural use. Furthermore, degradation depends heavily on the polymer type and environmental context, including temperature, humidity, material thickness, soil properties, and microbial composition. The lack of standardization and incomplete reporting of critical experimental parameters compromises the comparability of studies and hinders robust risk assessment.

To address this limitation, we propose an integrative conceptual framework linking degradation pathways, analytical tools, and biological responses. This framework places carbon traceability and mass balance at the heart of the assessment. This approach clarifies that disintegration does not equate to complete mineralization, nor does biological activity imply functional integration into soil biogeochemical cycles. Biodegradability alone does not ensure environmental safety. Therefore, contextual, systemic, and risk-oriented assessments are necessary to guide the responsible use of bioplastics in agriculture.

Acknowledgements.
This research has been developed within the PHAntastic project, funded by the European Union's Horizon Europe Programme under grant agreement No 101130073.

Study of the photolytic degradation of the antihypertensive drugs candesartan and irbesartan: Analytical strategy using liquid chromatography with QTOF and QqQ mass spectrometry

Rosa Peñalver,[a] Claudia Giménez-Campillo,[a] Lixy Olinda León-Morán,[a] Natalia Campillo,[a,*] Marta Pastor-Belda,[a] Natalia Arroyo-Manzanares,[a] Pilar Viñas,[a] Carmen María Martínez-Escudero[b], Isabel Garrido[b], Fulgencio Contreras[b], Pilar Hellín[b], Pilar Flores[b], José Fenoll[b]

[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, Regional Campus of International Excellence "Campus Mare Nostrum", E-30100 Murcia, Spain.
[b] Research Group on Sustainability and Quality of Fruit and Vegetable Production. Instituto de Investigación y Desarrollo Agrario y Medio Ambiental. C/ Mayor s/n. La Alberca, 30150, Murcia, Spain.

E-mail: rosamaria.penalver@um.es

Drugs in the sartan family, such as candesartan and irbesartan, are widely prescribed to treat high blood pressure [1]. These compounds have been identified as emerging pollutants due to their high consumption and incomplete removal in wastewater treatment plants, resulting in their persistent detection in surface and wastewaters [2]. Studying their transformation products (TPs) is particularly relevant, as these may be more persistent, mobile or toxic than the parent compounds.

The aim of this study is to evaluate the photolytic stability and degradation profile of candesartan and irbesartan by treating them in a photoreactor. This will help to identify the main TPs and propose possible chemical degradation pathways. To this end, individual solutions of both drugs were irradiated using ultraviolet light-emitting diode lamps in a photoreactor, monitoring the kinetics of the parent compounds and the sequential appearance of TPs at different irradiation times. To ensure the detection of TPs at trace levels, the samples were subjected to a two-step preconcentration strategy based on salt-assisted liquid-liquid extraction, involving the extraction of 10 mL of sample in acetonitrile. The TPs were identified using ultra high-performance liquid chromatography (UHPLC) coupled with time-of-flight (QTOF) mass spectrometry, employing exact masses and strict mass error criteria. Two untargeted approaches were applied: suspect screening based on a homemade database compiled from previously reported TPs, and the search for novel TPs through spectral analysis of a deconvoluted and aligned peak list exhibiting appropriate degradation trends. The TPs were structurally confirmed by UHPLC with triple quadrupole (QqQ) tandem mass spectrometry, based on the analysis of their fragmentation patterns. The results demonstrated the formation of multiple TPs, some of which were detected in the early stages of photolytic treatment.

The authors acknowledge financial support received from grant PID2022-143118OR-I00 funded by MICIU/AEI/ 10.13039/501100011033 and by ERDF/EU and PID2024-156671NB-I00 funded by MCIN/AEI/10.13039/501100011033/ FEDER, EU.

[1] R. Li, C. Liang, S. B. Svendsen, V. Kisielius, K. Bester, *Water Res*. **2023**, *229*, 119352.
[2] A. Siciliano, A. Medici, M. Guida, G. Libralato, L. Saviano, L. Previtera, G. Di Fabio, A. Zarrelli, *Appl. Sci.* **2023**, *13*, 8170.

Evaluation of different microextraction approaches for the comprehensive determination of plastic additives in fish

Rosa Peñalver,[a] María Dolores Pérez-Álvarez,[a] Ana Belén Martínez-Piernas,[a] Natalia Campillo,[a] Natalia Arroyo-Manzanares,[a] Ángel Pérez-Ruzafa[b] and Pilar Viñas[a,*]

[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, Regional Campus of International Excellence "Campus Mare Nostrum", E-30100 Murcia, Spain.
[b] Department of Ecology and Hydrology, University of Murcia, Regional Campus of International Excellence "Campus Mare Nostrum", E-30100 Murcia, Spain.

E-mail: rosamaria.penalver@um.es

Marine ecosystems are highly vulnerable to plastic pollution, as more than 9 million tons of plastic waste end up in the oceans every year. These materials can persist in the environment for hundreds of years, gradually degrading and fragmenting to form one of the most worrying emerging pollutants: microplastics (MPs). MPs not only pose a physical risk to marine organisms but also act as vectors for potentially toxic chemical compounds. During the production of plastics, a significant number of additives are used to improve their properties. However, many of these additives are incorporated into polymers without forming chemical bonds, which facilitates their release into the environment during degradation processes. Numerous studies have pointed out that many of these compounds have adverse ecotoxicological effects on marine organisms [1]. In this context, it is essential to develop efficient analytical methodologies that allow the determination of compounds associated with MPs in biological matrices, such as marine organisms. Recently, miniaturised extraction approaches have gained popularity due to their alignment with the principles of green chemistry, as they significantly reduce the consumption of organic solvents, minimise waste generation, and decrease the environmental impact of analytical procedures. The application of microextraction techniques not only improves analytical sensitivity but also contributes to the development of more sustainable and environmentally friendly analytical procedures, reinforcing the role of green chemistry in the analysis of emerging pollutants associated with MPs. In this study, different microextraction techniques based on solid-phase extraction were evaluated for the determination of phthalate and non-phthalate plastic additives using high-performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (HPLC-QTOF).

The authors thank the Spanish MCIN project PID2024-156671NB-I00 financed by MCIN/AEI/10.13039/501100011033/ FEDER, EU. M.D. Pérez-Álvarez acknowledges a fellowship 22319/FPI/23 from Fundación Séneca (Murcia, Spain).

[1] Banaee, M., Multisanti, C.R., Impellitteri, F., Piccione, G., Faggio, C., *Comp. Biochem. Physiol. C*. **2025,** *287*, 110042.

Simple Chloride Salts as Catalysts for the Synthesis of Cyclic Di- and Tri-thiocarbonates by Insertion of CS_2 into Epoxides.

Marcos López-Aguilar, Nicolás Ríos-Lombardía, Joaquín García-Álvarez,* Carmen Concellón,* Vicente del Amo.*

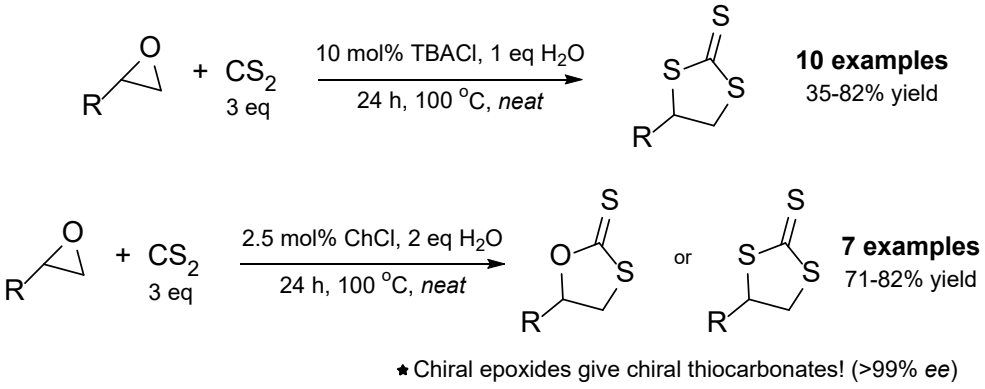
Laboratorio de Química Sintética Sostenible (QuimSinSos). Departamento de Química Orgánica e Inorgánica (IUQOEM). Centro de Innovación en Química Avanzada (ORFEO-CINQA). Facultad de Química. Universidad de Oviedo. C/Julián Clavería 8, 33006, Oviedo (Spain)

E-mail: lopezamarcos@uniovi.es

The insertion of heterocumulenes in epoxides is a well-known reaction as it allows the valorisation of CO_2 into cyclic carbonates. In an analogous way, the use of CS_2 enables the synthesis of heterocyclic compounds with different content in sulphur (mono-, di- and tri-thiocarbonates).[1] However, the synthesis of these sulphur-based heterocycles typically relies on harsh reaction conditions[2] or metal- or carbene-mediated catalysis.[3,4]

Herein, we describe a straightforward and efficient procedure where these di- and tri-thiocarbonates are obtained as the major products with good selectivities and yields by only using readily-available and simple chloride salts [in our case tetrabutyl ammonium chloride (TBACl) or choline chloride, ChCl)] as catalysts, in low loadings (2.5 – 10 mol%) and in the presence of water (1-2 eq.), working under neat conditions.[5]

This work reveals that both chloride salts show different reactivities. Thus, while TBACl provides trithiocarbonates with a greater variety of substrates through a S_N1 mechanism, ChCl allows the regio-selective synthesis of dithiocarbonates (1,3-oxathiolane-2-thiones isomer) or trithiocarbonates depending on the substrate used. As this latter last salt involves a S_N2 mechanism, it allows the synthesis of chiral thiocarbonates when chiral epoxides are used.



Scheme 1. Synthesis of cylic di- and tri-thiocarbonates by chloride salts catalysis.

[1] C. Díez-Poza, L. Álvarez-Miguel, M. E. G. Mosquera, C. J. Whiteoak, *Org. Biomol. Chem.*, **2023**, *21*, 3733-3755.

[2] C. C. J. Culvenor, W. Davies, K. H. Pausacker, *J. Chem. Soc.*, **1946**, 1050-1052.

[3] W. Clegg, R. W. Harrington, M. North, P. Villuendas, *J. Org. Chem.*, **2010**, *75*, 6201–6207.

[4] C. Mei, X. Li, L. Liu, C. Cao, G. Pang, Y. Shi, *Tetrahedron*, **2017**, *73*, 5706-5714.

[5] M. López-Aguilar, N. Ríos-Lombardía, M. Gallegos, D. Barrena-Espés, J. García-Álvarez, C. Concellón, V. del Amo, *Chem. Commun.*, **2025**, *31*, 3488-3491.

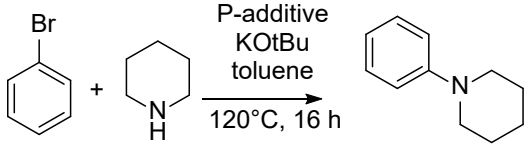
Ionic Liquids and beyond: catalytic innovations for coupling reactions

Eleonora Palmerini,[a] Mustapha Hamdaoui,[a] Katalin Barta*[a]

[a] *Universitätsplatz 3, 8010, Graz, Austria, Institute of Chemistry, Graz University of Graz*

eleonora.palmerini@uni-graz.at

Nitrogen-containing compounds are widespread in nature and play a central role in pharmaceuticals, materials, and biologically active molecules.[1] As a result, C–N bond formation is one of the most important transformations in synthetic chemistry. Amination of electron-neutral aromatic systems typically requires transition-metal catalysts,[2] although transition-metal-free approaches have been reported and are often proposed to proceed via benzyne intermediates.[3] Conventional benzyne generation generally relies on specialized precursors such as Kobayashi in combination with fluoride sources, or if starting from an aryl-halide, it would require much stronger bases.[4] In this work, we describe a transition-metal-free amination protocol starting directly from simple bromobenzene. The reaction is promoted by a widely available base such as potassium tert-butoxide (KOtBu), in combination with a cheap phosphonium-based additive. KOtBu has previously been shown to enable similar transformations,[5] particularly in polar aprotic solvents such as DMSO, where cation coordination enhances its basicity.[6] In contrast, our system operates in toluene, an apolar solvent typically considered unsuitable for *in situ* benzyne formation, where the phosphonium additive plays a key role in enabling the reaction, allowing metal-free C(sp^2)–N bond formation between bromobenzene and piperidine under operationally simple conditions. The reaction proceeds under air without the need for an inert atmosphere or specially pretreated reagents. Although elevated temperatures and extended reaction times are required, likely due to benzyne generation, the method offers a practical and accessible route to transition-metal-free aromatic amination. To elucidate the effective contribution of the phosphonium additive, reaction parameters were systematically examined using a One Variable At a Time (OVAT) approach. In addition, to study the system in greater depth and evaluate how different factors together influence the reaction outcome, a Design of Experiments (DoE) methodology was applied, in which multiple parameters were varied systematically according to a statistical approach.



Scheme 1. Phosphonium-assisted direct amination of bromobenzene (1) and piperidine (2).

[1] *Advances in Organometallic Chemistry* 67, **2017**, 401-481
[2] R. Singh, E. Sathish, S. Goyal, *Tetrahedron* **2021**, *100*
[3] H. Heaney, *Chem. Rev.* **1962**, 62 (2), 81–97
[4] D. Chang et al., *Tetrahedron* **2018**, *74*
[5] M. Beller, C. Breindl, T. H. Riermeier, A. J. Tillack, *Org. Chem.* **2001**, 66, 1403
[6] (a) Y. Fang, Y. Zheng, Z. Wang *Eur. J. Org. Chem*. **2012**, 8,1495–1498. (b) M. Beller, C. Breindl, T. H. Riermeier, *J. Org. Chem.* **2001**, 66, 4, 1403–1412 (d) C. R. Johnson, M.I. Ansari, A. Coop, *ACS Omega* **2018**, 3, 10886−10890.(e) L. Shi, M. Wang, C. A. Fan, F. M. Zhang, Y. Q. Tu, *Org. Lett.*, **2003**, *5*, 3515-3517.

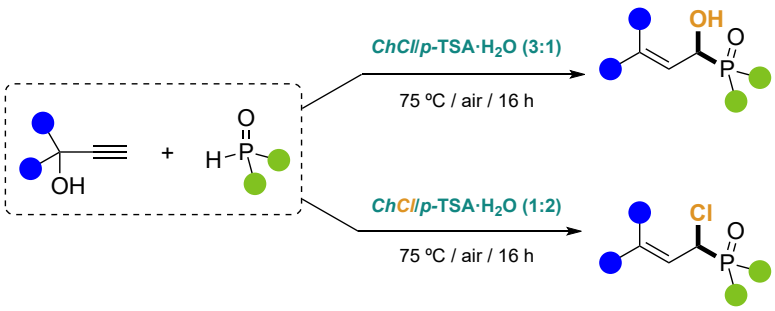
Modulated selectivity in *B*rønsted *A*cidic *D*eep *E*utectic *S*olvents (*BADESs*) *via HBA*/*HBD* Ratio to Enable the Green and Efficient One-Pot Tandem Concurrent Synthesis of Allyl Phosphine Oxides

Gloria Morís-Menéndez,[a] Nicolás Ríos-Lombardía,[a] Marina Ramos-Martín,[a,b] Alejandro Presa Soto,[a,*] and Joaquín García-Álvarez[a,*]

[a] Laboratorio de Química Sintética Sostenible (QuimSinSos): Departamento de Química Orgánica e Inorgánica (IUQOEM), Centro de Investigación en Química Avanzada (ORFEO-CINQA), Facultad de Química, Universidad de Oviedo. C/ Julián Clavería 8, 33006, Oviedo (Spain).

E-mail: morisgloria@uniovi.es

One-pot tandem methodologies offer powerful opportunities to enhance step economy while reducing waste, energy input and operational complexity [1], thereby directly aligning with the *Principles of Green Chemistry* [2]. Herein, an unprecedented fully concurrent, metal-free Meyer Schuster/C-P (and C-Cl) bond-forming protocol enabled by Brønsted Acidic Deep Eutectic Solvents (*BADESs*), which act simultaneously as solvent, promoter and chemoselectivity controller of the reaction outcome [3]. Remarkably, and just by simple modulation of the *HBA*/*HBD* ratio within the same *BADES* system, this methodology allows predictable switching between the selective formation of *α*-hydroxy or *α*-chloro allyl phosphine oxides. Moreover, the products generally precipitate from the reaction medium and can be isolated by simple filtration, thus avoiding the use of toxic and non-renewable volatile organic solvents during the synthesis or the final isolation/purification steps.



Scheme 1. Chemoselective one-pot tandem concurrent Meyer-Schuster/C-P (and C-Cl) bond formation promoted by Deep Eutectic Solvents based on different mixtures of choline chloride (*ChCl*) and *p*-toluenesulfonic acid *p*-TSA·H_2O.

[1] Y. Hayashi, *Acc. Chem. Res.* **2021**, *54*, 1385-1398.
[2]. P. T. Anastas, J. C. Warner, *Green Chemistry Theory and Practice*, Oxford University Press, Oxford, **1998**.
[3] For other examples related with the use *BADESs* in organic synthesis, see: a) G. Morís-Menéndez, S. E: García-Garrido, P. García-Álvarez, A. Presa-Soto, N. Ríos-Lombardía, J. García-Álvarez, *Adv. Synth. Catal.* **2025**, *367*, e20250038; b) M. Ramos-Martín, J. García-Álvarez, A. Presa-Soto, *ChemSusChem* **2025**, *18*, e202500679.

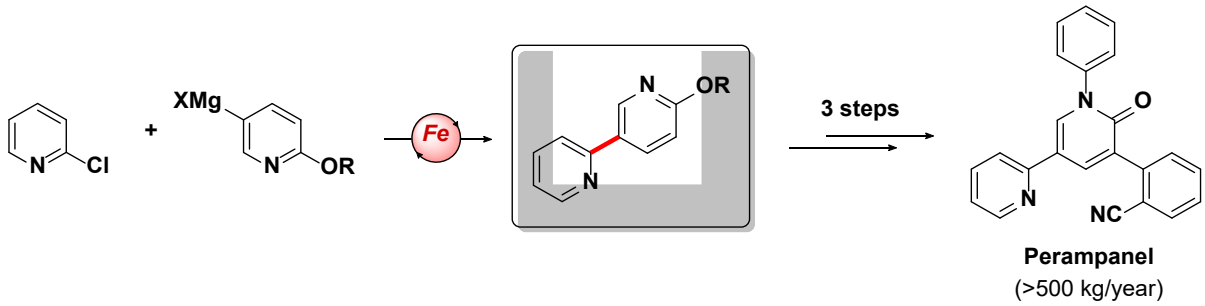
Sustainable synthesis of pharmaceutical bipyridine intermediates via iron-catalysis

Ferenc Minya,[a] Luca Buzzetti,[a] Simone Zaramella,[a,*] Alfredo Paio[a]

[a] *F.I.S. Fabbrica Italiana Sintetici S.p.A., 36075 Montecchio Maggiore, Vicenza, Italy*

Email:ferenc.minya@fisvi.com

The general topic of investigation lies in the discovery and development of various iron-catalyzed cross coupling reactions. For this class of transformation, iron catalysis is anticipated to serve as a greener alternative compared to the more established procedures featuring noble metals [1]. A particular focus of the research is related to the use of organomagnesium halide reagents (Grignard) as coupling partners, thus delving deep in Kumada-type reactions. These reagents are particularly established in industrial settings and they feature several advantages compared to other nucleophilic reagents used in transition metal-catalyzed cross-couplings. The chemical target of this investigation is the construction of bipyridine scaffolds through heteroaryl-heteroaryl cross coupling in green alternative solvents for industrial application. These structures are featured in many pharmaceutically active compounds and their importance as ligands is also prevalent [2]. One compound stands out, a key intermediate of the anti-epileptic medication, a 2,3'-bipyridine, Perampanel, which requires a palladium-catalyzed Kumada coupling to produce [3]. Working with the originator of this patent (F.I.S.), we set out to develop and optimize a reaction utilizing iron as a catalyst to produce this intermediate on-scale considering a greener alternative approach.



Scheme 1. Iron-catalyzed Kumada coupling step for the synthesis of Perampanel key intermediate

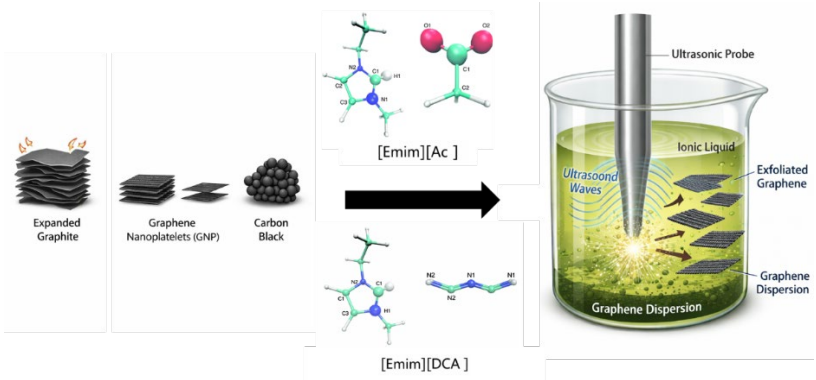
[1] Sherry, B. D.; Fürstner, A. The Promise and Challenge of Iron-Catalyzed Cross Coupling. *Accounts of Chemical Research* **2008**, *41 (11)*, 1500–1511.
[2] Kaes, C.; Katz, A.; Hosseini, M. W. Bipyridine: The Most Widely Used Ligand. A Review of Molecules Comprising at Least Two 2,2'-Bipyridine Units. *Chemical Reviews* **2000**, *100 (10)*, 3553–3590.
[3] Fontana, F.; Stabile, P. Process for the preparation of 2-alkoxy-5-(pyridin-2-yl)pyridine, an intermediate of perampanel, EP2586777B1, Fabbrica Italia Sintetici F.I.S. **2014**.

Green Exfoliation of Carbon Materials Using Ionic Liquids

José Javier Delgado-Marín, Imane Moulefera, Jesús García-León, Leonel Salazar-Aguilar, Ignacio Carnerero-Hinojosa, Mercedes G. Montalbán, Gloria Víllora*

Chemical Engineering Department, Faculty of Chemistry, CEIR Campus Mare Nostrum (CMN), University of Murcia, 30071 Murcia, Spain.
E-mail: josejavier.delgado@um.es

Graphene has attracted widespread attention due to its exceptional mechanical, electrical, and thermal properties, which enable applications across energy storage, electronics, and biomedicine. Traditional chemical exfoliation methods, such as the Hummers method, can effectively produce graphene oxide but involve harsh oxidizing agents and generate environmentally hazardous by-products, highlighting the need for more sustainable approaches. In this context, ionic liquid-assisted exfoliation of carbon materials has emerged as a promising alternative, providing both mild reaction conditions and improved stability of the exfoliated graphene sheets [1]. In this study, we investigated the exfoliation of graphite and carbon black using two ionic liquids (ILs), 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) and 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]). The materials were dispersed in the ILs and subjected to probe-type ultrasonic treatment for three hours, allowing the delamination of layered carbon structures into few-layer graphene sheets (Scheme 1). The ILs act as stabilizing media, preventing restacking and aggregation of the exfoliated sheets, thereby facilitating the formation of uniform dispersions suitable for subsequent applications. The exfoliated carbon materials were characterized to assess the degree of exfoliation and particle size using dynamic light scattering (DLS). This work demonstrates the potential of ILs as green exfoliating agents and stabilizers for carbon nanomaterials, offering a more environmentally friendly approach compared to conventional chemical methods.



Scheme 1. Exfoliation process for the different carbon sources.

Funding: This work is part of the following research projects: Ref. PID2023-150761OB-C21 funded by MICIU/AEI/10.13039/501100011033 and by FEDER, UE and Ref. 22129-PI-22 funded by the research support program of the Seneca Foundation of Science and Technology of Murcia, Spain. J.J. Delgado-Marín and J. León-García acknowledge support from the Juan de la Cierva contract (Ref. JDC2023-052774-I) and FPI contract (Ref. PID2023-150761OB-C21), respectively, funded by MICIU/AEI /10.13039/501100011033 and the FSE+.

[1] Freeman, J. S., Goloviznina, K., Li, H., Saunders, M., Warr, G. G., Pádua, A. A., & Atkin, R. *J. Ion. Liq.* **2021**, 1(1), 100001.

Sustainable Gypsum–Lime–Slag Binders: Overcoming the mechanical limits of gypsum

Mauro Mitsuuchi Tashima *[a], **Andrea Sanabria Tiscar**[b], **Sávio Alcântara** [c], **Luca Spiridigliozzi** [c], **Francisco José Castellón** [d], **David Navarro** [b], **Marcos Lanzón** [b]

[a] *Departamento de Ingeniería Minera y Civil, Universidad Politécnica de Cartagena, Paseo Alfonso XIII 52, 30203, Cartagena, Spain.*
[b] *Departamento de Arquitectura y Tecnología de Edificación, Universidad Politécnica de Cartagena, Calle Real 3, 30201, Cartagena, Spain.*
[c] *Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Via G. de Biasio 43, 03043, Cassino, Frosinone, Italy.*
[d] *Departamento de Estructuras, Construcción y Expresión Gráfica, Universidad Politécnica de Cartagena, Doctor Fleming s/n, 30202, Cartagena, Spain.*

E-mail: mauro.mtashima@upct.es

Portland cement is one of the most widely used construction materials worldwide. Cement manufacturing involves energy-intensive processes [1], which generate about 5-8% of anthropogenic CO_2 emissions [1,2]. Despite its environmental impact, Portland cement remains widely used across a broad range of building applications. In some cases, it is employed even where its use is not strictly essential, such as in exterior coatings, renders, and architectural finishes, thus further increasing its overall environmental footprint. Therefore, the development and implementation of sustainable binder systems with reduced emissions is an urgent issue. Creating sustainable binders with lower CO_2 emissions while maintaining adequate mechanical performance represents a key challenge for the construction sector and a critical step toward more environmentally responsible infrastructure.

This study evaluates the feasibility of developing a novel sustainable gypsum-lime-slag binder intended for use in exterior coatings, renders, and architectural finishes. The binder is designed to reduce CO_2 emissions in comparison with conventional Portland cement-based materials, while achieving adequate mechanical performance, surface hardness, and softening coefficient. Prismatic specimens with dimensions of 40 x 40 x 160 mm^3 were produced using different mass proportions of gypsum-lime-slag (100-0-0; 90-5-5; 80-5-15; and 65-5-30), with a constant water:binder ratio of 0.45. Mechanical mixing was performed for 1 minute, after which the fresh mixtures were compacted into molds. Mechanical testing was conducted after 7 and 28 days of curing. Flexural and compressive strengths were determined using a universal testing machine, while surface hardness was assessed using Shore C durometer equipment. Compared to gypsum plaster, the gypsum-lime-slag binders exhibited improved surface hardness, along with similar mechanical strength, mainly at early curing ages. Overall, the results indicate that gypsum-lime-slag binders represent a promising and sustainable alternative for exterior coatings, renders, and architectural finishing applications.

[1] K. Zhang, P. Shen, L. Yang, M. Rao, S. Nie, F. Wang, *J. Clean. Prod.* **2021**, 327, 129487.
[2] I.C. Carvalho, J.S. Andrade Neto, P.R. Matos, B. Lothenbach, A.P. Kirchheim, *Cem. Concr. Comp.* **2025**, 159, 105989.

Gypsum-lime–slag mortars as sustainable and durable alternatives to cement

Mauro Mitsuuchi Tashima [a], Andrea Sanabria Tiscar[b], Sávio Alcântara [c], Francisco José Castellón [d], Antonio J. Tenza-Abril [e], Victoria García-Vera [b], Juan Antonio Madrid [b], Marcos Lanzón [b*]

[a] Departamento de Ingeniería Minera y Civil, Universidad Politécnica de Cartagena, Paseo Alfonso XIII 52, 30203 Cartagena, Spain.
[b] Departamento de Arquitectura y Tecnología de Edificación, Universidad Politécnica de Cartagena, Calle Real 3, 30201 Cartagena, Spain.
[c] Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Via G. de Biasio, 43, 03043 Cassino, Frosinone, Italy.
[d] Departamento de Estructuras, Construcción y Expresión Gráfica, Universidad Politécnica de Cartagena, Doctor Fleming s/n, 30202 Cartagena, Spain.
[e] Departamento de Ingeniería Civil, Universidad de Alicante, San Vicente del Raspeig 03690 Alicante, Spain

E-mail: marcos.lanzon@upct.es

The transition towards low-carbon construction materials is a key challenge for green chemistry and sustainable materials design. The cement industry is widely reported as one of the largest industrial sources of CO_2 emissions worldwide and cement production contributes approximately 7-8 % of total global anthropogenic CO_2 emissions [1,2]. Preventing CO_2 emissions at source can be much more effective than decarbonisation strategies. This can be done by selecting raw materials that may notably reduce or even eliminate the cement demand and stimulate by-product valorisation (waste).

Limestone Calcined Clay Cement (LC3) are considered a promising low-carbon alternative to cement, but they also contain about 50% clinker and require calcination temperatures between 700 and 800 °C [3]. The present study investigates novel mortars made with limestone (40% w/w) and a ternary binder mixture based on gypsum, lime, and granulated blast furnace slag (60% w/w) delivering suitable mechanical performance. The materials are conceived for outdoor uses and do not contain cement, which significantly reduce their environmental footprint compared to conventional mortars and/or LC3 mixtures. The low firing temperatures of gypsum, the absence of cement and the valorisation of industrial by-products (slag), offer a resource-efficient and lower-CO_2 binding solution. Yet, a major disadvantage of gypsum is its limited rain durability, the reason why low doses of metallic soaps were used to repel water [4]. The water resistance performance was studied by absorption tests, contact angle measurements and ionic leaching. The results indicate a substantial reduction in water penetration, added contact angle and residence time of water droplets deposited on the surface. Even at this exploratory stage, the study provides strong evidence that gypsum-based ternary mortars may offer durable and greener alternatives to cement and LC3 materials in usual applications, such as coatings, renders, and plasters.

[1] S. Wu, Z. Shao, R.M, Andrew, R.M. et al, *Sci Data.* **2024**, 11, 1409.
[2] M. Hanifa, R. Agarwal, U. Sharma, P.C. Thapliyal, L.P. Singh, J. CO_2 Util. **2026**, 67, 102292.
[3] K. Hosen, B. Chen, J. Build. Eng. **2025**, 112, 113672.
[4] M. Lanzón, P.A. García-Ruiz, Constr. Build. Mater. **2009**, 23, 3287-3291.

Sustainable lignin recovery from tiger nuts waste via process intensification and bio-based solvents

Manuel Salgado-Ramos,[a,*] Alberto J. Huertas-Alonso,[b] Lucía López-Blanco,[c] Laura Hernández-García,[a] Pedro V. Martínez-Culebras,[a] Francisco J. Martí-Quijal, [a] Francisco J. Barba,[a] Albert Sebastià[a,*]

[a] Research group in Innovative Technologies for Sustainable Food (ALISOST), Department of Preventive Medicine and Public Health, Food Science, Toxicology and Forensic Medicine, Faculty of Pharmacy and Food Science, Universitat de València (UV), Burjassot, Spain
[b] Department of Chemistry, Stockholm University, SE-106 91, Stockholm, Sweden
[c] Food Hygiene, Inspection and Control Laboratory (LHICA), Department of Analytical Chemistry, Nutrition and Bromatology, Veterinary School, Campus Terra, Universidade de Santiago de Compostela (USC), Lugo, Spain

E-mail: manuel.salgado-ramos@uv.es

The increasing resistance of the current pathogenic agents exposes the need to develop new functional compounds with enhanced biological action. Lignin, a bio-based framework present in lignocellulosic biomass, puts forwards as a strong candidate for chemical, pharmaceutical, and biomedical applications. This work tackles a sustainable recovery of lignin from tiger nut (*Cyperus esculentus* L.) biomass and the assessment of its biological activity. Following Green Chemistry principles, a protocol that includes process intensification and bio-based solvents was implemented. Namely, high-pressure techniques such as Accelerated Solvent Extraction (**ASE**) were used in combination with natural deep eutectic solvents (**NaDES**). The methodology enabled a noted 50% delignification through the system choline chloride-lactic acid (ChLA). While this performance was maintained at major level of operation (41%). Cytotoxicity and antioxidant activity were assessed in CaCo-2 cell lines to determine the biological safety and potential biomedical applicability of the extracts. In addition, antibacterial potential was confirmed in presence of *S. aureus* and *S. entecus*. A sustainability assessment by **green chemistry metrics** such as eco-scale, PMP or E-factor confirmed the low environmental footprint of the methodology.

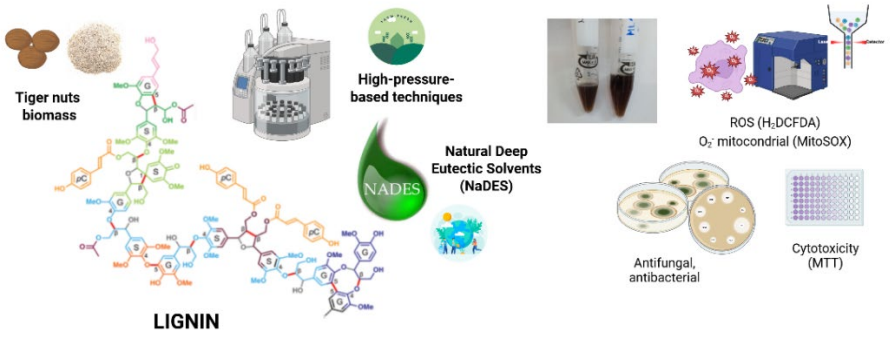


Figure 1. General overview of the study.

ACKNOWLEDGEMENTS: This study forms part of the research project AGROBIOMAT (Ref. **CIGE/2024/97**), supported by Generalitat Valenciana (GVA) through *Subvenciones para grupos de investigación emergentes* (2024 I+D program). The work is also supported by Banco Santander and Universitat de València (International Mobility Grant 2025). M. S-R expresses gratitude to GVA for financial support through APOSTD program (**CIAPOS/2023/236**).

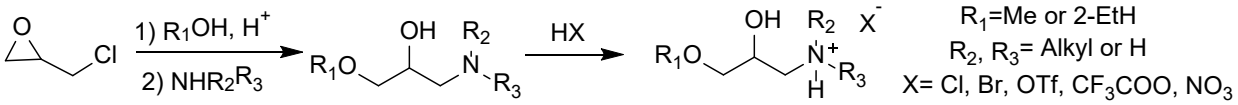
Tailored acid–base renewable solvents from glycerol: amines and protic ionic liquids

Carlos David Mur, Clara Isabel Herrerías,* and José María Fraile*

ISQCH (Universidad de Zaragoza-CSIC), Facultad de Ciencias, C/Pedro Cerbuna 12,50009 Zaragoza
E-mail: cmur@unizar.es

The transition towards a more sustainable chemical paradigm demands the integration of efficient catalytic processes with renewable resources. In this context, renewable-based solvents—commonly known as green solvents—are key to reduce the environmental footprint of chemical transformations [1]. Glycerol, an abundant by-product of biodiesel production, stands out as an attractive platform due to its availability, low cost, and versatile chemical structure. Glycerol-derived solvents have been extensively investigated by our research group owing to their remarkable chemical stability and the possibility of fine-tuning their physicochemical properties through structural modification [2]. Herein, we report the design and preparation of glycerol-derived amines and their corresponding protic ionic liquids (PILs).

A series of functionalized amines was synthesized through selective transformation of epichlorohydrin (produced from glycerol by Solvay's Epicerol®), enabling modulation of steric and electronic properties. Bio-based amines have been widely reviewed as key building blocks in sustainable chemistry, serving as reactive intermediates, organocatalysts, ligands, and monomers for advanced materials [3]. Subsequent protonation afforded protic ionic liquids (PILs) with tunable acid–base behavior. Protic ionic liquids have been extensively described as multifunctional media combining solvent and catalytic roles, with applications in catalysis, biomass valorization, separations, and electrochemical systems [4]. All compounds were fully characterized by NMR and MS analyses, confirming their structures and purity, and some of them have been tested in acid- or base-catalyzed organic reactions.



Scheme 1. Preparation of glycerol-derived amines and protic ionic liquids.

[1] F. G. Calvo-Flores, J. A. Dobado, J. Isac-García, F. J. Martín-Martínez, *Top. Curr. Chem.* **2018**, *376*, 18.
[2] A. Leal-Duaso, P. Pérez, J. A. Mayoral, J. I. García, E. Pires, *ACS Sustainable Chem. Eng.* **2019**, *7*, 13004–13014.
[3] V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault, B. Boutevin, *Chem. Rev.* **2016**, *116*, 14181–14224.
[4] J. Bailey, E. L. Byrne, P. Goodrich, P. Kavanagh, M. Swadźba-Kwaśny, *Green Chem.* **2024**, *26*, 1092–1131.

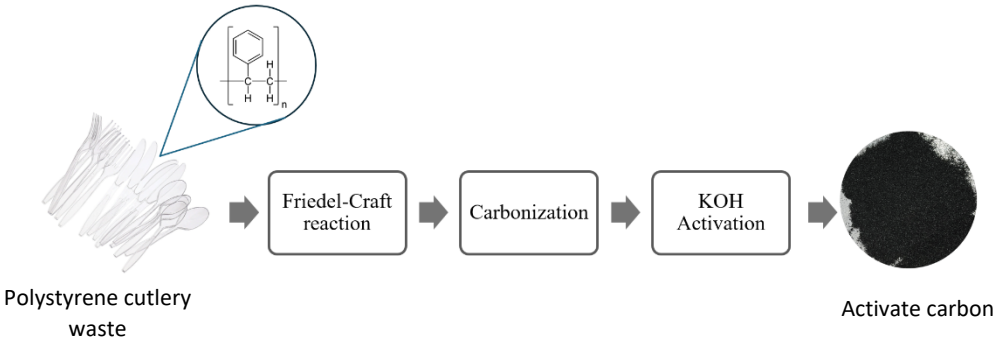
Conversion of post-consumer polystyrene into activated carbon for advanced functional applications

Panarat Rattanaphanee,*, Anuntita Juykrathok, Nareerat Seesuebma, Phimlada Kingcha, and Natnipa Boonpluk

School of Chemical Engineering, Institute of Engineering, Suranaree University of Technoloy Nakhon Ratchasima, Thailand

E-mail: panarat@sut.ac.th

Thailand, which normally generates over 2–3 million tons of plastic waste annually, has faced the worsening situation since the COVID-19 pandemic in 2020. Lockdown measures, hygiene concerns, and the rapid expansion of app-based food delivery services led to a marked increase in solid waste accumulation with single-use plastics including food packaging and disposable cutlery become one of the major contributors. This study explores the valorization of plastic waste into high-value functional materials through the synthesis of porous carbon from discarded polystyrene (PS) cutlery. A hyper-crosslinked polymer (HCP) derived from waste polystyrene was first prepared via Friedel–Crafts crosslinking reaction using ferric chloride as a reaction catalyst and dimethoxymethane as a crosslinker [1]. The resulting HCP was subsequently carbonized under a nitrogen atmosphere at 600°C before it was chemically activated with potassium hydroxide (KOH) at 800°C to obtain the highly porous activated carbon.



Scheme 1. Conversion of post-consumer polystyrene into activated carbon.

The pore structure of the synthesized activated carbons was characterized and found to be strongly governed by both the cross linker-to-PS (CL/PS) ratio and the heating rate. Increasing the crosslinker ratio enlarged the average pore diameter but significantly reduced micropore volume and micropore surface area, indicating that excessive crosslinking suppresses micropore development by forming a dense carbon framework. The CL/PS ratio of 2.7 produced the highest total BET surface area (2420.56 $m^2 g^{-1}$), demonstrating a balance between structural rigidity and activation accessibility. In contrast, increasing the heating rate from 2 to 5 °C min^{-1} consistently decreased micropore volume, micropore area, and total surface area, confirming that slower heating promotes more effective pore formation through controlled devolatilization and uniform activation. This work demonstrates a sustainable pathway to convert plastic waste into high-surface-area porous carbon suitable for advanced functional carbon applications.

[1] G. Gatti, M. Errahali, L. Tei, E. Mangano, S. Brandani, M. Cossi, L. Marchese, *Nanomaterials*, **2019**, 9, 726-737.

Subcritical water enabling the production of platform molecules and bioactive compounds from tiger nuts waste: A dual valorization strategy for chemical and food sector

Manuel Salgado-Ramos[a*], Noelia Pallarés[a*], Alberto J. Huertas-Alonso[b], Francisco J. Martí-Quijal[a], Juan Castagnini[a], Francisco J. Barba[a], and Albert Sebastià[a]

[a] *Research group in Innovative Technologies for Sustainable Food (ALISOST), Department of Preventive Medicine and Public Health, Food Science, Toxicology and Forensic Medicine, Faculty of Pharmacy and Food Science, Universitat de València (UV), Burjassot, Spain*
[b] *Department of Chemistry, Stockholm University, SE-106 91, Stockholm, Sweden*

E-mail: noelia.pallares@uv.es; manuel.salgado-ramos@uv.es

Tiger nuts (TN) represent a valuable food source in Mediterranean areas, such as Valencia. Albeit the production of *horchata* from TN generates a huge amount of discarded materials with a lignocellulosic composition that make them suitable for valorization. This study outlines a chemical upcycling of wasted TN through process intensification and clean solvents, in line with Green Chemistry principles. In particular, a processing with subcritical water (10 MPa, 100-200ºC) was proposed for sustainable, bidirectional production of platform molecules (PM) and bioactive compounds (BC). Conversion to PM or BC was strongly influenced by the experimental conditions, enabling a dual valorization pathway of interest in chemical and food sector. Regarding PM, higher temperatures (175-200ºC) favored the conversion to levulinic acid (LA) and 5-hydroxymethylfurfural (HMF), intermediates to synthetize fuels or materials. Alternatively, inferior temperatures (100-150ºC) boosted the production of BC. An in-depth assessment in terms of biological activity (antioxidant), nutritional profile (minerals), or food safety (heavy metals, cytotoxicity) was conducted to confirm the suitability of these crudes to develop novel functional compounds. Finally, Green Chemistry Performance Metrics (GCPMs) such as E-factor, PMP, or Eco-scale revealed the low environmental footprint associated to the protocol and support its industrial feasibility.

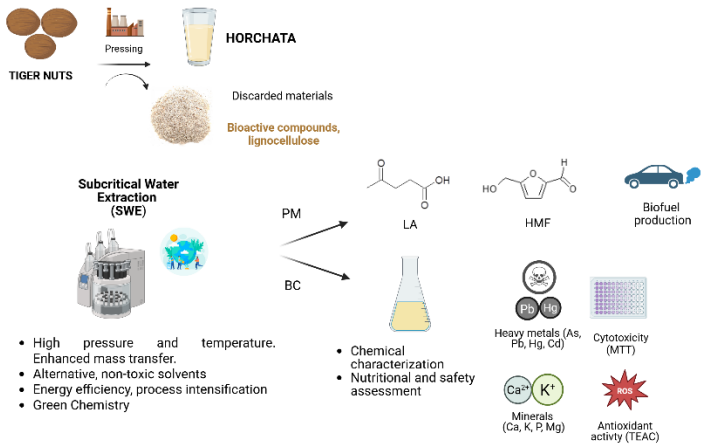


Figure 1. General overview of the work.

ACKNOWLEDGEMENTS: This work forms part of the research project AGROBIOMAT (Ref. **CIGE/2024/97**), supported by Generalitat Valenciana (GVA) (2024 I+D program). M. S-R expresses gratitude to GVA for financial support through APOSTD program (**CIAPOS/2023/236**).

Sustainable Lactone Production in a Micro-Aqueous Reaction System Using an Alcohol Dehydrogenase

Dominik Meißner[1,2], Sven Sörensen[3], Sonja Herres-Pawlis[3], Dörte Rother[1,2]

[1]Institute of Bio- and Geoscience 1: Biotechnology, Forschungszentrum Jülich GmbH, Jülich, Germany; [2]Aachen Biology and Biotechnology, RWTH Aachen University, Aachen, Germany; [3]Aachen Bioinorganic Chemistry, RWTH Aachen University, Aachen, Germany

Biocatalysts offer highly selective, biodegradable, and environmentally compatible solutions for sustainable chemical processes. To overcome the inherent limitations of aqueous media in lactone synthesis, we explored the oxidation of 1,5-pentandiol using an alcohol dehydrogenase in a Micro-Aqueous Reaction System (MARS), enabling enzymatic reactions in predominantly organic media with minimal water content.

In contrast to aqueous and biphasic reference systems, the use of MARS allows nearly complete conversion at 100 mM substrate concentration while effectively suppressing lactone hydrolysis. The biocatalyst maintained activity at elevated substrate loadings, and acetone-mediated cofactor regeneration enabled product titers up to 350 mM. Systematic evaluation identified solvent hydrophobicity as a key factor controlling enzyme performance and product stability under non-conventional conditions.

These results demonstrate that controlling water activity via the MARS overcomes intrinsic limitations of traditional biocatalysis, intensifies enzymatic lactone synthesis, and aligns with principles of green chemistry. The produced δ-valerolactone represents a renewable building block for biobased polymers, highlighting the platform's potential for sustainable material synthesis and integration with water-sensitive downstream chemical transformations.

IRED-catalysed reduction of pre-formed aromatic imines: Influence of organic co-solvents

Marisa Sánchez,[a] Stephan Vrabl,[a] Sarah Berger,[a] Serena Bisagni, Hans Iding,[b] Kurt Puentener,[b] Wolfgang Kroutil,[a] Joerg Schrittwieser*[a]

[a] *Institute of Chemistry, University of Graz: Heinrichstrasse 28, 8010 Graz, Austria*
[b] *F. Hoffmann-La Roche Ltd., Process Chemistry and Catalysis: Grenzacherstrasse 124, 4070 Basel, Switzerland*

E-mail: marisa.sanchez-quinteros@uni-graz.at, https://www.uni-graz.at

Chiral amines are important intermediates in the synthesis of biologically active molecules. [1]A straightforward method for producing these compounds involves the formation of a C=N bond by reacting carbonyl compounds with amines, followed by the selective reduction of the resulting imine. In this regard, the use of imine reductases (IREDs) and reductive aminases (RedAms) with NADPH as a hydride donor has shown great potential for the asymmetric reduction of C=N bonds,[2] crucially avoiding the reduction of the carbonyl group.

While the reduction of cyclic imines and the direct reductive amination of ketones and amines by IREDs and RedAms have been intensively explored, the reduction of pre-formed, open-chain imines by these enzymes has not been systematically studied yet. Despite their intrinsic sensitivity to hydrolysis in aqueous media, we have found that pre-forming imines before their reduction using IREDs leads to high conversion rates and excellent enantiomeric excess (*ee*). Particularly, for imines derived from aromatic ketones (*e.g.*, acetophenone) and aromatic amines (*e.g.*, aniline), this method generally offers better conversion compared to direct reductive amination (**Figure 1**).

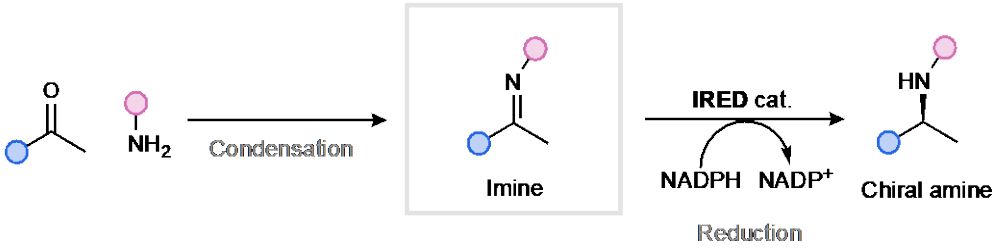


Figure 3. Imine preformation and biocatalytic imine reduction

In this study, we demonstrate that IRED-catalysed stereoselective reduction of chemically pre-formed imines is broadly applicable across a wide range of aromatic scaffolds. However, the intrinsic susceptibility of single-stabilised imines to hydrolysis in aqueous media remains a significant limitation. Consequently, the incorporation of co-solvents may offer an effective strategy to enhance reaction performance.

[1] D. Ghislieri, N. J. Turner, *Top. Catal.* **2014**, *57*, 284-300.
[2] A. K. Gilio, T. W. Thorpe, N. Turner, G. Grogan, *Chem. Sci.* **2022**, *13*, 4697-4713.

Synthesis and characterization of Ag and Cu dopped zeolites as potential catalysts for bioelectrochemical systems

Korichi Ferial[a,*], Nabila Bouchiba[a], Florencio Santos Cutillas[b], Víctor Manuel Ortiz-Martínez[c,*], María José Salar-García[*,b], Sergio Sánchez Segado[c]

[a]Laboratoire de Chimie des Matériaux L.C.M, Université Oran1 Ahmed Ben Bella, BP 1524, El-Mnaouer, Oran 31000, Algeria
[b]Department of Chemical and Environmental Engineering, Technical University of Cartagena (UPCT) member of European University of Technology EUT+, Campus Alfonso XIII, Aulario C, 30203, Cartagena, Spain
[c]Department of Chemical and Environmental Engineering, Technical University of Cartagena (UPCT) member of European University of Technology EUT+, Campus Muralla Del Mar, 30202, Cartagena, Spain

E-mail: korichiferial@outlook.com , mariajose.salar@upct.es

This work reports the synthesis of four Mazzite-type zeolites/M nanocomposites (M = Ag, Cu) prepared through a hydrothermal route [1] followed by ion exchange and chemical reduction with $NaBH_4$ to incorporate metallic nanoparticles into the zeolitic framework.

The resulting materials were comprehensively characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX), and X-ray photoelectron spectroscopy (XPS), confirming the preservation of the zeolitic structure and the successful dispersion of metal nanoparticles.

Their electrocatalytic performance was evaluated using rotating ring-disk electrode (RRDE) measurements in neutral and alkaline media, enabling determination of the electron transfer number and elucidation of the oxygen reduction reaction (ORR) pathway.

The findings indicate that these materials are promising catalysts for bioelectrochemical systems such as microbial fuel cells (MFCs) [2], owing to their demonstrated catalytic activity toward the ORR.

Acknowledgments

This work is supported by project PID2023-1510000A-I00 funded by MICIU/AEI/10.13039/501100011033 and by FEDER, EU.

[1] Z. Sun, Q. Shu, Q. Zhang, S. Li, G. Zhu, C. Wang, J. Zhang, H. Li, Z. Huang, *Separations* **2024**, 11, 39.
[2] A. Chaturvedi, P. P. Kundu, *ACS Appl. Mater. Interfaces* **2022**, 14, 33219-33233.

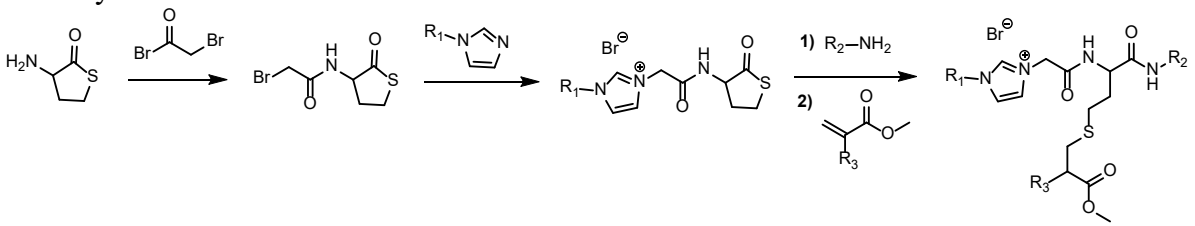
Pseudopeptidic ionic liquids as multifunctional platforms for biocatalysis and antibacterial

Samira Akki,[a] María Maciá,[a] Raúl Porcar,[a,b] Scott Mitchell,[c] Pedro Lozano[d] and Eduardo García-Verdugo[a,*]

[a] *Dept. of Inorganic and Organic Chemistry, Jaume I University, Av. Vicent Sos Baynat s/n, E-12071. Castellon, Spain.*
[b] *Dept. of Organic and Bio-Organic Chemistry, Faculty of Sciences, UNED, Avenida de Esparta s/n, 28232. Las Rozas-Madrid, Spain.*
[c] *Institute of Nanoscience and Materials of Aragon, R&D Building, Río Ebro Campus, Mariano Esquillor St. s/n, 50018 Zaragoza, Spain.*
[d] *Dept. of Biochemistry and Molecular Biology B and Immunology. Faculty of Chemistry, University of Murcia. Campus de Espinardo, E-30100, Murcia, Spain.*

E-mail: al410025@uji.es

Ionic liquids (ILs) constitute a versatile platform for the design of functional materials due to the high tunability of their molecular structure, which allows precise modulation of their physicochemical properties for specific applications. Recently, ILs have attracted increasing attention as bioactive systems, particularly for antibacterial and biocatalytic applications [1]. In this work, new orthogonal synthetic strategies are developed for the preparation of Psp-ILs (pseudopeptidic units–ionic liquids) and Psp-PILs (pseudopeptidic units–polymeric ionic liquids) [2], using click chemistry methodologies, specifically thiol–ene and thiol–yne reactions. These efficient and modular approaches enable the synthesis of new families of compounds with well-defined architectures and tunable amphiphilic properties [3]. From a biocatalytic perspective, the amphiphilic nature of these systems promotes self-assembly in aqueous media into micellar aggregates, generating IL-based microenvironments capable of stabilizing and immobilizing enzymes while maintaining their catalytic activity and facilitating the transformation of hydrophobic substrates. In parallel, the antibacterial activity of the synthesized compounds was evaluated against *E. coli* and *B. subtilis*, showing, in some cases, excellent antibacterial performance (MIC = 32 µg/mL, MBC = 8 µg/mL). Overall, these results highlight the potential of Psp-ILs and Psp-PILs as multifunctional platforms for applications in biocatalysis and antimicrobial materials.



Scheme 1. Synthetic route for ILs derived from DL-homocysteine thiolactone.

Acknowledgements: This work is part of the project PID2022-142897OA-I00 funded by MCIN/AEI/10.13039/501100011033, the project CPP2023-010883 funded by MCIN/AEI/10.13039/501100011033/ FEDER, UE, and the project PID2024-159264OB-C21 funded by MCIN/AEI/10.13039/501100011033.

[1] K.S. Egorova, E.G. Gordeev, V.P. Ananikov. *Chem. Rev.*, **2017**, *117*, 7132-7189.
[2] D. Valverde, I. Muñoz, E. García-Verdugo, B. Altava, S.V. Luis. *Polymers*, **2021**, *13*, 3110.
[3] Greaves, T. L.; Drummond, C. J., *Chem. Soc. Rev.*, **2008**, *37*, 1709-1726.

CaLB Immobilization on ZIF-8 towards Green Synthesis

Álex Fernández[a], Eduardo García-Verdugo[a]* and Pedro Lozano[c]*

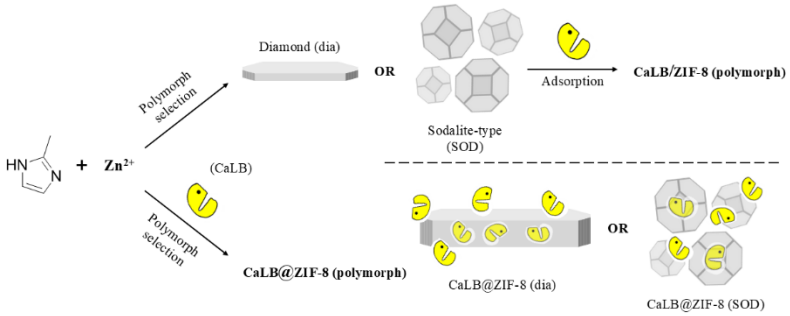
[a] *Universitat Jaume I, Inorganic and Organic Chemistry Department: Av. Vicent Sos Baynat, s/n, Castelló de la Plana, Spain.*
[b] *University of Murcia, Biochemistry and Molecular Biology and Immunology "B" Department: C. Campus Universitario, 5, Epinardo, Spain.*

E-mail: aleferna@uji.es

Rising ecological concerns have driven a paradigm shift in both the chemical industry and academia towards the sustainable production of chemicals. Subsequently, new and greener ways to perform chemical transformations must be developed under the framework of the 12 Principles of Green Chemistry [1]. In this context, immobilized biocatalysis offers key advantages due to its unparalleled selectivity and enhanced stability, making it a robust and powerful tool for green organic synthesis [2].

In this regard, this work focuses on the study of structural and biocatalytic features of the resulting biocomposites from the combination of the readily tuneable supporting material zeolitic imidazolate framework 8 (ZIF-8) and the biocatalyst *Candida antartica* lipase B (CaLB). Enzyme immobilization was achieved by following two main strategies: adsorption and entrapment (biomineralization). Biocomposite structures were characterized by ATR-FTIR and PXRD measurements and SEM imaging. Catalytic performance was evaluated by performing two model transesterification reactions using either non-chiral and chiral substrates (geraniol and (±)-1-phenylethanol, respectively) and an activated ester (vinyl propionate). Furthermore, enzyme structural integrity was examined by ATR-FTIR amide I band analysis.

Results show that the highest immobilization yields were obtained from using low concentrations and molar relationships of ZIF-8 precursors in solution whereas buffered media at pH 8.5 and tris buffer presence at low concentrations promotes biocomposite formation and CaLB structural preservation. High thermal stability is also achieved with great activity retention upon incubation in cyclohexane at 80ºC.



Scheme 1. CaLB immobilization approaches in ZIF-8 phases.

Grant PREP2024-002859 funded by MICIU/AEI/10.13039/501100011033 and, as appropriate, by "ESF+".

[1] R. A. Sheldon, J. M. Woodley. *Chem. Rev.* **2018**, *118*, 801–838.
[2] R. A. Sheldon. *Catal. Today.* **2024**, *431* ,114571.

Racemization-free L-proline amidation in organic media using ammonia

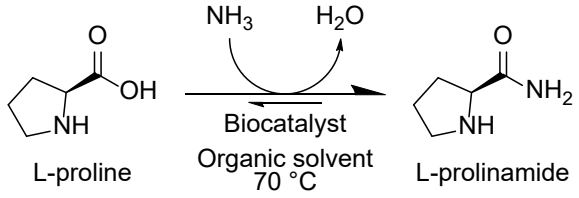
Julia Pitzer,[a] Magdalena Abramiuk,[a,d] Kerstin Steiner,[a] Christian Schmid,[a] Karl Gruber,[b] Anton Glieder[c] and Wolfgang Kroutil*[,a,d]

[a]acib GmbH, Krenngasse 37, 8010 Graz, Austria
[b]Institute of Molecular Biosciences, University of Graz, 8010 Graz, Austria
[c]Institute of Molecular Biotechnology, Graz University of Technology, 8010 Graz, Austria
[d]Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria

E-mail: magdalena.abramiuk@acib.at

The amide moiety is prevalent in many commercial pharmaceuticals, agrochemicals, and polymers, as well as in nature in peptides and proteins.[1] New and efficient amidation methods are therefore continuously in demand for industrial applications, especially as many currently utilized approaches require substrate activation and suffer from significant disadvantages regarding process sustainability and scalability.[2, 3, 4]

The aforementioned challenges were addressed in this work using biocatalysis. A racemization-free, enzyme-catalyzed method for unprotected L-proline amidation using ammonia in organic solvent was developed and optimized.[5]



Scheme 1. Enzymatic amidation of L-proline in organic solvent with ammonia, forming L-prolinamide and water.

At 145 mM substrate loading, conversions up to 80% were achieved using an immobilized CalB variant (CalBopt-24 T245S) as a catalyst in 2-methyl-2-butanol at 70 °C. The product was obtained with excellent optical purity (ee >99%). The use of a stable immobilized biocatalyst in the process allowed for a significant atom economy improvement as compared to chemical methods. The developed biocatalytic approach avoids the use of halogenated solvents, simultaneously minimizing racemization and the amount of waste produced.

[1] J. Pitzer. K. Steiner, *J. Biotechnol*. **2016**, *235*, 32–46.
[2] H. Lundberg, F. Tinnis, N. Selander, H. Adolfsson, *Chem. Soc. Rev*. **2014**, *43*, 2714–2742.
[3] M. Lubberink, W. Finnigan, S. L. Flitsch, *Green Chem*. **2023**, *25*, 2958-2970.
[4] D. J. C. Constable, P. J. Dunn, J. D. Hayler, G. R. Humphrey, J. J. L. Leazer, R. J. Linderman, K. Lorenz, J. Manley, B. A. Pearlman, A. Zaks and T. Y. Zhang, *Green Chem.* **2007**, *9*, 411–420.
[5] J. Pitzer, K. Steiner, C. Schmid, V. K. Schein, C. Prause, C. Kniely, M. Reif, M. Geier, E. Pietrich, T. Reiter, P. Selig, C. Stückler, P. Pöchlauer, G. Steinkellner, K. Gruber, H. Schwab, A. Glieder, W. Kroutil, *Green Chem.* **2022**, *24*, 5171–5180.

Exploring the performance of High Entropy Oxides as catalyst for selective oxidation of alcohols.

José Luis Serrano,[a]* Sávio Alcântara,[b] Luca Spiridigliozzi,[b] Francisco Cirujano, [c] Nuria Martín, [c] Ágata Karkosik, [c] José Pérez. [a]

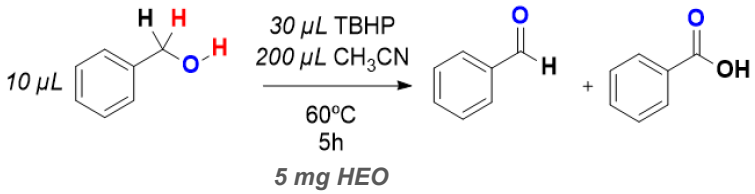
[a]Universidad Politécnica de Cartagena member of European University of Technology EUT+, Department of Chemical Engineering, Campus Muralla, 30202 Cartagena, Spain.
[b]University of Cassino and the Southern Lazio member of European University of Technology EUT+, Department of Civil and Mechanical Engineering, , Via G. Di Biasio, Cassino, Italy.
[c]Department of Inorganic and Organic Chemistry, Universitat Jaume I, Castelló de la Plana, Castelló, Spain.

E-mail: jose.serrano@upct.es

High Entropy Oxides (HEOs) are a new class of ceramic materials produced using entropy as a driving force, consisting of 5 or more components in a single-phase solid solution. Since their discovery, their concept is being extended to systems as fluorites, bixbyites and perovskites, among others.[1]

By alternating their potential composition and ratios of metals used, their properties can be tuned. HEOs started to be applied for catalysis due to advantages as tailorable compositional matrices and multi-active site interactions, with homogenization of metallic constituents. Their characteristic multi-component presence in the same lattice and the oxygen effect (due to the lattice distortion) contribute to the catalytic advantages of these materials.

Following the Pechini method for the synthesis of advanced ceramics, a selection of HEOs containing elements such as Mg, Co, Ni, Cu, and Zn have been prepared and tested as catalytic systems. The oxidation of alcohols has been the targeted reaction using conditions as displayed in Scheme 1, which allow obtaining the corresponding aldehyde with quantitative yields under mild conditions.



Scheme 1. Representative alcohol oxidation under study.

[1] L. Spiridigliozzi, M. Biesuz, V.M. Sglavo, G. Dell'Agli, *Journal of the European Ceramic Society*, **2024**, *44*, 2223-2232.

Green Bioproduction and Bioactivity of Novel Trehalose Glycolipids as Promising Sustainable Therapeutic Agents

Maria H Ribeiro,[a*] André Teixeira,[a+] Lucio Mauro[a+], Célia Faustino[a]

[a] *Research Institute for Medicines, Faculty of Pharmacy, Universidade de Lisboa, Av.Gama Pinto, Lisboa, Portugal*

Email: mhribeiro@ff.ulisboa.pt

Growing global environmental concerns are driving research toward the development of sustainable, eco-friendly alternatives to polluting chemicals. Trehalose lipids (TLs) are glycolipid biosurfactants distinguished by their high surface activity, biodegradability, low toxicity, and antimicrobial properties. Structurally, TLs consist of a non-reducing disaccharide in which two glucose units are linked through an α,α-1,1-glycosidic bond. Owing to these features, TLs have attracted increasing interest for applications as emulsifiers, foaming agents, wetting agents, solubilizers, and antimicrobial agents in the pharmaceutical, cosmetic, and food industries.

This work aimed to optimize both the production and downstream processing of TLs to enhance their biological activity and overall process sustainability. New microbial sources, cultivation conditions, medium compositions, purification strategies, and physicochemical properties were systematically investigated.

TLs can be produced by various microorganisms from renewable resources under controlled cultivation conditions. However, production yields are strongly influenced by parameters such as carbon and nitrogen sources and their ratio (C/N). In addition, downstream processing, particularly purification, remains a major bottleneck for bioprocess implementation.

At the microscale level, TL production was successfully achieved using *Rhodotorula* sp. under different culture conditions, including glucose-based media and salt media supplemented with glucose and *n*-hexadecane. The influence of the C/N ratio on biosurfactant production was evaluated. Liquid extraction and ultrasound were employed for compound recovery, followed by characterization using UHPLC.

This study identifies *Rhodotorula* sp. as a promising and sustainable trehalose lipid producer, exhibiting enhanced productivity and highlighting its potential as a green biocatalytic platform for bio-based surfactant production from renewable resources within a circular bioeconomy framework.

Biocatalytic synthesis of new bioactive compoundswith merged properties

Susana Nieto,[a*] Maite Nuño,[a] Francisco J. Ruiz,[a] Rocío Villa,[a] Pedro Lozano[a,*]

[a] Departamento de Bioquimica y Biologia Molecular B e Inmunologia, Facultad de Quimica, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain.

E-mail: susanani@um.es

Concerns regarding the efficiency, safety, and environmental impact of everyday consumer products have stimulated the search for new molecules, primarily derived from natural feedstocks, to replace those conventionally synthesized. Within this context, the cosmetic industry is at the forefront of developing novel compounds that deliver outstanding performance while meeting strict requirements of safety and sustainability.[1]

Herein, we report for the first time the synthesis of a dual-function molecule that combines the bioactive properties of panthenol (pro-vitamin B5; hydrating, moisturizing, and wound-healing) [2] and hydrocaffeic acid (HCaF; antioxidant and UV-filtering agent)[3]. Careful selection of the reaction medium proved crucial to overcoming the high melting point and hydrophilicity of both substrates, thereby enabling the biocatalytic transformation to proceed under mild conditions (60 °C, 8 h) with high efficiency (70% yield and 88 μmol mg^{-1} N435 h^{-1}).

Importantly, the bioactivities of the parent compounds were preserved in the final product, which exhibited excellent free radical scavenging and iron-reducing capacities. Furthermore, the rational design of the reaction medium enabled the isolation of the pure product with minimal waste generation, highlighting the remarkable sustainability of the process, as assessed through different green metrics (AE, SF, E-f, PMI, TCR).

[1] https://cosmeticseurope.eu/key-actions/driving-sustainability/ (accessed on March 2026)

[2] P. Lozano, E. Alvarez, S. Nieto, R. Villa, J. M. Bernal, A. Donaire. *Green. Chem*. **2019**, 21, 3353-3361.

[3] S. Nieto, F. Martínez-Mora, I. Lozano, F. Ruiz, R. Villa, P. Lozano, P., *Catal. Tod.* **2024.** 114500.

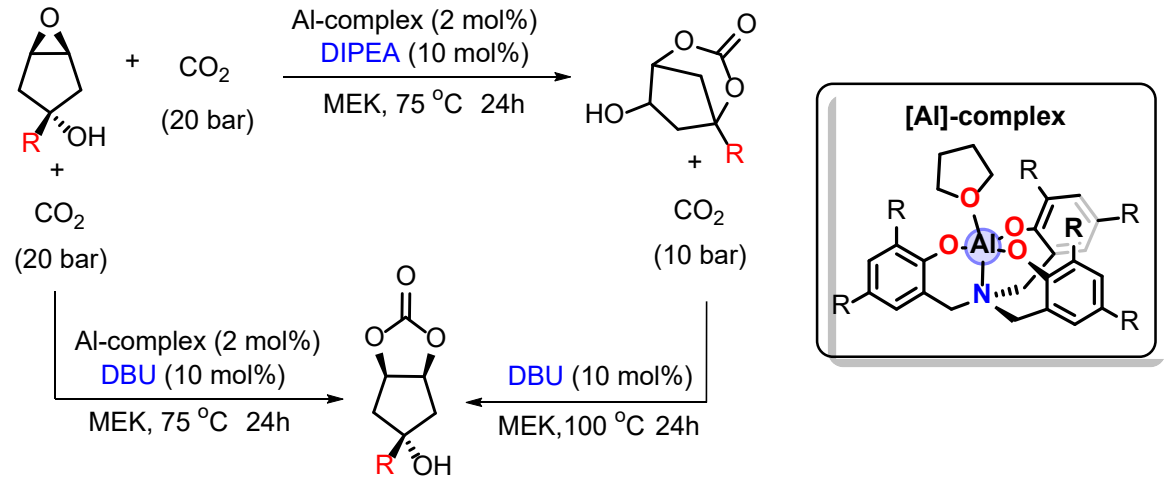
Halide-Free Heterocyclic Divergence from Carbon Dioxide Enabled by a Binary Lewis Acid/Base Catalyst

Chenyang Chang [a] **and Arjan W. Kleij** [a, *]

[a] *Institute of Chemical Research of Catalonia (ICIQ-Cerca), Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain*
* *Catalan Institute for Research and Advanced Studies (ICREA), Pg. Lluis Companys 23, 08010 Barcelona (Spain)*

E-mail: cchang@iciq.es

A new catalytic process has been developed for the coupling of cyclic epoxides and CO_2 affording either five- or seven-membered bicyclic carbonates. *Anti*-configured epoxides equipped with a *beta*-positioned OH group can be transformed into structurally diverse bicyclic cyclic carbonates in good yields and with high chemoselectivity. Key to the latter is the difference between the reactivity of *syn*- and *anti*-configured epoxy alcohols, and the control that is exerted by the base catalyst. Five-membered ring products are favored in the presence of a binary Al^{III}-aminotriphenolate/DBU dual catalyst, and seven-membered bridged ring carbonates after replacing DBU by DIPEA under similar process conditions.



[1] M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2014**, *4,* 1893–1896.
[2] C. Qiao, A. Villar-Yanez, J. Sprachmann, B. Limburg, B. Carles, A. W. Kleij, *Angew. Chem. Int. Ed.* **2020**, *59,* 18446–18451.
[3] C. Qiao, W.-Y. Shi, A. Brandolese, J. Benet-Buchholz, E.-C. Escudero-Adan, A. W. Kleij, *Angew. Chem. Int. Ed.* **2022**, *61,* e202205053.
[4] W.-Y. Shi, J. Benet-Buchholz, A. W. Kleij, *Nat. Commun.* **2025**, *16,* 1372.
[5] C.-Y. Chang, S. G. E. Amos, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2025**, *27,* 6794−6799.

Mesoporous Silica-Supported Palladium Catalysts Functionalized with Ionic Liquids for Aqueous CO_2 Hydrogenation under Mild Conditions

Marc Cuesta-Álvaro[a], Francisco G. Cirujano[a], Eduardo García-Verdugo[a], Raúl Porcar[b], **Nuria Martín***[a]

[a] Department of Inorganic and Organic Chemistry, Universitat Jaume I, Castelló de la Plana, Castelló, Spain; [b] Departamento de Química Orgánica y Bio-orgánica, Facultad de Ciencias, Universidad Nacional de Educación a Distancia (UNED), Las Rozas, Madrid, Spain

E-mail: numartin@uji.es

A series of palladium-based catalysts were synthesized by grafting a silylated imidazolium ionic liquid onto two types of silica supports: mesoporous SBA-15 and commercial silica. [1] The ionic liquid served as both a stabilizing matrix and anchoring platform for palladium ions, introduced via aqueous impregnation (Figure 1). The influence of support activation temperature, reduction treatment, and textural properties on catalytic performance was systematically studied. Catalysts were tested in the aqueous-phase hydrogenation of CO_2 to formic acid under mild conditions (40 bar H_2/CO_2, room temperature). SBA-15-based catalysts showed superior performance, achieving up to 50 $mol_{HCOOH} \cdot mol^{-1}_{Pd} \cdot h^{-1}$ — over three times higher than the flash silica counterpart. High support surface area and pore volume enabled greater ionic liquid loading and palladium dispersion, as confirmed by TEM, SEM-EDX and ICP analyses. Pre-reduction with $NaBH_4$ eliminated induction periods in the kinetic profile and further enhanced activity, whereas no such improvement was observed for flash silica, likely due to palladium aggregation.

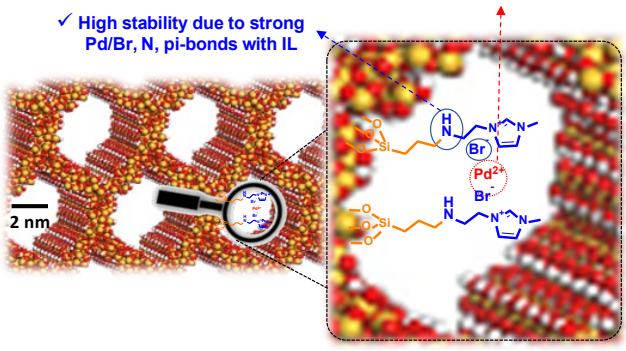


Figure 1. Isolated palladium sites on ionic liquid functionalized mesoporous silica.

[1] Martín, N.; Porcar, R.; Serrano, J. L.; Pérez, J.; Lozano, P.; Cirujano, F. G.; García-Verdugo, E. *ChemSusChem* **2024**, *18*, 1, e202401192.

Design of novel amino acid-derived macrocyclic organometallic complexes with applications in green chemistry

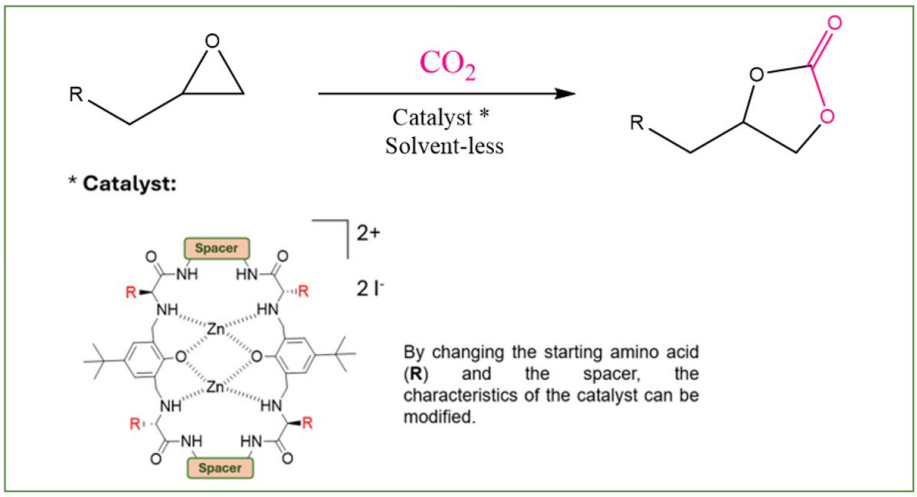
Juan Chiva,[a] Belén Altava,[a]* Julián Sáchez-Velandia,[a] and Eduardo García-Verdugo[a]*

[a]*Department of Inorganic and Organic Chemistry, Jaume I University, Av. Vicent Sos Baynat, s/n, 12071, Castelló de la Plana, Spain*

E-mail: jcelades@uji.es

The continuous increase of carbon dioxide emissions into the atmosphere has intensified research efforts aimed at its capture, activation, and transformation into value-added chemicals.[1] Within the range of available strategies for CO_2 utilization, the development of efficient catalytic systems for the production of cyclic carbonates has attracted significant attention.[2] Our group has previously shown that these complexes exhibit outstanding catalytic performance under mild reaction conditions in the cycloaddition of CO_2 to epoxides, without the need for additional co-catalysts (Scheme 1).[3]

Based on these results, this study proposes the modification of the organometallic catalyst to improve its catalytic performance, as well as the exploration of new green chemistry model reactions in which these catalysts could be applied.



Scheme 1. Zn-based macrocyclic catalysts for the cycloaddition of CO_2 to epoxides.

Acknowledgements

Proyecto PID2024-159264OB-C21 financed by MCIN/AEI/10.13039/501100011033, and the CIACIF program financed by Generalitat Valenciana and ESF+ from European Union.

[1] N. M. Cavalleri, N. Panza, A. di Biase, G. Tseberlidis, S. Rizzato, G. Abbiati, A. Caselli. Eur. *J. Org. Chem*. **2021**, 19, 2764-2771.
[2] K. Takaishi, B. D. Nath, Y. Yamada, H. Kosugi, T. Ema. Angew. Chem. Int. Ed. **2019**, 58, 9984-9988.
[3] F. Esteve, R. Porcar, M. Bolte, B. Altava, S. V. Luis, E. García-Verdugo. Chem Catal. **2023**, 3, 100482.

Experimental Assessment of Cu-Based Electrodes for High-Efficiency Alcohol Production via Continuous CO_2 Electroreduction

Jose Antonio Abarca[a], Felicia Di Costola,[b] Juqin Zeng,[b] Angel Irabien[a] and Guillermo Díaz-Sainz,[a,*]

[a]Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Av. de los Castros s/n, 39005 Santander, España

[b]Department of Applied Science and Technology (DISAT), Politecnico di Torino, Italy.

E-mail: abarcaja@unican.es

Carbon capture, storage, and utilization technologies have emerged as key strategies for industrial decarbonization. Among utilization pathways, the electrochemical reduction of CO_2 (CO_2RR) into value-added chemicals is particularly attractive. In this context, alcohols such as ethanol and propanol stand out due to their high industrial relevance and energy density [1]. This work investigates continuous CO_2 electroreduction in a filter-press reactor using Cu electrodes synthesized by cathodic sputtering with different deposition times (Cu100, Cu200, Cu400, Cu600, and Cu800). The primary objective is to evaluate how surface morphology influences catalytic selectivity and Faradaic efficiency (FE) toward oxygenated C_2+ products, particularly ethanol (C_2H_6O) and propanol (C_3H_8O) (C_3H_8O) [2].

Electrochemical tests were performed at current densities ranging from 45 to 200 $mA \cdot cm^{-2}$, using a Sustainion anion-exchange membrane and a 1 M KOH aqueous electrolyte. The results demonstrate a strong correlation between electrode morphology and catalytic performance. The Cu800 electrode, characterized by a highly rough and porous surface, achieved FEs of 32.2% for ethanol and 4.3% for propanol at 45 $mA \cdot cm^{-2}$, evidencing enhanced activity toward oxygenated products. In contrast, Cu200 and Cu600 exhibited higher selectivity toward ethylene (C_2H_4), reaching FEs between 25% and 46% at 90 and 200 $mA \cdot cm^{-2}$. These findings suggest that surfaces with intermediate roughness favor CO desorption and subsequent C-C coupling in the gas-phase coupling. Meanwhile, less developed morphologies such as Cu400 showed a greater tendency toward C_1 products, indicating limited capability to sustain multi-electron and C–C coupling pathways.

Current density also played a decisive role in product distribution. At low currents, the hydrogen evolution reaction (HER) predominated. Alcohol production was maximized at intermediate current densities (45–90 $mA \cdot cm^{-2}$), whereas operation at 200 $mA \cdot cm^{-2}$ led to decreased overall efficiency due to CO_2 mass-transport limitations and increased ohmic losses.

In summary, porous Cu electrodes demonstrate significant potential for the selective production of C_{2+} compounds via continuous CO_2 electroreduction. The use of a filter-press reactor enabled stable and reproducible operation, representing a meaningful step toward industrial scalability. Future work will focus on further tuning surface morphology to enhance ethylene selectivity and evaluating alternative ion-exchange membranes to optimize system performance and energy efficiency.

Acknowledgements

The authors gratefully acknowledge financial support through project PDC2025-165116-I00 (MICIU/AEI/10.13039/501100011033). Jose Antonio Abarca gratefully acknowledges the predoctoral research grant (FPI) PRE2021-097200.

[1] M. Rumayor, A. Domínguez-Ramos, A. Irabien, *J. Clean. Prod.,* **2019**, 225, 426-434.

[2] N.B.D. Monti, G.A. El-Nagar, F. Di Costola, S. Gupta, M.T. Mayer, C.F. Pirri, J. Zeng, *Mat. Today Sustain*., **2025**, 30, 101124.

Towards stable photoelectrochemical glycerol oxidation coupled with CO_2 reduction using Ni-decorated photoanodes

Sara Crespo[a], Ivan Merino-Garcia[a], Jose Antonio Abarca[a,*], Elena Bujedo-Saiz[b], Jose Solla-Gullón[b], Jonathan Albo[a]

[a]*Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, España.*

[b]*Instituto de Electroquímica, Universidad de Alicante, Apdo. 99, E-03080 Alicante, España.*

**E-mail: joseantonio.abarca@unican.es*

Replacing the oxygen evolution reaction (OER) with glycerol oxidation (GOR) is a promising strategy to enhance the Full Energy Efficiency (FEE) of photoelectrochemical (PEC) CO_2 conversion systems [1]. The aim of this work is to develop stable multilayer photoanodes, decorated with Ni, for efficient GOR coupled with CO_2 reduction to formate ($HCOO^-$) at a dark Bi/C gas diffusion cathode. The multilayered photoelectrodes are composed of commercial semiconductor materials ($BiVO_4$, WO_3 and $CaTiO_3$) [2], decorated with Ni nanoparticles synthesized via an ethanol-based chemical reduction method, and fabricated by automated deposition, ensuring uniform material deposition. PEC characterization (CP, LSV, and EIS) is performed in a filter-press flow cell under visible light illumination (100 mW cm^{-2}) [3], and anodic (DHA, GLAD, ACET, GLYA, $HCOO^-$) and cathodic ($HCOO^-$) products are quantified by HPLC and ion chromatography.

At constant 45 mA cm^{-2}, the photoanodes allows reaching a FEE of 60.1%, producing DHA (184.8 µmol m^{-2} s^{-1}) together with GLAD, ACET, GLYA and $HCOO^-$, while a cathodic $HCOO^-$ production rate of 2200 µmol m^{-2} s^{-1} is obtained after 1 h of continuous operation. Stability analyses show a slight decrease in DHA production rate after 8 h of continuous operation (~11%) with an anodic FE of ~30%. The $HCOO^-$ production rate at the cathode decreases by ~19% with a cathodic FE of 77%. The required cell potential, however, doubled from the initial 4.5 V, resulting in a ~50% decrease in the FEE (Figure 1). This higher overpotential is attributed to surface photoelectrode modifications [4], whose optimization is currently ongoing.

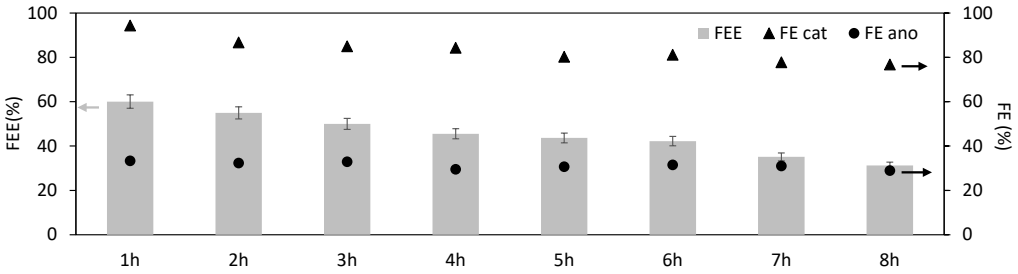


Figure 4. FEE and FEs during 8 h of continuous operation.

Acknowledgements

Grants PID2022-138491OB-C31 and PID2022-138491OB-C32 funded by MICIU/AEI/10.13039/501100011033 and by ERDF/EU. Ivan Merino-Garcia also acknowledges Grant RYC2023-043378-I, funded by MICIU/AEI/10.13039/501100011033 and by ESF+.

[1] K. Fernandez-Caso, A. Peña-Rodríguez, J. Solla-Gullón, V. Montiel, G. Díaz-Sainz, M. Álvarez-Guerra, Á. Irabien, *J. CO2 Util.* **2023**, 70, 102431.

[2] I. Merino-Garcia, S. Crespo, M. Perfecto-Irigaray, G. Beobide, A. Irabien, J. Albo, *Catal. Today* **2024**, 432, 114581.

[3] S. Crespo, I. Merino-Garcia, M. Perfecto-Irigaray, G. Beobide, J. Albo, *J. Environ. Chem. Eng.* **2025**, 13, 118854.

[4] G. Wang, Y. Ling, X. Lu, T. Zhai, F. Qian, Y. Tong, Y. Li, *Nanoscale* **2013**, 5, 4129.

Magnetically enhanced CO_2 electroreduction to ethanol using MOF-based catalysts

Jose Antonio Abarca,[a] Mariana Ferreira,[b] Rodrigo Hernández,[c] Sara Realista,[b] Paulo Nuno Martinho,[b] , Jenifer Gómez-Pastora[c], Angel Irabien[a] and Guillermo Díaz-Sainz[a,*]

[a] *Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Avenida de los Castros s/n, Santander, 39005, Spain*
[b] *Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Lisboa, 1749-016, Portugal*
[c] *Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*
E-mail: diazsg@unican.es

The electrochemical reduction of CO_2 ($ERCO_2$) is a promising strategy within the circular carbon economy. However, its practical implementation remains limited by challenges such as low selectivity toward multi-carbon products (e.g., alcohols) and competition with the hydrogen evolution reaction (HER) [1].

This work investigates metal–organic framework (MOF)-based catalysts, specifically Ni-MOF-74 and Mg-MOF-74, evaluating their performance in a flow-cell configuration and assessing the effect of external magnetic fields on ethanol production [2,3].

In the flow-cell system, both MOFs produced ethanol, though with distinct behaviours. Experiments were conducted under galvanostatic control at current densities of –3, –6, and –9 $mA \cdot cm^{-2}$, using 0.5 M $KHCO_3$ as the recirculating catholyte and 1 M KOH as the anolyte. Ni-MOF-74 exhibited superior stability and selectivity, achieving a Faradaic efficiency (FE) of 29.8 % at –3 $mA \cdot cm^{-2}$, whereas Mg-MOF-74 showed a pronounced decrease in performance with increasing current density.

The application of an external magnetic field led to markedly different outcomes for the two materials. Mg-MOF-74 showed no significant change, whereas Ni-MOF-74 experienced a dramatic enhancement in ethanol selectivity. At –3 $mA \cdot cm^{-2}$ under the magnetic field, the FE increased from 29.8 % to 83.4 %, representing a threefold increase in ethanol production. These findings demonstrate that $ERCO_2$ selectivity and efficiency can be significantly improved through MOF-based catalysts and magnetic field application. Ni-MOF-74, in particular, performed well under mild conditions and benefited substantially from the magnetic field.

The results suggest that spin-related effects may promote reaction pathways leading to C_2^+ products. The galvanostatic operation rules out magnetic effects on charge transport, indicating that the enhanced performance is not due to magnetohydrodynamic (MHD) phenomena. Instead, spin-state effects, strongly influenced by the central metal ion, are the likely origin of the improved selectivity observed for Ni-MOF-74.

Acknowledgements

This research was funded by CETPartnership, under the 2023 joint call for research proposals (CETP-FP-2023-00378), co-funded by the European Commission (GA N°101069750) and with the funding provided by the Spanish Research Agency through project PCI2024-155027-2, funded by MICIU/AEI/10.13039/501100011033. Jose Antonio Abarca gratefully acknowledges the predoctoral research grant (FPI) PRE2021-097200.

[1] S. Dongare, N. Singh, H. Bhunia, P. K. Bajpai, & A. K. Das. Electrochemical reduction of carbon dioxide to ethanol: A review. ChemistrySelect, **2021,** 6(43), 11603–11629
[2] C. González-Fernández, G. Díaz-Sainz, A. Gutierrez-Carballo, E. Bringas, I. Ortiz, G. G. Botte, J. Gomez-Pastora, *ACS Sustain. Chem. Eng.* **2024**, 12, 3390–3401.
[3] J. A. Abarca, X. Wu, C. González-Fernández, I. H. Karampelas, A. Gutiérrez-Carballo, J. A. Gauthier, G. G. Botte, J. Solla-Gullon, G. Díaz-Sainz, Á. Irabien, J. Gomez-Pastora, *Chem. Eng. J.* **2025**, 515, 163614.

Monoethanolamine-assisted Cu/Cu_2O composites for efficient CO_2 electroreduction to formate

Paulo Henrique Eleuterio Falsetti,[a,b,*] Jéssica Cristina de Almeida,[c] Douglas Mendes da Silva Del Duque,[d] Caue Ribeiro de Oliveira,[c] Vagner Romito de Mendonça,[b,d] Guillermo Díaz-Sainz[a]

[a] Chemical and Biomolecular Engineering Department, University of Cantabria, Avenida de los Castros, 46, Santander, Cantabria, 39005, Spain
[b] Federal University of São Carlos: Rodovia João Leme dos Santos, Km 110, SP-264, Itinga District, Sorocaba, São Paulo, 18052-780, Brasil
[c] Embrapa Instrumentação: Rua 15 de Novembro, 1452, Centro, São Carlos, São Paulo, 13561-206, Brasil
[d] Federal Institute of Education, Science and Technology of São Paulo: Avenida João Olímpio de Oliveira, 1561, Vila Asem, Itapetininga, São Paulo, 18202-000, Brasil

E-mail: pef499@alumnos.unican.es

In recent periods, the increase in energy demand that is accompanied by population growth has intensified CO_2 emissions into the atmosphere, disrupting the carbon cycle and enhancing the greenhouse effect. In this context, CO_2 capture and conversion have emerged as promising strategies. Among them, CO_2 electrochemical reduction (CO_2ER) has gained particular attention [1]. Accordingly, the present work aimed to develop gas diffusion electrodes (GDEs) with layers of CuO or Cu/Cu_2O composites for CO_2ER. The catalyst were synthesized by preparing an ethanolic solution of copper acetate (0.05 M), either with or without the addition of monoethanolamine (Cu:ETA = 2:3). The solution was then subjected to 20 h in a solvothermal reactor, resulting in CuO (JCPDS 48-1548) or the Cu/Cu_2O composite (JCPDS 04-0836 and 71-3645), as confirmed by X-ray diffraction analysis. The samples were deposited onto carbon paper via spray coating to produce the GDEs [3]. CO_2ER tests were performed in a membrane electrode assembly (MEA) cell (2 cm^2) under galvanostatic conditions (150 $mA \cdot cm^{-2}$, 2 h) with a CO_2 flow of 30 $mL \cdot min^{-1}$, using nickel foam as the counter electrode and an anion exchange membrane. Gas and liquid products were quantified by gas chromatography (GC) and proton nuclear magnetic resonance (1H NMR)

After 2 h, formate ($HCOO^-$) was the predominant liquid-phase product, reaching 1051 µmol in CuO and 2274 µmol in Cu/Cu_2O. The faradaic efficiency (FE) for formate formation was 14.1% for CuO and 30.5% for Cu/Cu_2O, indicating that the Cu/Cu_2O composite synthesized with ETA exhibited higher selectivity toward formate and greater energy efficiency, operating at 2.5 V compared to 2.9 V for CuO. Formate formation is particularly relevant, as it represents a selective two-electron reduction pathway and serves as a valuable chemical feedstock and energy carrier in sustainable technologies [4]. ETA plays a key role in stabilizing Cu/Cu_2O phase, enhancing both selectivity and efficiency for formate production.

[1] J.C. de Almeida et al., Adv. Funct. Mater. 2025, 2502901.
[2] A.E. Nogueira, A.S. Giroto, A.B.S. Neto, C. Ribeiro, Colloids Surf. A 2016, 498, 161-167.
[3] J.C. de Almeida, et al., Nanoscale 2024, 16, 18455-18467.
[4] K. Fernández-Caso et al., ACS Energy Lett. 2023, 8, 1992-2024.

Ionic Liquids-based CO_2 Direct Air Capture and Catalytic Transformation to Formate

Alejandra Cortés[a,b], Vitória Gonçalves Pina[a,b], Julian E. Sánchez-Velandia[c], Víctor Sans[a], Eduargo García-Verdugo[c], Marcileia Zanatta[a,b]

[a] *Institute of Advanced Materials (INAM), Universitat Jaume I, Avda Sos Baynat s/n, 12071, Castellón, Spain*
[b] *Departament de Química Física i Analítica, Universitat Jaume I, Avda Sos Baynat s/n, 12071 Castellón de la Plana, Spain*
[c] *Departamento de Química Orgánica y Inorgánica, Grupo de Química Sostenible y Supramolecular,Universidad Jaume I, Castellón, Spain*

E-mail: gonalves@uji.es

The continuous rise in atmospheric CO_2 levels, driven by human activities, poses a significant environmental challenge. Developing efficient CO_2 mitigation strategies is therefore essential. Integrating direct air capture with catalytic conversion to value-added products, particularly hydrogenation to formate, offers a promising approach due to formate's role as a hydrogen storage vector and chemical intermediate.
Ionic liquids (ILs) are promising media for CO_2 capture and conversion because of their high CO_2 solubility, tunable physicochemical properties, and ability to stabilize reactive species. In this work, we explore the use of hydroxide ILs under basic conditions to promote CO_2 absorption and its subsequent catalytic hydrogenation to formate.
A systematic experimental investigation was carried out with ionic liquids (ILs) to evaluate the effect of different organic cations) in combination with various solvents (DMSO, H_2O, and MeOH). The results reveal that solvent composition plays a decisive role in both CO_2 sorption capacity and speciation. Notably, a maximum capture efficiency of 1.0 mol CO_2 per mol of TBA^+ was achieved in a DMSO/H_2O mixture, with water significantly enhancing the overall sorption process. Subsequent hydrogenation of the captured bicarbonate species was optimized using Ru-based catalysts. Among the complexes tested, $Ru_3(CO)_{12}$ exhibited good performance, delivering formate yields up to 99% under a mild hydrogen pressure of 5-15 bar. Overall, this study demonstrates that fine-tuning the interplay between cation structure and solvent environment is essential for maximizing CO_2 capture efficiency and facilitating its catalytic conversion. By significantly lowering hydrogen pressure requirements while maintaining near-quantitative formate yields, this work contributes to the advancement of practical and energy-efficient DACC technologies, offering a promising route toward sustainable CO_2 valorization and carbon cycle closure.

[1] M. Zanatta, E. García-Verdugo, V. Sans, ACS Sustainable Chem. Eng., 2023, 11, 9613–9619.
[2] J. E. Sanchez-Velandia, V. Gonçalves Pina, M. Oliva, V. S. Safont, C. Echeverría-Arrondo, E. Garcia-Verdugo, V. Sans, M. Zanatta, ChemSusChem, 2025, 18, e202501284.

Biobased NIPU materials formation from eugenol cyclic carbonates

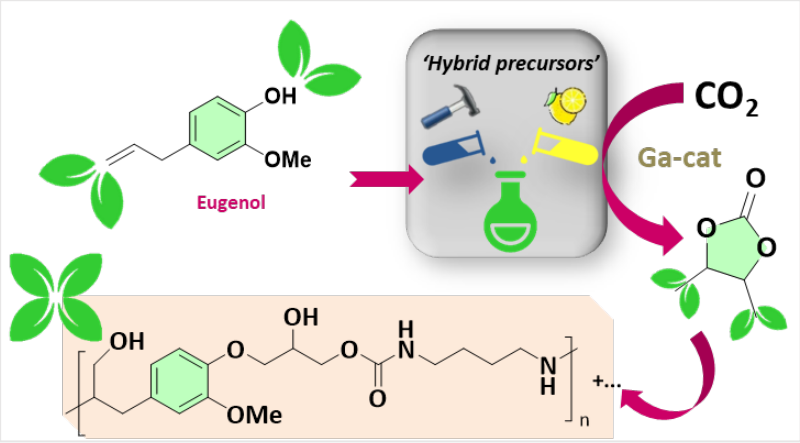
Lucía Álvarez-Miguel[a], Marta E. G. Mosquera[b] and Christopher J. Whiteoak[b,*]

[a] *Universidad de Valladolid, Grupo MIOMeT, Dpto Química Física y Química Inorgánica, Paseo de Belen 7, 47011, Valladolid, Spain*
[b] *Universidad de Alcalá, Grupo SOSCATCOM, Dpto. de Química Orgánica y Química Inorgánica, Facultad de Farmacia and Instituto de Investigación Química Andrés M. del Río (IQAR), Campus Universitario, Ctra. Madrid-Barcelona Km. 33,600, 28871 Alcalá de Henares, Madrid, Spain*

E-mail: lucia.alvarezm@uva.es

The valorisation of CO_2 and its use as a chemical feedstock provides an opportunity for the scientific community to be at the heart of attempts to design and develop a circular economy. To date, a wide range of synthetic applications have emerged to utilise this non-toxic and highly abundant C1 source.[1]

One reaction of interest is the atom-efficient coupling of CO_2 and epoxides to form cyclic carbonates (CCs). We recently reported the use of a highly active gallium aminotrisphenolate complex as catalyst for the synthesis of CCs, at low and elevated temperatures across a wide substrate scope including terminal, internal, multiple, and fully deuterated epoxides.[2] Lately, we have embarked on the development of simple and useful post-functionalization strategies to transform natural substrates into bio-derived epoxides and thereafter, into the corresponding CCs.[3] With this optimal pathway behind us, we moved to the challenging *Non-Isocyanate PolyUrethane* area. Herein, we present the eugenol-based NIPU materials from the reaction of the eugenol-CCs and diamines. Preliminary characterization and mechanical studies suggest that these polymers possess potential applications extending beyond sustainability.



[1] (a) C. Kim, C.-J. Yoo, H.-S. Oh, B. K. Min, U. Lee, *J. CO_2 Util*. **2022**, *65*, 102239; (b) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun*. **2015**, *6*, 5933.
[2] L. Álvarez-Miguel, J. D. Burgoa, M. E. G. Mosquera, A. Hamilton, C. J. Whiteoak, *ChemCatChem* **2021**, *13*, 4099-4110.
[3] L. Álvarez-Miguel, M. E. G. Mosquera, C. J. Whiteoak, *Org. Biomol. Chem.* **2022**, *20*, 9629. (b) V. Aomchad, À. Cristòfol, F. Della Monica, B. Limburg, V. D'Elia, A. W. Kleij, *Green Chem.* **2021**, *23*, 1077.

Biocatalytic Epoxidation of Oils in Ionic Liquid Media for CO_2 Valorization

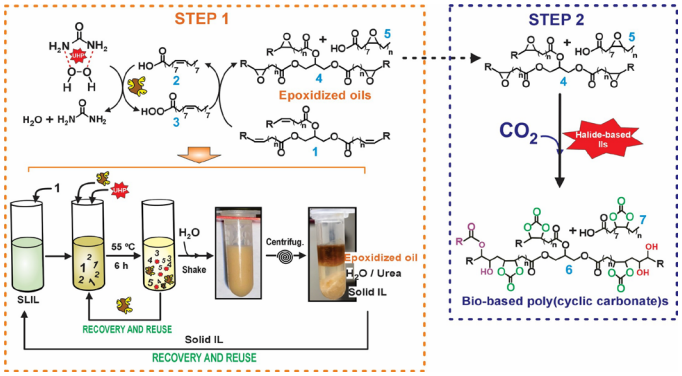
Pedro Lozano,[a] Francisco J. Ruiz,[a] Rocío Villa,[a,*] Francisco Velasco,[a] Jorge Parra,[a] Susana Nieto,[a] Eduardo Garcia-Verdugo,[b] and Jairton Dupont[a]

[a] Departamento de Bioquímica, Facultad de Química, Universidad de Murcia, España
[b] Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad Jaume I, España

E-mail: plozanor@um.es

The continuous generation of carbon dioxide (CO_2) through natural and anthropogenic oxidative processes highlights the urgent need for efficient CO_2 capture and valorization strategies.[1] Among (bio)catalytic routes, the synthesis of cyclic carbonates via CO_2 cycloaddition to epoxides is particularly attractive, especially when renewable fats and oils are used as sustainable feedstocks for non-isocyanate polyurethane (NIPU) production.[2]

This work reports a sustainable chemo-enzymatic route for the synthesis of poly(cyclic carbonate)s from CO_2 and renewable oils using sponge-like ionic liquids (SLILs) as a monophasic reaction medium.[3] The process integrates biocatalysis and IL technologies in two consecutive steps. In the first step, a lipase catalyzes the *in situ* formation of peracids from free fatty acids and oils using urea hydrogen peroxide as oxidant, enabling the epoxidation of C=C bonds. In the second step, the cycloaddition of CO_2 to the epoxidized oils was carried out using halide-based IL catalysts (*e.g.* tetrabutylammonium bromide, [TBA][Br]), yielding up to 54% carbonated soybean oil after 72 h at 100 °C and 1 MPa CO_2.



Scheme 1. Chemo-enzymatic synthesis of poly(cyclic carbonate)s from oils through a two-step process. Step 1. Novozym 435-catalyzed epoxidation of the selected oil in a monophasic sponge-like ionic liquid (SLIL) medium. Step 2. Halide-based IL-catalyzed cycloaddition of CO_2 to the epoxide rings, affording poly(cyclic carbonate)s.

Acknowledgments: This work has been partially supported by MICIU-AEI-FEDER 10.13039/501100011033 (PID2024-159264OB-C21/C22, and CPP2023-010883) grants. F.V. has a MICIU PhD-fellowship (FPU23/03041).

[1] J. Dupont, P. Lozano, *Angew. Chem. Int. Ed.*, **2025**, *64*, e202416459.
[2] V. Jasek, S. Figalla, *ACS Polym. Au*, **2025**, *5*, 105-128.
[3] F. J. Ruiz, R. Villa, F. Velasco, J. Parra, S. Nieto, E. García-Verdugo, J. Dupont, P. Lozano, *ChemSusChem*, **2026**, *Accepted - in press*.

.

Recombinant production of FDH isoforms in *E. coli*

Juan Martínez, [a] Julia Gallego-Jara,[a] Francisco J. Ruiz,[a] Teresa de Diego,[a] Susana Nieto,[a] and Pedro Lozano[a]*

[a] *Departamento de Bioquímica y Biología Molecular B e Inmunología, Facultad de Química, Universidad de Murcia.*

Email: julia.gallego@um.es

The massive use of fossil fuels has led to an uncontrolled increase in CO_2 emissions, resulting in alarming environmental consequences. CO_2 fixation using enzymes is one of the most promising strategies to address the greenhouse effect [1]. Formate dehydrogenases (FDHs) catalyze the reversible conversion of CO_2 to formate, offering a promising enzymatic pathway for CO_2 capture and utilization. In this study, we expressed, purified, and evaluated the catalityc activity of three metal-independent FDHs using *Escherichia coli* BL21 as the host organism. The selected enzymes included native FDH from *Thiobacillus* sp. (TsFDH) and *Myceliophthora thermophila* (MtFDH), as well as a variant of the *Chaetomium thermophilum* FDH engineered via directed evolution (CtFDH) [2]. Expression of the recombinant proteins was optimized by assessing different culture media, carbon sources and inducer IPTG concentrations. To evaluate expression, a western blot assay was performed using an anti-$(His)_6$ antibody, which specifically recognized the recombinant enzymes (Fig. 1A). All three proteins were successfully purified by Ni-affinity chromatography with an automated FPLC system (Fig. 1B).

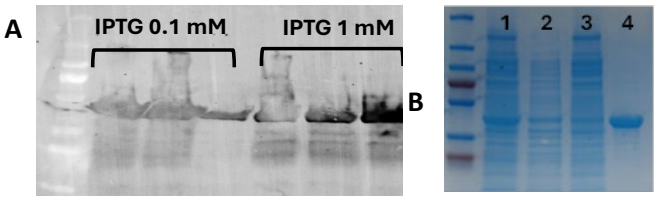


Figure 1. A. Western blot of FDH. Growing with minimal medium and glucosa or glycerol, or LB at different IPTG concentrations. **B**. FDH purification SDS-PAGE. Lane 1: protein extract, lane 2: precipitated proteins, lane 3: unbound proteins, lane 4: purified FDH.

After purification, oxidase and reductase activities were measured by monitoring the NADH formation or consumption [3] (Table 1). As shown, engineered CtFDH showed the highest reductase activity. Furthermore, this enzyme showed no oxidase activity, which represents a significant advantage by avoiding the undesirable reversibility. However, the final protein concentration was substantially low, indicating that further optimization of expression is required to obtain higher enzyme yields suitable for developing a competitive CO_2-fixation process.

Table 1. Concentration and activity measurements of recombinant FDHs

FDH	Concentration (mg/mL)	Oxidase activity (mU/mg)	Reductase activity (mU/mg)
TsFDH	8,68 ± 4,84	2373,20 ± 1093,99	7,89 ± 1,25
MtFDH	3,57	337,31	1,89
CtFDH	0,57 ± 0,31	0,00 ± 0,00	12,93 ± 2,57

[1] R. Villa, S. Nieto, A. Donaire, and P. Lozano, Molecules, **2023**, 28, 5520.
[2] M. M. Çakar *et al.*, *Biotechnol. Lett.*, **2020**, 42, 11, 2251–2262.
[3] H. Choe *et al.*, *PLoS One*, **2014**, 9,7.

Protein-Engineered Carbon Nanotubes for Selective Platinum Group Metal Recovery

Pedro S. Teixeira[a], Amir Nobahar[b], Flávia N. Braga [a,b], Rita M. Carvalho [a,c], João A.P. Coutinho[b,c], Cláudia G. Silva[a,*], Helena Passos[a,*]

[a] LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810–193 Aveiro, Portugal
[c] RYA - Purification Technologies, PCI - Creative Science Park, 3830-352 Ílhavo, Portugal

E-mail: hpassos@fe.up.pt cgsilva@fe.up.pt

The recovery of Platinum Group Metals (PGMs), classified by the European Commission as critical raw materials [1], has become increasingly relevant due to their scarcity and high demand across several industrial sectors, particularly in emerging green technologies. Conventional mining processes are energy-intensive and generate toxic byproducts, whereas spent automotive catalytic converters (SACCs) - the most significant secondary source of PGMs - contain significantly higher PGMs concentrations than natural ores. Therefore, developing efficient, environmentally benign PGMs recovery strategies from secondary sources is key to improving material circularity and supply resilience [2]. Bio-derived materials emerged as alternatives for metal recovery through adsorption, demonstrating high selectivity, sustainability, and environmental benefits [3].

In this work, ovalbumin (OVA) functionalized multiwalled carbon nanotubes (CNTs) were studied as adsorbents for selective PGMs recovery from synthetic HCl-based multi-metallic solutions. The protein immobilization process was optimized, achieving Langmuir-type adsorption with OVA loading of ~126 $mg \cdot g^{-1}$ at pH 7 within 30 min, yielding a strong, durable bioconjugate material. In metal adsorption tests, OVA-CNTs consistently demonstrated its potential for PGMs recovery, achieving high Pd and Pt adsorption capacities (6.94 and 4.41 $mg \cdot g^{-1}$). Characterization techniques like Raman, FTIR, TEM, TGA, and especially XPS, shed light on the adsorption mechanisms and advantages OVA brings to this process, proving that while CNTs provide durability and loading capacity, OVA functional groups are indispensable for achieving selective and efficient metal adsorption.

This work was supported by FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). This work was further financially supported by FCT, I.P. /MCTES through national funds: LSRE-LCM, UID/50020/2025 (DOI: 10.54499/UID/50020/2025); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); and CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI: 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI: 10.54499/UIDP/50011/2020), LA/P/0006/2020 (DOI: 10.54499/LA/P/0006/2020). F. Braga and R. Carvalho acknowledge FCT for Ph.D. grants 2023.01749.BD (DOI:10.54499/2023.01749.BD) and 2025.06718.BDANA. P. Teixeira acknowledges the fellowship funded by the project CIVITAS - Pontes entre Cidadania e Ciência para a Adaptação Climática em Comunidades da Região Norte (NORTE2030-FEDER-02717100), co-financed by the European Union, through the NORTE 2030 Regional Program, of Portugal 2030.

[1] I. E. European Commission: Directorate-General for Internal Market, Smes, M. Grohol and C. Veeh, Publications Office of the European Union, 2023.
[2] C. Saguru, S. Ndlovu, D. Moropeng, Hydrometallurgy, 2018, 182.
[3] S. Ndlovu, A. Kumar, Biological Metal Recovery from Wastewaters, 2024, pp. 119–146.

Assessment of Ergot Alkaloids in Urine with Magnetic Molecularly Imprinted Polymers

Blas Rocamora-Rivera, Natalia Arroyo-Manzanares, and Pilar Viñas*

Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, 30100 Murcia, Spain

E-mail: blas.rocamorar@um.es

Ergot alkaloids are mycotoxins produced by fungi of the *Clavicipitaceae* family and are frequently found in cereals crops. Consumption of contaminated food may pose health risks to both humans and animals. Therefore, the European Union has established maximum limits for 12 of these compounds in cereal: ergometrine, ergotamine, ergokryptine, ergocristine, ergosine, ergocornine and their corresponding epimers [1]. Direct determination of mycotoxins in food presents several limitations, including sample heterogeneity, the impact of cooking, variability in food intake, and differences in the toxicokinetics and toxicodynamics of individual ergot alkaloids. By contrast, the monitoring of mycotoxins biomarkers in biological fluids has gained increasing attention, as it enables assessment of short- or long- term exposure and may predict future health problems [2]. In this work, urinary biomarkers are proposed to assess human exposure to ergot alkaloids. To achieve the low levels of these compounds and minimize interferences, sample pretreatment plays an important role. Here, core-shell magnetic molecularly imprinted polymers (MMIPs) synthetized onto ferrite-based nanoparticles were developed and applied for the selective extraction of the 12 ergot alkaloids. Metergoline, previously assessed in non-magnetic MIPs, was selected as the template [3].

Analytical measurements were carried out by liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS). The methodology was validated in terms of recovery, precision, limits of detection (LOD), limits of quantification (LOQ) and with the construction of matrix-matched calibration curves for the 12 ergot alkaloids. The best results (R^2>0.995, precision with relative standard deviation< 6.5% and apparent recovery of 100-106%) were obtained for ergometrine and ergometrinine due to its high structural similarity to the template. The remaining analytes also showed acceptable parameters such as R^2>0.950. The methodology achieved low concentration levels, with LODs ranging from 0.08 to 0.40 ng/mL and LOQs between 0.15 and 1.34 ng/mL. MMIPs integrate the high selectivity of MIPs with rapid and straightforward separation of the nanomaterial through the application of an external magnetic field. Owing to these advantages and the excellent results, MMIPs represent a promising approach for the assessment of ergot alkaloids in urine.

Acknowledgements. The authors thank the Spanish MCIN project PID2024-156671NB-I00 financed by MCIN/AEI/10.13039/501100011033/ FEDER, EU. Blas Rocamora-Rivera acknowledges a FPU fellowship from the Spanish Ministry of Science and Innovation.

[1] Commission Regulation (EU) 2023/915 of 25 April 2023, Official Journal of the European Union **2023**, *L119*, 103-157.
[2] E. N. Ediage, J. D. Di Mavungu, S. Song, A. Wu, C. Van Peteghem, S. De Saeger, *Anal. Chim. Acta.* **2012**, *741*, 58-69.
[3] P. Lenain, J. Diana Di Mavungu, P. Dubruel, J. Robbens, S. De Saeger, *Anal. Chem.* **2012**, *84*, 10411–10418.

Effect of surface Ni^0 exposure in $Ni_xAl_yO_4$ spinel catalysts on selective furfural hydrogenation using in situ H_2 via methanol aqueous phase reforming

Norberto Vera-Hincapie[1], Nelson Manuel Domínguez-Fernández[1], Unai Iriarte-Velasco[2], Miguel Angel Gutiérrez-Ortiz[1], Jose Luis Ayastuy[1,*]

[1] *Dept. of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Sarriena S/N, 48940 Leioa, Spain*
[2] *Dept. of Chemical Engineering, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria, Spain*

E-mail: joseluis.ayastuy@ehu.eus

Furfural is a key biomass-derived platform molecule, and its selective hydrogenation to furfuryl alcohol (FOL) remains a central challenge for sustainable catalytic upgrading, as it requires suppressing over-hydrogenation, hydrogenation of the furan ring, and ring-opening side reactions [1]. The state-of-the-art shows that the furfural hydrogenation pathways are categorized into three main types: hydrogenation with external H_2, electrochemical hydrogenation, and hydrogenation using in situ produced H_2 [2]. This final approach is the most sustainable from an environmental standpoint.

The aqueous-phase hydrogenation of furfural was investigated over $Ni_xAl_yO_4$ spinel catalysts at varying Ni^0 exposure. Several catalysts, named as NiAlr-zC, were synthesized by sol–gel route at varying Ni/Al ratios (r=0.4, 0.5, 0.6), chelating agent (C=citric acid-CA, ethylene glycol-EG), and chelating agent/metal ratio (z=1.2-2.4). Comprehensive characterization of catalysts was performed to elucidate structure–performance correlations. Catalytic experiments were performed in a fixed-bed reactor at 180 °C and 20 bar, feeding aqueous 5 wt.% furfural and 1 wt.% methanol. Structural analyses showed that the stoichiometric Ni/Al ratio maximizes the metal site density, and Ni-rich samples generate larger metallic particles. Furfural was mainly converted to FOL and furan (FU), with minor cyclopentanone formation. The detection of H_2 and CO_2 in the gas phase confirmed in situ H_2 generation via methanol APR. A volcano-type dependence of FOL selectivity on the metal sites density was observed (Figure 1), maximizing for NiAl0.5-1.2EG.

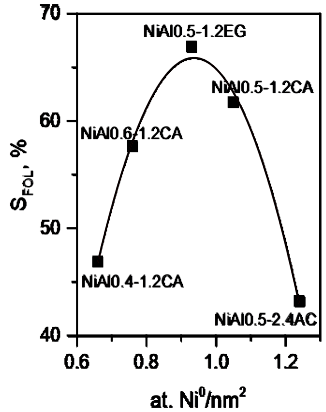


Figure 1. FOL selectivity vs. metal site density.

Alternating feeds of furfural with and without methanol induced immediate and reversible changes in conversion and selectivity, demonstrating that the reaction network is directly governed by local hydrogen coverage generated via methanol APR. Post-reaction characterization showed partial oxidation and growth of Ni^0 particles, mesopore narrowing, and the formation of moderately disordered carbon. The results indicate that performance of $Ni_xAl_yO_4$ catalysts in aqueous-phase furfural hydrogenation is balanced by the metal sites density and hydrogen availability, where the stoichiometric composition using EG maximized the selective furfuryl alcohol production.

[1] A. Zhidong, L. Jiang, *Green Chem.*, **2022**, *24*, 1780-1808.
[2] Y. Zhang, Q. Fu, X. Zhao, *Chem Eng J.*, **2025**, *521*, 166588.

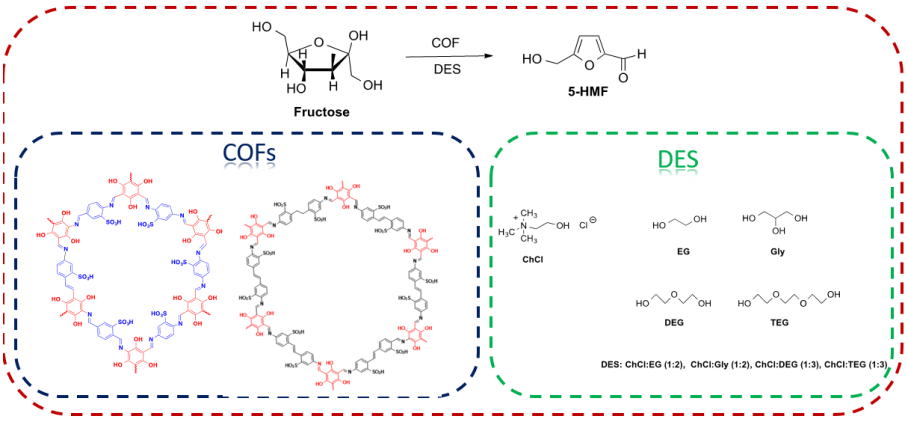
Joining Covalent Organic Frameworks and Deep Eutectic Solvents for Fructose Dehydration to 5-HMF

Salvatore Marullo,[a] Giovanna Raia,[a] Martina Silaco,[a] and Francesca D'Anna[a,*]

[a] *Università degli Studi di Palermo, Dipartimento STEBICEF, Viale delle Scienze, Ed. 17, 90128 Palermo (Italy)*

E-mail: salvatore.marullo@unipa.it

Lignocellulosic biomass valorization into industrially relevant chemicals is widely recognized as a cornerstone to curb the current reliance on fossil feedstocks. In this context, 5-hydroxymeyhylfurfural (5-HMF) is a useful biomass-derived intermediate for the synthesis of polymers or fuels.[1]
Herein, we studied the conversion of fructose to 5-HMF, catalyzed by sulfonic acid-appended covalent organic frameworks (COF), based on iminic linkages. COFs are porous solids constituted by an extended network of covalent bonds.[2] We prepared and characterized iminic COFs based on 1,3,3,5-trihydroxy phloroglucinol and used it as catalyst for the dehydration of fructose to 5-HMF, in cholinium-based deep eutectic solvents (DES).



Optimization of reaction conditions showed that these COFs are efficient and recyclable catalysts for the reaction, with high yield in relatively short reaction times.

Acknowledgments:
We thank MUR, PRIN 2022, 20222H43S2 - Hybrid Porous Materials for Eco-sustainable Catalytic Organic Processes, CUP_ B53C24005940006.

[1] A. Mittal, H. M. Pilath, D. K. Johnson, *Energy Fuels* **2020**, *34*, 3284-3293.
[2] S. Kandambeth, K. Dey, R. Banherjee, *J. Am. Chem. Soc.* **2019**, *141*, 1807-1822.

Influence of the Ni/Cu ratio on selective furfural hydrogenation using in situ H_2 from formic acid over spinel-derived catalysts

Nelson Manuel Domínguez-Fernández[1], Norberto Vera-Hincapie[1], Unai Iriarte-Velasco[2], Miguel Angel Gutiérrez-Ortiz[1], Jose Luis Ayastuy[1,*]

[1] *Dept. of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Sarriena S/N, 48940 Leioa, Spain*
[2] *Dept. of Chemical Engineering, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria, Spain*

E-mail: joseluis.ayastuy@ehu.eus

Furfural (FUR), a key strategic compound derived from lignocellulosic biomass, is a versatile platform molecule for the synthesis of a wide range of value-added chemicals. Among them, furfuryl alcohol (FOL) stands out due to its extensive use as a monomer and chemical intermediate in several industries [1]. This transformation is typically carried out in the liquid phase, which provides higher selectivity toward FOL than gas-phase systems. Conventionally, molecular hydrogen is supplied externally [2]. An alternative strategy that enhances atom efficiency and process sustainability involves the in situ generation of H_2 via aqueous-phase reforming (APR) of hydrogen donors such as formic acid, following a tandem catalytic scheme that integrates H_2 production and selective hydrogenation in a single liquid-phase step.

In this work, a series of bimetallic NiCu catalysts based on alumina spinel structures ($Ni_XCu_{1-X}Al_2O_4$) were synthesized via the sol–gel method with citric acid, and tested to study the effect of catalyst composition on activity and selectivity towards FOL. The catalyst were named as X(NiCu)Al, where X is the Ni/Cu atom ratio. The catalytic experiments were performed in a fixed-bed reactor at 180 °C and 20 bar, feeding aqueous 5 wt.% furfural and 3 wt.% formic acid.

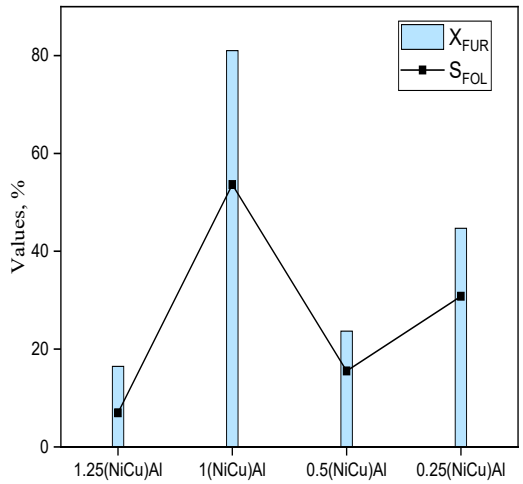


Figure 1. FUR conversion and S_{FOL}.

The results demostrate that the Ni/Cu ratio has significant influence on both FUR conversion and FOL selectivity. The catalyst with stoichiometric Ni/Cu ratio shows the highest activity due to the balanced role of both metals. Catalysts with higher Cu content show slightly lower activity but still perform better than Ni-rich catalysts, indicating that Cu metal favors selective hydrogenation while Ni activates the hydrogen donor. Upon usage, all catalysts present carbon deposits. Ni leaching (up to 4.17 wt.%) is higher than Cu and Al (<0.5 wt.%); however, the overall metal leaching is low, indicating good catalyst stability.

In conclusion, the results confirm a synergistic effect between Ni and Cu, where a proper balance between hydrogen activation and selective hydrogenation leads to high activity and selectivity toward furfuryl alcohol.

[1] A. Racha, C. Samanta, S. Sreekanta, Energy Fuels, **2023**, 37, 11475-11496
[2] D. Silva Sanches, L. Franzo de Lima, D. Richard, M. Fraga, S. Fernanda Moya, Raphael Soeiro, Molecular catalysis, **2023**, 547, 113294.

Turning Sunflower Residual Biomass into Valuable Resources Through Advanced Pretreatment Strategies

Raquel Cañadas,[a] Anderson Correa,[b] Cristina Álvarez,[a] Alfonso Vidal[c], José Miguel Oliva [a,*], and Aleta Duque [a,*]

[a] *Advanced Biofuels and Bioproducts Unit, Energy Department, Research Centre for Energy, Environment and Technology (CIEMAT), Avda. Complutense 40, 28040, Madrid, Spain*

[b] *Universidade Federal de Uberlândia, Minas Gerais, Brazil*

[c] *Institute of Biorefineries Research, Universidad de Jaén, Jaén, Spain*

E-mail: raquel.canadas@ciemat.es

Sunflower residual biomass has a high valorization potential. The efficient fractionation and conversion of this biomass into high-value bioproducts represents a promising pathway for the development of sustainable biorefineries.

In this study, the experimental strategy focused on evaluating several emerging technologies for the comprehensive fractionation of residual sunflower biomass, with the aim of obtaining differentiated process streams enriched in the main components of lignocellulosic biomass (cellulose, hemicellulose, and lignin), as well as extractable compounds [1,2]. Two innovative pretreatment strategies (a Tornado Overhead Stirring System equipped with a Carousel 6 Plus and a Microwave Digestion System) were evaluated to enhance delignification and subsequent enzymatic saccharification, both using environmentally friendly solvent systems in line with the principles of green chemistry. Microwave technology is a well-established intensified extraction method with low environmental impact that promotes the efficient recovery of compounds of interest, while the Tornado-Carousel system allows the simultaneous processing of multiple samples under controlled agitation and uniform temperature, even at high solids loading, improving efficiency, reproducibility, and scalability.

The study explored the influence of key operational parameters to identify conditions that maximize process efficiency. Comparative experiments were conducted using different solvent systems, including deep eutectic solvents based on choline chloride, ionic liquids, and organosolv processes. In addition, a detailed characterization of the structure and composition of the recovered lignin was carried out to assess its potential for high-value applications. The results of this work support the use of the evaluated technologies to improve the production of various bioproducts from sunflower waste biomass, contributing to the development of an integrated and sustainable biorefinery platform.

Acknowledgements
These results are part of the R&D project PID2023-147594OB-C31, funded by MICIU/AEI/10.13039/501100011033

[1] S. Murat, A. Alparslan, B. Levent, *Renew. Energy*, **2018**, 118, 993-1000.
[2] V. Havrysh, A. Kalinichenko, P. Pysarenko, M. Samojlik, *Processes*, **2023**, 11, 630.

Optimization of Lactic Acid Production from Aqueous Carob Extracts Using *Lactobacillus delbrueckii*

Fernando Ródenas Pérez-Cuadrado,[a] María José Salar García,[a] Luis Javier Lozano Blanco,[a] Víctor Manuel Ortiz Martínez [*a] and Sergio Sánchez-Segado,[*a]

[a] *Department of Chemical and Environmental Engineering, Polytechnic University of Cartagena, C/ Dr. Flemming s/n, 30202 Cartagena, Spain.*

E-mail: sergio.segado@upct.es

The growing demand for sustainable bioprocesses has increased interest in alternative, low-cost substrates for lactic acid production. Carob (*Ceratonia siliqua*) pods are rich in fermentable sugars and represent an underutilized agro-industrial resource[1]. This study aimed to optimize lactic acid production from aqueous carob extracts using *Lactobacillus delbrueckii* under controlled fermentation conditions.

Aqueous extracts were prepared from milled carob pods and characterized for sugar composition, pH, and total soluble solids. Batch fermentations were conducted under varying conditions of temperature, initial pH, inoculum size, and supplementation with nitrogen sources. Process optimization was performed using a response surface methodology (RSM) to evaluate the interaction effects of key variables on lactic acid production and productivity. Results demonstrated that carob aqueous extract provides an effective carbon source for *L. delbrueckii*, achieving high lactic acid concentrations without extensive pretreatment.

Optimal conditions were identified at 40 °C, pH 5,5, and 20% inoculum concentration, leading to a maximum lactic acid concentration of 90,5 g/L and a productivity of 1,88 g/L·h. Statistical analysis confirmed the significant influence of the variables studied.

These findings highlight the potential of carob-derived substrates as a sustainable alternative for lactic acid production and contribute to the valorization of agro-industrial by-products within a circular bioeconomy framework[2].

Acknowledgements

The authors wish to acknowledge the Fundación Séneca financial support under the action FSRM/10.13039/100007801(22620/PI/24). Spain.

[1] S. Sánchez, L.J. Lozano, C. Godínez, D. Juan, A. Pérez, F.J. Hernández, *Appl. Energy*. **2010**, 87, 3417–3424.
[2] E. Yatmaz, I. Turhan, *Biocatal. Agric. Biotechnol.* **2018**, 16, 200–208.

Predicting Partition Coefficients of Biomolecules in Aqueous Biphasic Systems

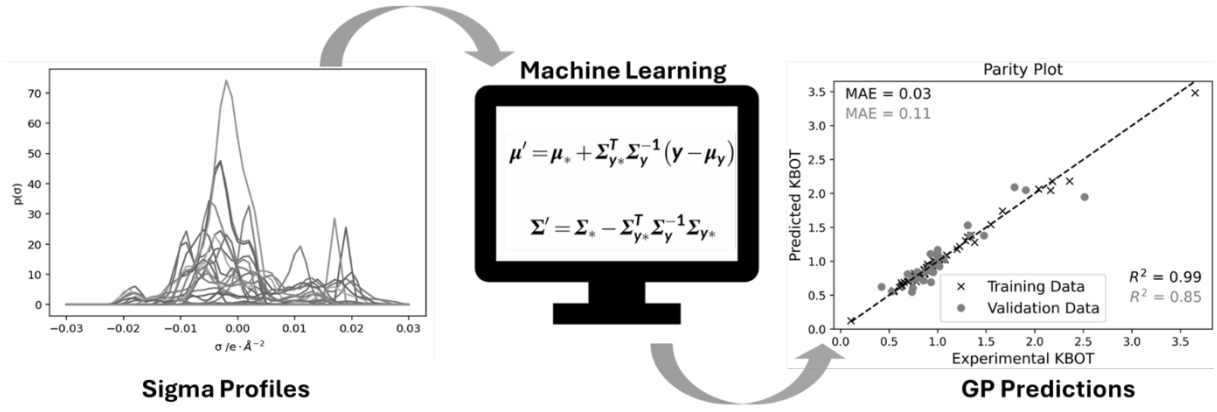
Margarida D. Pinhão,[a] Emanuel V. Capela,[a] João A. P. Coutinho,[a] Mara G. Freire[a*] and Dinis O. Abranches[a*]

[a]CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

E-mail: jcoutinho@ua.pt

Aqueous Biphasic Systems (ABSs) have emerged as a viable approach in the purification of biomolecules without loss of biological activity. Unlike traditional water-organic biphasic systems, ABSs consist of two immiscible aqueous phases and are non-toxic, non-flammable, and biocompatible. Ionic liquids (ILs) are often used as ABS constituents to better control biomolecule-solvent interactions and enhance separation performance. However, given the vast library of ILs, the selection of suitable systems for each target biomolecule relies on laborious trial-and-error campaigns. Machine learning (ML), particularly Gaussian process (GP) models have been shown to be capable of predicting physicochemical properties of materials, and emerge as a viable alternative to help design IL- based ABSs.

In this work, GP models were developed to predict the partitioning behavior of several biomolecules, such as caffeine, nicotine, phenylalanine, gallic acid and levodopa, in different polyethylene glycol-dextran (PEG-DEX) ABSs. Sigma profiles, molecular descriptors derived from quantum chemistry calculations, were employed. The GP models were able to predict the partition coefficients of all biomolecules across several different ABSs. Overall, coefficients of determination of 0.99 and 0.85 were attained for the training and testing sets, respectively. The testing set consisted of novel ABSs never seen before by the model, highlighting its predictive and generalization capability. The methodology developed in this work significantly accelerates the design of separation and purification processes based on ABSs, guiding the experimental design and reducing trial and error screening.



Scheme 1. Sigma profiles of all the Ionic Liquids added as adjuvants to the Aqueous Biphasic Systems, given to the Gaussian Process model to predict the relative Partition Coefficients of the solutes in the DEX-rich, bottom phase, achieving R-Squared values of 0.99 and 0.85 for the training and testing sets, respectively.

Integrated Multi-Catalytic System for Sustainable Valorization of Biomass-Derived Feedstocks

Annatelli Mattia,[a] **Eduardo García-Verdugo Cepeda**,[a]

[a] *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I*
Av Sos Baynat , E-12071 – Castellón, Spain

E-mail: annatell@uji.es

The growing demand for bio-based monomers for sustainable materials and polymers requires the development of efficient chemical processes with reduced environmental impact. Among renewable platform molecules, 2,5-furandicarboxylic acid (FDCA) has attracted significant attention as a sustainable alternative to fossil-derived counterparts. In this work, we present a bio-inspired "synthetic cell" system designed for the direct conversion of readily available sugars and polysaccharides into FDCA.[1]

The proposed strategy relies on a multi-catalytic one-pot approach that integrates sequential reaction steps within a single operational platform. By combining dehydration and oxidation processes in a confined environment, the system minimizes intermediate handling, lowers energy consumption, and reduces waste generation, thereby improving overall process sustainability. At the core of this concept is the use of Metal-Organic Frameworks (MOFs), whose high structural regularity, tunable porosity, and controlled distribution of active sites enable spatially organized catalytic functions, facilitating cascade reactions and enhancing selectivity toward FDCA.[2]

The synergistic employment of Ionic Liquids (ILs) or Deep Eutectic Solvents (DES) as reaction media further promotes biomass solubilization, improves mass transfer, and boosts catalytic efficiency.[3] Overall, this integrated and biomimetic platform offers a promising and sustainable pathway for FDCA production, contributing to the advancement of biomass valorization strategies and green chemistry principles.

Acknowledgements: This project has received funding from the European Union's Horizon Europe research and innovation program under the Marie Skłodowska-Curie grant agreement HORIZON-MSCA-2024-PF-01-01, P.N: 101204879. This work was partially funded by the Generalitat Valenciana through project CIPROM/2023/57 and by Universitat Jaume I under the PPITC25 program (Action 5.1, reference 19I001.06).

[1] Q. Hou, X. Qi, M. Zhen, H. Qian, Y. Nie, C. Bai, S. Zhang, X. Bai, M. Ju, *Green Chem.*, **2021**, *23*, 119–231.
[2] A. Yuan, Y. Lu, Xiaodan Zhang, Q. Chen, Y. Huang, *J. Mater. Chem. B*, **2020**, *8*, 9295-9303.
[3] a) J. N. Pedersen, B. Pérez, Z. Guo, *Sci Rep*, **2019**, *9*, 17479; b) A. Verger, H. Kichou, N. Huang, X. Perse, I.-M. Ardeza, C. Pradel, R. Goncalves Martins Da Conceicao, B. Atanasova, F.-X. Legrand, A. Despres, L. Boudesocque-Delaye, E. Munnier, *ACS Sustainable Chem. Eng.*, **2024**, *12*, 7187−7199

Sustainable recovery of resveratrol from vine pruning waste via biobased solvents and process intensification technologies

Andrea Sánchez-Monedero[a], Diego Cobo[a], Julia Huertas[a], Mencía Guerra[a], Emilio J. González[a], María González-Miquel[a]*

[a] *Dpto. ingeniería química Industrial y del Medio Ambiente, ETSI Industriales, Universidad Politécnica de Madrid, C/José Gutiérrez Abascal 2, 28006 Madrid, Spain*

E-mail: maria.gonzalezmiquel@upm.es

Wine production is an activity with global impact, particularly in the Mediterranean region. In Spain, grape production exceeds 5 million tons per year, most of which is devoted to winemaking, an activity that generates more than 2 million tons of vine pruning waste (VPW) annually [1]. However, VPW remains an underutilized lignocellulosic residue, despite being rich in value-added polyphenolic compounds that are highly sought after for food, pharmaceutical, and cosmetic applications. One of the major polyphenolic compounds found in VPW is resveratrol, a natural antioxidant known for its potential cardiovascular and metabolic benefits, anti-aging effect and anti-tumoral properties [2].

Conventional methods for recovering polyphenolic compounds from natural matrices typically rely on petrochemical solvents, which have negative impacts on both human health and the environment. In this context, the aim of this work is to develop a sustainable process for VPW valorization through the extraction of resveratrol using biobased solvents and assisted extraction technologies for process intensification purposes.

To this end, three VPW varieties from the D.O. Valdeorras region (Godello, Mencía, and Garnacha) were studied to evaluate the effect of grape variety on extract composition. The potential of various biosolvents (including alcohols, ethers, esters, and terpenes) for the solid–liquid extraction of resveratrol from VPW was evaluated and optimized in terms of extraction time, temperature, and solvent load. The resulting extracts were analyzed using chromatographic and spectrophotometric techniques to determine their phenolic profiles and antioxidant capacities. Subsequently, ultrasound and microwave-assisted extraction were assessed to improve extraction efficiency while reducing energy requirements. Overall, gamma-valerolactone proved to be the most effective solvent for selective resveratrol recovery, with process intensification technologies enabling significant reductions in both extraction time and energy consumption compared to conventional methods.

[1] Ministerio de Agricultura, Pesca y Alimentación (Mapa), 2024
[2] M. S. Jesus, Z. Genisheva, A. Romaní, R. N. Pereira, J. A. Teixeira, L. Domingues, *Industrial Crops and Products* **2019**, *132*, 99-110.

Natural pigments from agroindustrial byproducts for wood coatings

MªCarmen Garcia-Poyo,[a,*] Marta Muñoz-Martí,[a] Ainoa Candela-Gil,[a] Carlos Castaño-Forte,[a] and Mª Virtudes Navarro-Bañón[a,*]

[a] *Author affiliation: Calle Perales S/N, 30510 Yecla, Murcia, Spain, Technology Centre of Furniture and Wood (CETEM)*

E-mail: mc.garcia@cetem.es

The growing environmental and health concerns associated with synthetic pigments have intensified the search for sustainable alternatives in coatings applications. The Region of Murcia (Spain), one of the main agroindustrial production areas in Europe, generates large volumes of agricultural residues from crops such as tomato, peach, green and red pepper, and red grape. These underutilized by-products entail a renewable and locally available source of natural pigments, including carotenoids, chlorophylls, and anthocyanins. Their valorization offers a promising strategy to integrate regional biomass management within a circular economy framework while advancing green chemistry approaches for sustainable coating formulations.

This study investigates pigment extraction by using various green solvents, including ethanol, 2-methyltetrahydrofuran (MeTHF), their mixtures, and several natural deep eutectic solvents (NADES). Optimal extraction was, pigment and solvent, specific: MeTHF:EtOH 50:50 for tomato and green pepper, EtOH for peach and red pepper, and EtOH 70% v/v at pH 1 for red grapes. Extractions were performed at ambient temperature (~1.5 h) with low energy input. Pigments were characterized to assess their composition, color, stability, and structural features. Scaling up the process from 0.5 g to 50 g maintained the relative absorbance profiles and color, demonstrating the reproducibility and robustness of the extraction procedure.

Purified pigments have been incorporated into water- and solvent-based varnishes and lacquers for wood coatings. Ongoing studies evaluate color performance, stability, and formulation compatibility. This approach demonstrates the versatility of green solvents for selective pigment recovery, promotes circular economy strategies for agro-residues, and provides an environmentally and industrially relevant alternative to synthetic colorants.

DETERMINATION OF AGRICULTURAL AND FORESTRY BIOMASS PYROLYSIS KINETICS BY THERMOGRAVIMETRIC ANALYSIS

A.M. Montero-Csanady[1,2], J.M. Escola[1,2], G. Gómez-Pozuelo[1*], J.A. Botas[1,2*]

[1]Chemical and Environmental Engineering Group. ESCET, Rey Juan Carlos University. c/ Tulipán s/n, 28933, Móstoles (Madrid), Spain.
[2]Instituto de Investigación de Tecnologías para la Sostenibilidad, Rey Juan Carlos University, c/ Tulipán s/n, 28933, Móstoles (Madrid), Spain.

email: alicia.montero@urjc.es

Lignocellulosic biomass pyrolysis represents a promising pathway to produce biofuels and high-value chemicals [1]. Improving the efficiency of these processes requires a better understanding of the complex kinetics involved in biomass thermal decomposition. Non-isothermal thermogravimetric analysis combined with model-free isoconversional methods enables the evaluation of apparent kinetic parameters (activation energy and pre-exponential factor of Arrhenius equation), avoiding the need to assume a specific reaction mechanism [2].

The pyrolysis behavior of wheat straw (WS), acid-washed wheat straw (ac-WS), eucalyptus (EU) and oak (OAK) was investigated by thermogravimetric analysis (TG) under nitrogen atmosphere from room temperature to 1000 ºC and using heating rates (HR) of 10, 15, 25 and 50 ºC/min. Kinetic parameters were calculated using Kissinger, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. While the Kissinger method provides a single apparent activation energy associated with the maximum degradation rate (DTG_{max}), the FWO and KAS methods describe the multi-step character of biomass pyrolysis by evaluating activation energy over the conversion range.

Clear differences were found between agricultural (WS and ac-WS) and forestry biomasses (EU and OAK). WS showed the highest average apparent activation energy (311.3^{FWO} kJ/mol), while ac-WS biomass presented lower values (279,6^{FWO} kJ/mol), demonstrating the role of inorganic species in the thermal decomposition process. In contrast, EU and OAK exhibited more moderate and relatively similar apparent activation energy values (EU: 284,6^{FWO} kJ/mol and OAK: 276.4^{FWO} kJ/mol), suggesting a comparable kinetic response between both forestry biomasses. In FWO and KAS methods, the increase in apparent activation energy was accompanied by similar trends in the pre-exponential factor, consistent with the complex and overlapping reactions occurring during biomass pyrolysis [2].

The obtained results show that lignocellulosic biomass composition and its inorganic matter content affect the thermal reactivity and energy requirements of the pyrolysis process. The calculated kinetic parameters contribute to a better understanding and optimization of this biomass thermochemical conversion method.

The authors gratefully acknowledge the financial support to the HYPYCAT Project (PID2023-147355OB-C22) by the MCIU and the AEI through MICIU/AEI/10.13039/501100011033, and Alicia M. Montero-Csanady for her predoctoral grant (PREP2023-001049).

[1] P. Yan et al., *Green Chem.* **2025**, *27*, 10444-10477.
[2] S. Vyazovkin et al., *Thermochim. Acta* **2011**, *520*, 1-19.

Integral valorization of vine shoots within a biorefinery framework: Production of glucose, bioactive compounds, and furfural

Camila C. Muñoz-Realpe*, María del Mar Contreras, Alfonso M. Vidal, Eulogio Castro, Inmaculada Romero

Department of Chemical, Environmental and Materials Engineering, Universidad de Jaén, 23071 Jaén, Spain.
Institute of Biorefineries Research (I3B), Universidad de Jaén, 23071 Jaén, Spain

E-mail: ccmunoz@ujaen.es

Vine cultivation generates large amounts of agricultural waste annually, primarily vine shoots, yielding approximately 1 to 2 tons per hectare. Within the framework of the circular economy, there is a growing interest in developing sustainable processes that maximize the utilization of this lignocellulosic biomass under the biorefinery concept. This study presents an integral valorization strategy for vine shoots to obtain value-added products, combining the extraction of phenolic compounds, the recovery of hemicellulosic sugars, and their subsequent conversion into furfural.

Ultrasound and microwave-assisted extraction were evaluated for the recovery of phenolic compounds. The main extraction variables were optimized for the two technologies using experimental designs. The resulting extracts were analyzed to determine their total phenolic content (Folin–Ciocalteu) and antioxidant activity (ABTS and FRAP), and bioactive compounds (*trans*-resveratrol and *trans*-ε-viniferina) were quantified by HPLC. Ultrasound extraction optimization aimed to maximize all responses simultaneously, reaching an optimum at 62% amplitude, 59% ethanol, and 6 min (55 °C). For microwave-assisted extraction, two scenarios were proposed: the first focused on maximizing stilbenoids recovery only (80 °C, 4 min, 69% ethanol); and the second, aligned with the ultrasound approach, optimized all responses, which required an increase in temperature (155 °C, 3.5 min, 58% ethanol). Both methods demonstrated high efficiency in recovering biocompounds within short processing times [1]. Additionally, the hemicellulosic fraction was valorized through microwave-assisted acid hydrolysis, maximizing xylose recovery. Under optimized conditions of 0.8% (w/v) H_2SO_4, 160 °C, and 5 min, a xylose recovery of 80% was achieved. Subsequently, the hemicellulosic liquor was used as a substrate for furfural production at 200 °C using 0.3 M LiCl as a catalyst, and a yield of 80% (94% selectivity) was reached in 5 min. In comparison, when the chemical conversion was carried out without added salt, a maximum yield of 75.5% (86% selectivity) was achieved, although a longer reaction time (10 min) was required. Concerning the pretreated solid (optimized conditions), it was hydrolyzed using Cellic® CTec2 and β-glucosidase, releasing 11 g/L at 5% substrate loading (enzymatic digestibility of 41.25%).

In conclusion, this work demonstrates the potential of vine shoots as a renewable feedstock within a biorefinery framework. Their valorization enables the production of natural antioxidants and platform chemicals such as furfural, consolidating a sustainable industrial model applicable to the energy, chemical, food, and pharmaceutical sectors.

[1] C. C. Muñoz-Realpe, M. del Mar Contreras, A. M. Vidal, E. Castro, I. Romero, Sustain. Chem. Pharm. 2025, 43, 101899.

From thecnical maximum to green optimum: Balancing yield and energy in the ultrasound extraction of phenolic compounds

Luis Carlos Morán-Alarcón,[a,b] María del Mar Contreras,[a,b,*] Ángel Galán-Martín,[a,b] and Eulogio Castro[a,b]

[a] *Department of Chemical, Environmental and Materials Engineering, Universidad de Jaén, Campus Las Lagunillas, Jaén, 23071, Spain*
[b] *Institute of Biorefineries Research (I3B), University of Jaén, Campus Las Lagunillas, 23071, Jaén, Spain.*

E-mail: mcgamez@ujaen.es

The valorization of exhausted olive pomace (EOP) is key to the circular economy of the olive oil industry [1]. Although it is rich in bioactive compounds such as hydroxytyrosol (HT) and its acetylated derivative (HT-Ac), conventional extraction strategies usually focus exclusively on maximizing yield, ignoring the energy impact required for a viable industrial scale-up.

In this work, a Box-Behnken Design of Experiments was applied for the ultrasound-assisted extraction (UAE) of HT and HT-Ac from EOP, evaluating three variables: ethanol concentration (20-100%), ultrasonic amplitude (20-80%), and time (2-10 min). In addition to quantifying the chromatographic yield, the real energy consumption (kWh) of each experiment was monitored [2]. Data analysis went beyond maximizing traditional yield, and minimizing energy consumption at the laboratory scale using the Response Surface Methodology and the desirability function.

Results revealed that the use of pure ethanol (100%) drastically reduces the extraction yield (<205 mg/100 g), demonstrating the affinity of HT and HT-Ac for more polar solvent mixtures and by adding water to favor the extraction. The mathematical optimum for yield (880 mg/100g) required 50% ethanol, 50% amplitude, and 10 min for extraction, consuming 0.008 kWh. However, energy optimization identified a greener compromise point at 2 min: rapid acoustic cavitation recovered 90% of the theoretical maximum (799 mg/100 g) with only 0.002 kWh. Extending the process quadruples the energy expenditure to gain barely 10% more phenolic compounds.

The viability of EOP biorefineries depends critically on process efficiency. This study demonstrates that UAE technology, considering not only yield but also the energy expenditure of the process, enables a highly effective and energetically sustainable extraction, avoiding the blind pursuit of maximum mathematical yield.

Acknowledgments: Pre-doctoral grants for the training of research personnel under Action 8.a) of the Operational Plan to Support Research at the University of Jaén (UJA) (2021-2022), projects PID2023-149614OB-C21 and PID2023-151855OA-I00 funded by MICIU/AEI/10.13039/501100011033, FEDER and EU, and Action 8.a) grant.

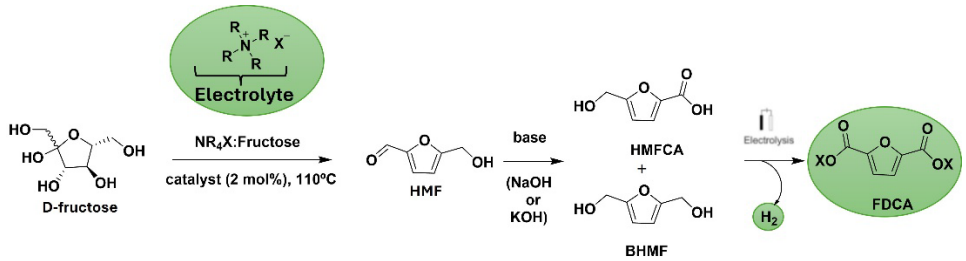
[1] L.C. Morán-Alarcón, Á. Galán-Martín, M.d.Mar Contreras, E. Castro. *Renew. Sustain. Energy Rev*. **2026**, 226, 116438.
[2] I. Gómez-Cruz, M.d.M. Contreras, I. Romero, E. Castro, *Antioxidants* **2021**, 10, 1781.

An Integrated DES-Based Strategy for the Purification-Free Conversion of Fructose into FDCA

Iván Muñoz,[a] Eduardo García-Verdugo,[a] Belén Altava[a], Kikaru Tabata,[b] Carmen Mejuto,[b] Francisco Fabregat,[b] and Elena Mas[b]

[a]Author affiliation: Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, Av. Vicent Sos Baynat, s/n 12071, Castellón, España.
[b]Author affiliation: Institute of Advanced Materials (INAM), Universitat Jaume I, 12071 Castellón, España.
E-mail: munozi@uji.es

The development of sustainable routes to produce bio-based platform chemicals requires efficient multistep processes that minimize waste, energy consumption, and intermediate handling. In this context, 2,5-furandicarboxylic acid (FDCA) has emerged as a key renewable building block; however, its synthesis from carbohydrates is often limited by the instability of intermediates and the need for sequential purification steps [1]. Herein, we report an integrated one-pot platform for the direct conversion of fructose into FDCA without intermediate isolation. The strategy combines ammonium-based deep eutectic solvents (DESs) with a sequential reaction design, enabling fructose dehydration to HMF under favourable solubility and selectivity conditions within a single reaction system. [2].To address the inherent instability of HMF under alkaline conditions, a controlled Cannizzaro disproportionation is incorporated as an intermediate stabilization step, enabling the direct transfer of the reaction medium to a final electrochemical oxidation stage. This approach provides a sustainable route for the conversion of biomass-derived intermediates into FDCA under mild conditions [3]. Overall, this work highlights the role of DESs as enabling components in the design of integrated and purification-free platforms for carbohydrate valorization.



Scheme 1. Schematic representation of the purification-free route via DES-mediated dehydration, Cannizzaro stabilization, and electrooxidation.

Acknowledgements: This work was partially funded by Generalitat Valenciana through project CIPROM/2023/57, by Grant PID2024-159264OB-C21 funded by MCIN/AEI/10.13039/501100011033 and by ERDF A way of making Europe, and by Universitat Jaume I under the PPITC25 programme (Action 5.1, reference 19I001.06).

[1] Cong, H.; Yuan, H.; Tao, Z.; Bao, H.; Zhang, Z.; Jiang, Y.; Huang, D.; Liu, H.; Wang, T. *Catalysts* **2021**, *11*, 1113.
[2] Chen, B.; Peng, Z.; Li, C.; Feng, Y.; Sun, Y.; Tang, X.; Zeng, X.; Lin, L. *ChemSusChem* **2021**, *14* (6), 1496-1506.
[3] Kwon, Y.; Schouten, K. J. P.; van der Waal, J. C.; de Jong, E.; Koper, M. T. M. *ACS Catalysis* **2016**, *6* (10), 6704-6717.

Hydrothermal Liquefaction of Sludge Digestate for Sustainable production of Biocrude and Hydrochar

David Gbenga Oke,[ab]* Giovanni Manente,[a], Giuseppe Mele,[a]

[a] *Department of Engineering for Innovation. University of Salento, Italy.*
[b] *Industrial Chemistry Programme, Bowen University, Iwo, Nigeria.*

E-mail: davidgbenga.oke@unisalento.it

The ability to manage wet biomass and particularly sewage sludge is still a significant concern nowadays. This is because of their high moisture content and extremely low energy density. Hydrothermal liquefaction (HTL) provides a green and sustainable method of chemical conversion of wet biomass into liquid and solid products rich in energy and value. Over seventy HTL experiments were conducted in this work using a 500 mL Parr batch reactor and sludge digestate as feedstock containing 85 % of water. These reactions were conducted in the absence of catalyst at 300 °C and 320 °C, with corresponding pressures in the range of 100-120 bar, and residence times of 30, 45, and 60 minutes. The research was aimed at biocrude and hydrochar production and characterization.

The raw sludge digestates had poor fuel qualities (C-38.9 wt%, H-5.6 wt%, N-4.6 wt%, S-0.9 wt%) and very low calorific values (HHV- 4.2 MJ/kg and LHV- 2.0 MJ/kg). After the HTL process, the biocrude oil product was significantly enriched in carbon and hydrogen (C-70.8 wt%, H-10.0 wt%), had a lower sulphur content (0.4 wt%) and similar nitrogen (4.3 wt%). This confirms that thermochemical upgrading through dehydration and decarboxylation occurred successfully. The maximum biocrude oil yield was 25 wt% at 300 C and 30 minutes indicating that moderate temperature and reduced residence time favour the formation of liquids and reduce the formation of secondary repolymerization reactions. Approximately 650 mL of biocrude oil was obtained from the experimental campaign, with an average of 9 grams per experiment. The resulting mixed biocrude oil had a density of 0.997 g/cm3 and a viscosity of approximately 5000 cSt which is characteristic of heavy HTL oils. The biocrude oil exhibited remarkably high calorific values of HHV of 40.6 MJ/kg and LHV of 38.4 MJ/kg, which is almost ten times higher than the raw digestate and is very close to fossil fuels. Hydrochar was also produced in reasonable proportions. It is carbon-based implying that condensation and aromatization reactions took place in HTL. Such solid fraction can be potentially processed into solid fuel, soil amendment, or carbon sequestration storage, which will facilitate the circular economy.

Among the variables of the process that were under investigation, temperature played the most important role in the distribution of products. Increased temperature (320 °C) favoured secondary reactions leading to more gases and higher viscosity whereas longer residence time favoured the hydrochar formation. Subcritical conditions of water were provided by pressure although it did not exert the same effect on elemental upgrading as temperature. These experiments have shown that low-value sludge digestates may be effectively liquefied using hydrothermal methods to high-energy biocrude and highly valued hydrochar in the absence of catalysts. The significant improvement of the calorific values and carbon contents point out the prospects of HTL to be a sustainable waste-to-energy technology in the context of green and sustainable chemistry. To further improve fuel application, there are attempts to enhance upgrading procedures to lower viscosity and heteroatom contents.

Tailored Fractionation of Tomato Pruning Residues within a Biorefinery Framework

Raquel Cañadas Soler,[a] Cristina Álvarez Vaquerizo,[a] José Miguel Oliva Domínguez,[a] Ignacio Ballesteros Perdices,[a] Alberto González Sáez, [a] Sara Parrondo Manrique [a], Antonio David Moreno García [a] and María del Prado García-Aparicio [a*]

[a] Advanced Biofuels and Bioproducts Unit, Department of Energy, CIEMAT, Avenida Complutense 40, 28040 Madrid, Spain

E-mail: raquel.canadas@ciemat.es

The transition toward sustainable crop protection requires the development of bio-based alternatives derived from residual lignocellulosic biomass. Tomato cultivation, for instance, generates more than 3 million tons of agricultural residues annually, including pruning branches and lignocellulosic material remaining after the growing cycle [1]. In this context, the European ZELDA project (Zero-waste Lignocellulose-Derived biorefinery products for smart plant protection, GA 101214981), is focused on developing innovative fractionation strategies to valorize these agricultural residues into functional bio-based compounds.

Lignocellulosic tomato crop residues represents a particularly challenging feedstock due to its high content of extractives (~38%), significant inorganic fraction (~14% ash), and elevated nitrogen content, corresponding to an estimated crude protein fraction of about 11% based on Kjeldahl analysis. These characteristics can interfere with conventional hydrothermal processing by increasing buffering capacity and limiting the efficiency and selectivity of autohydrolysis [2].

In this work, a tailored conditioning and fractionation approach is proposed, combining selective removal of nitrogenous and extractive components prior to hydrothermal treatment. Different strategies are being explored, including enzymatic treatments (proteases), green solvent systems such as natural deep eutectic solvents (NADES), and aqueous or mild acid washing to reduce inorganic content and buffering effects, while preserving the structural carbohydrate fraction.

The resulting solid fraction is then subjected to liquid hot water pretreatment to promote the selective solubilisation of hemicellulosic components, enabling the production of bio-based intermediates with potential application in plant protection. In parallel, the recovered nitrogen-rich streams offer additional valorisation opportunities, contributing to a zero-waste biorefinery concept.

Overall, this work highlights the importance of adapting fractionation strategies to biomass-specific characteristics, particularly for extractives- and ash-rich agricultural residues, in order to improve process efficiency and develop sustainable bio-based solutions.

[1] T. Løvdal, B.V. Droogenbroeck, EC Eroglu, S. Kaniszewski, G Agati, M. Verheul, D. Skipnes, *Foods*. **2019**, *8*, 229.
[2] A.D. Moreno, A. Duque, A. González, I. Ballesteros, M.J. Negro, *Foods*, **2021**, *10*, 814.

Continuous fixed-bed biosorption of Cr(III) by *Posidonia oceanica* leaves

Juan Francisco Ortuño, Ana Belén Pérez-Marín, Víctor Meseguer, María Isabel Aguilar, Mercedes Lloréns, Blasa Martínez-Ruiz

Departamento de Ingeniería Química, Facultad de Química, Universidad de Murcia, Campus of Espinardo, 30100 Murcia, Spain

E-mail: jfortuno@um.es

Fixed-bed adsorption systems are widely used to remove contaminants from wastewater. The performance of packed beds is usually described by means of breakthrough curves, where the ratio of the effluent concentration (C_{eff}) to the influent concentration (C_0) is plotted against the service time of the column. A continuous up-flow fixed-bed study was carried out by using *Posidonia oceanica* leaves as a biosorbent for the removal of trivalent chromium ions from aqueous solution. The *Posidonia oceanica* leaves were washed, ground and sieved, with the fraction ranging in size from 0.6 mm to 2.5 mm being used as the adsorbent. The effect of bed depth (9 cm - 27 cm) and flow rate (7.4 mL·min^{-1} - 22.1 mL·min^{-1}) was investigated. To obtain the experimental breakthrough curves, the metal solution (C_0 = 20 mg·L^{-1}, pH = 4) was pumped upwards through the fixed-bed. Samples were periodically collected from the fixed-bed effluent, and their pH values and Cr (III) concentrations (C_{eff}) were determined.

The performance of the fixed bed was evaluated using the breakthrough curve, by determining the breakthrough (C_{eff}/C_0 = 0.05) and the saturation times (C_{eff}/C_0 = 0.95), as well as the amount of metal retained in the column. As expected, the experimental results confirmed that both the breakthrough time and the amount of Cr (III) sorbed increased with bed depth, due to the greater number of adsorption sites provided by larger beds. Conversely, these values decreased as the flow rate increased due to lower contact time between the metal solution and the sorbent.

Several simplified breakthrough curve models: two parameters, bed depth service time (BDST), Thomas, Clark and Yoon-Nelson [1], were applied to the experimental data to simulate and predict the breakthrough curves. The characteristic parameter values for each model, which are useful for process scale-up and design, were obtained by fitting the experimental data to the model equation using non-linear regression. The two-parameter model and the Yoon-Nelson model are the models that best describe the experimental breakthrough curves.

[1] H. Patel, *Int. J. Environ. Sci. Technol.* **2022**, 19, 10409–10426.

bagasse in fixed bed column

Víctor Meseguer, Juan Francisco Ortuño, María Isabel Aguilar, Mercedes Lloréns, Ana Belén Pérez-Marín, María Aránzazu Molina

Departamento de Ingeniería Química, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain

E-mail: vzapata@um.es

The use of bagasse (a by-product of the brewing industry) as a biosorbent for the removal of methylene blue (MB) (a cationic thiazine dye) from aqueous solution has been investigated through continuous fixed-bed experiments.

The bagasse from a brewing industry was washed with tap water, dried, ground and sieved. The solid material with a particle size ranging from 0.09 mm to 1.5 mm was then used. The experiments were generally carried out at a temperature of 25 °C by pumping a solution of MB (pH = 6) with a known concentration through a bed with a packed density of 0.2 $g \cdot cm^{-3}$ situated inside a 1.88 cm diameter methacrylate column. Samples of the solution were taken at the column outlet at different times and analysed using visible spectroscopy to determine the concentration of MB. The pH of the effluent was also measured. Experiments were conducted by varying the initial MB concentration (10 $mg \cdot L^{-1}$ - 30 $mg \cdot L^{-1}$), the bed height (4 cm - 16 cm) and the feed flow rate (5 $mL \cdot min^{-1}$ - 20 $mL \cdot min^{-1}$). The corresponding breakthrough curves were obtained and the characteristic parameters of the process (breakthrough time, saturation time, transfer zone length, amount of adsorbate adsorbed per unit mass of adsorbent, amount of adsorbate treated, and percentage of adsorption) were determined.

The behaviour of the fixed-bed was modelled by fitting the experimental breakthrough curves to various simplified models: Bed Depth Service Time (BDST), Thomas, Clark, Yoon-Nelson and dose-response [1].

The following conclusions can be derived from the achieved results:

- The pH of the effluent remains practically constant in all cases, with a value similar to that of the feed (pH ≈ 6).
- An increase in bed height results in longer breakthrough and saturation times as well as a higher percentage of dye adsorption.
- As the feed flow rate increases, the breakthrough and saturation times decrease, as does the percentage of dye adsorbed.
- Increasing the concentration of MB in the feed reduces breakthrough and saturation times, as well as the percentage of dye adsorbed.
- The behaviour of the brewery bagasse bed in the bioadsorption of methylene blue is best described by the dose-response model.

[1] H. Patel, *Int J Environ Sci Tech.* **2022,** 19, 10409–10426

.

Xylanase-Driven Hydrolysis of *Palmaria palmata* Xylan in a Cascading Biorefinery Approach

Diogo Coelho,[a,b] Cláudia Oliveira,[a,b] Helena Abreu,[c] Margarida Martins,[d] and Tony Collins[a,b*]

[a] *Centre of Molecular and Environmental Biology (CBMA)/Aquatic Research Network (ARNET), Department of Biology, University of Minho, 4710-057 Braga, Portugal*
[b] *Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, 4710-057 Braga, Portugal*
[c] *Independent Seaweed Consultant, 3870-322 Murtosa, Portugal*
[d] *ALGAplus, 3830-352 Ílhavo, Portugal*

E-mail: tcollins@bio.uminho.pt

Xylan is a structurally diverse hemicellulose that can be hydrolysed into xylooligosaccharides (XOS), a class of bioactive compounds with recognized prebiotic, antioxidant, and potential anticancer properties. While terrestrial xylans have been extensively explored, marine-derived counterparts remain largely underexploited. The red macroalga *Palmaria palmata* emerges as a sustainable and underexplored source of a novel xylan structure, characterized by mixed β-(1→3)/β-(1→4) linkages, phosphate and sulphate side-chains, and the absence of lignin, which facilitates extraction and may lead to the generation of structurally distinct XOS with enhanced or novel bioactivities. Enzymatic hydrolysis of xylan offers clear advantages over conventional harsh and hazardous chemical methods, enabling higher specificity, milder conditions, and improved control over product profiles.

Within a biorefinery-driven framework, a sustainable extraction strategy for xylan from *P. palmata* was established [1], followed by a systematic screening and comparative characterization of its enzymatic hydrolysis using a panel of five xylanases spanning distinct glycoside hydrolase (GH) families [2]. Kinetic parameters, including Michaelis–Menten constants, and temperature–activity profiles (10–80 °C) were determined for all enzymes, supporting the identification of the most promising candidates for integration into a tailored biorefinery process. Hydrolysis extension and product profiles were monitored using DNS and HPLC-SEC, enabling the correlation between enzyme specificity and XOS degree of polymerization. The bioactive potential of the obtained hydrolysates is being evaluated to elucidate structure–bioactivity relationships, focusing on antioxidant, prebiotic, and anticancer activities.

[1] D. Coelho, D.F. Costa, M. Barroca, S.A. Cunha, M.M. Pintado, H. Abreu, M. Martins, T. Collins, M*arine Drugs.* **2025**, *23(8)*, 1-18.
[2] M. Mendonça, M. Barroca, T. Collins, *Biotech. Advances.* **2023**, *65*,108148 1-23.

Analyzing enzymatic synergy through fractal modeling: Saccharification of alkaline mildly-pretreated rice straw

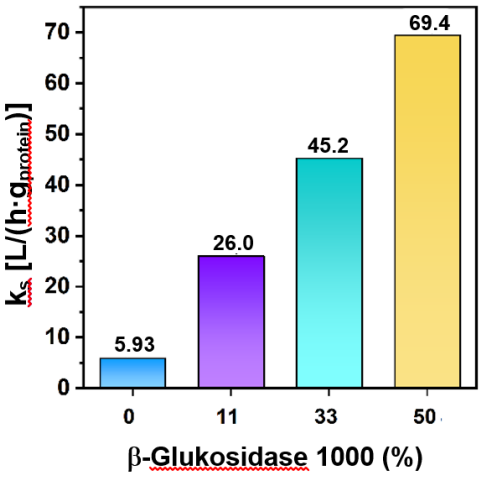
Celia Álvarez-González[a], Mauricio Zurita[b], Juan M. Bolivar [a,*], Miguel Ladero[a,c,*]

[a] *FQPIMA group, Chemical and Materials Engineering Department, Faculty of Chemical Sciences, Complutense University of Madrid, Madrid, 28040, Spain*
[b] *Materials and Sustainability group, Department of Engineering, Universidad Loyola Andalucía, Dos Hermanas, Seville, 41704, Spain*
[c] *Translational Research with iPS Cells Group, Research Institute of Hospital 12 de Octubre, imas12, 28041 Madrid, Spain*

E-mail: juanmbol@ucm.es; mladerog@ucm.es

In lignocellulosic and algae biorefineries, the sustainable use of energy and material resources advocates for mild pretreatments, good solid-liquid mixing and low enzyme loads, profiting for the cooperative action of all enzymes involved in biomass depolymerisation [1]. This work presents a detailed kinetic analysis of mildly alkaline pretreated rice straw, showing the effects on kinetic models and/or kinetic parameters of the adequate mixing of industrial cellulase and β-glucosidase cocktails (Biogazyme 2X –a cocktail rich in cellulase activity from *Trichoderma reesei*, and β-Glukosidase 1000, a cocktail rich in β-glucosidase and hemicellulase activities from *Aspergillus fumigatus*, both from ASA Biogazymes GmbH), monitoring saccharification reactions for pure and mixed cocktails by ion-exchange HPLC.

Fractal kinetic modelling is adequate to show progressive activation, deactivation and/or inhibition through the temporal evolution of the kinetic constant(s) as indicated by a fractal exponent [2]. Here, we deduced that a kinetic model that encompassed simple first-order kinetic fractal equations for the depolymerization and saccharification reactions and a firs-order total desactivation equation for the cellulase activity is the one that best fits to experimental results at 3 mg protein per gram dry solid (DS) with diverse enzyme cocktail mixtures. While the deactivation constant and the kinetic parameters for the saccharification reaction remain the same for all experiments, regarding the depolymerisation reaction, the fractal exponent values are slightly higher than those obtained for the pure cocktails, while the kinetic constant values are much higher, between 5 and 8 times higher, with values of 26, 45 and 69 h L/(h·$g_{protein}$), suggesting an extraordinary improvement in the hydrolysis/lysis of oligosaccharides and cellobiose to glucose associated with the increase in the enzyme cocktail of *Aspergillus fumigatus* (β-Glukosidase 1000), as shown in the figure. This model was also fine to be fitted at 6 and 9 mg/g DS, conditions at which total cellulose conversion was achieved at 2.5% DS.



[1] C. Alvarez-Gonzalez, J.A. Delgado, J.M. González, M. Zurita-Gotor, M. Ladero, J.M. Bolivar, J. M. *Results Eng*. **2025**, *27*, 106573.
[2] M. Wojtusik, P. Vergara, J.C. Villar, M. Ladero, F. García-Ochoa, *Bioresour. Technol.* **2020**, *318*, 124050.

Integrated recovery of lignin, phenolic extractives, and cellulose from vine shoots via oxalic acid-assisted ethanol organosolv pretreatment

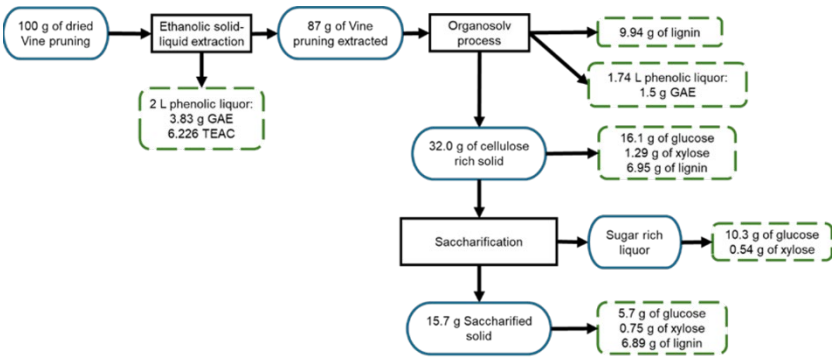
Jorge Garcia-Montalvo[a], Beatriz García-Sánchez[a], Sara Villarino-Viloria[a], Victoria Rigual[a], Juan M. Bolivar[a,*], Miguel Ladero[a,b,*]

[a]Chemical and Materials Engineering Department, Faculty of Chemical Sciences, Complutense University of Madrid, Madrid, 28040, Spain
[b] Translational Research with iPS Cells Group, Research Institute of Hospital 12 de Octubre, imas12, 28041 Madrid, Spain

E-mail: juanmbol@ucm.es; mladerog@ucm.es

Waste related to food production is a plentiful, scarcely used, emerging source of medium to high value-added compounds (cellulose, hemicellulose, lignin, and phenolic compounds), being usually employed for low-value applications, such as cattle-feed or composting, or disposed of via landfilling. However, complete utilization of these residues is required to develop a sustainable process within the second-generation biorefinery framework. Vine pruning is an abundant agro-industrial residue (about one million tons per year in Spain) with high lignin and phenolic content [1], yet their valorization is limited by the recalcitrant nature and the need to develop sustainable lignin extraction [2]. In this work a lignin-first biorefinery strategy is proposed, combining hydro-ethanol extraction applied to vine pruning to obtain a high yield in phenolic extractives with a novel ethanol-oxalic acid organosolv fractionation.

The solid-liquid extraction was optimized via RSM, enabling the recovery of a phenolic fraction with high antioxidant capacity (64.25 TEAC gds^{-1}). As a consequence, the remaining solid fraction was rich in structural biopolymers. The following optimal organosolv processing efficiently produced a native-like lignin fraction (114 mg gds^{-1}) and a cellulose-rich solid with 72.1 % cellulose and 5.1 % hemicellulose. The enzymatic saccharification of this latter fraction allowed to recover 0.62 grams of glucose yield pre gram of cellulose, with a six-fold yield improvement if compared to untreated biomass. Overall, this study demonstrates that the combination of a solid-liquid extraction with an oxalic acid-catalyzed organosolv process allows for a progressive fractionation of vine shoots into phenolic extractives, structurally preserved lignin, a highly digestible cellulose fraction and a lignin-rich final solid. This strategy seems to be an effective route to deploy vine pruning lignin-first biorefineries.



[1] M. Jesus, A. Romaní, F. Mata, L. Domingues, L. *Polymers* **2022**, *14*(9), 1640.
[2] M. Lara-Serrano, S. Morales-delaRosa, J.M. Campos-Martín, I. Romero, E. Castro, J.M. Oliva, P. Manzanares. *Ind. Crops Prod.* **2025**, *232*, 121240.

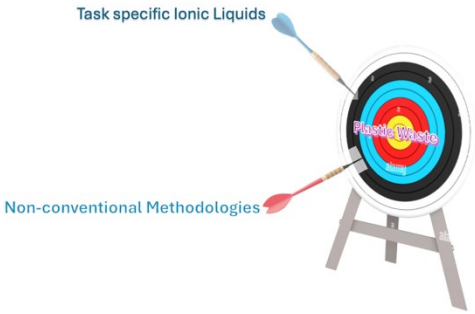
Two Arrows One Target: Task Specific Ionic Liquids and Non-Conventional Methodologies for Plastics Waste Recycling

Francesca D'Anna,[a*] Giovanna Raia,[a] Martina Silaco,[a] Salvatore Marullo[a]

[a]*Università degli Studi di Palermo, Dipartimento STEBICEF, Viale delle Scienze, Ed. 17, 90128 Palermo (Italy)*

E-mail: francesca.danna@unipa.it

Dispersion of plastic waste in the environment is one of the pressing issues of the modern society.[1] This is the reason why, in the last decade, researchers have dedicated a surge of interest to the identification of efficient strategies for plastic waste recycling. This would allow to achieve two main targets: *i*) the environment preservation; *ii)* the reduction of the dependence of modern society from fossil fuels.
With the above premises in mind, in this communication, we will present our last research dealing with the analysis of benefits deriving from the combined use of task specific ionic liquids (TSILs) and non-conventional methodologies (N-CMs) in plastic waste recycling.



Plastic polymers of different nature, like PET, PC, PLA and PCL, have been processed. Data collected show that the synergy between TSLIs and N-CMs allows performing plastic waste recycling and upcycling with high efficiency and energy saving.[2-6]

[1] H. Hibrahim, G. Alam, R. Amna, A. Faheem, *Green Technol. Sustain.* **2026**, *4(2)*, 100314
[2] S. Marullo, C. Rizzo, N. Tz. Dintcheva, F. D'Anna, *ACS Sustainable Chem. Eng.* **2021**, *9(45)*, 15157-15165.
[3] F. D'Anna, M. Sbacchi, G. Infurna, N. Tz. Dintcheva, S. Marullo, Green Chem. **2021** *23(24),* 9957-9967.
[4] G. Raia, S. Marullo, G. Lazzara, G. Cavallaro, S. Marino, P. Cancemi, F. D'Anna, *ACS Sustainable Chem. Eng.* **2023,** *11(50)*, 17870-17880.
[5] F. D'Anna, G. Raia, G. Di Cara, P. Cancemi, S. Marullo RSC Sustainability **2025**, *3(1)*, 580-591.
[6] S. Marullo, S.; M. Silaco, F. D'Anna, ACS Sustainable Chem. Eng. **2025**, *13(48)*, 20766-20775.

Enhancing the biodegradability of commercial cellulose-based glitter through a preliminary pretreatment using KrCl excilamp and hydrogen peroxide

María Claudia Montiel[a,*], Marta Doval-Miñarro[b], María Dolores Murcia[a], Javier Bayo[b], María Gómez[a], Ramón Pamies[c], Salvadora Ortega-Requena[a], Cristian Sánchez-Rodríguez[c]

[a] *Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30100 Murcia, Spain*
[b] *Department of Chemical and Environmental Engineering, Technological University of Cartagena, Doctor Fleming s/n, 30202 Cartagena, Spain*
[c] *Materials Science and Metallurgical Engineering Research Group, Technological University of Cartagena, Doctor Fleming s/n, 30202 Cartagena, Spain*

Email: cmontiel@um.es

Advanced Oxidation Processes (AOPs) have gained prominence as effective strategies for degrading persistent organic pollutants that resist conventional treatments. While traditional methods such as coagulation, filtration, and adsorption have been widely explored, they often fall short of achieving complete mineralization or require additional treatment steps. In contrast, photooxidation techniques, particularly those employing excimer radiation lamps in combination with hydrogen peroxide, have demonstrated notable success in degrading synthetic polymers like PET [1]. Building on these advances, the present study explores the use of krypton chloride (KrCl) excimer lamps, which emit high-energy monochromatic UV radiation at 222 nm, in combination with H_2O_2, as a preliminary pretreatment to enhance the biodegradability of commercial cellulose-based glitter. This approach promotes the generation of reactive oxygen species that accelerate polymer degradation and aims to assess the feasibility of this method as a first step toward facilitating subsequent biodegradation in marine environments. The study is especially relevant given the increasing use of so-called "eco-friendly" glitters made from modified regenerated cellulose, whose actual biodegradability under environmental conditions remains to be fully validated.

Photochemical degradation experiments were conducted in an open, batch-mode setup. Each reaction took place in a 250 mL borosilicate glass beaker positioned on a magnetic stirrer operating at 700 rpm to ensure thorough mixing. A mercury-free KrCl excimer lamp was mounted horizontally 3 cm above the liquid surface to provide irradiation. To monitor the degradation of commercial cellulose-based glitter, 500 µL aliquots were collected at predetermined time intervals and analyzed using high-performance liquid chromatography (HPLC). Additionally, the extent of organic pollutant mineralization was assessed by measuring Chemical Oxygen Demand (COD) and evaluating biological toxicity before and after treatment.

Acknowledgements: This work has been funded by University of Murcia and Technological University of Cartagena within the framework of "Proyectos Semilla" (Campus Mare Nostrum actions).

[1] A. Navarro-García, M. Gómez, M.D. Murcia, E. Gómez, A.H. Hidalgo, L.A. Dorado, J. Bastida, *Molecules*. **2025**, 30 (15), 3302.

Recycled PET waste as an adsorbent for bisphenol A removal

María Claudia Montiel[a], *, María Gómez[a], María Dolores Murcia[a], Elisa Gómez[a], Asunción María Hidalgo[a], Salvadora Ortega-Requena[a], Samy Dib[b]

[a] Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30100 Murcia, Spain
[b] Department of Chemistry and Physics of Inorganic Materials, University of Sciences and Technology Houari Boumediene, Algeria

Email: cmontiel@um.es

Polyethylene terephthalate (PET) is among the most widely used plastics thanks to its excellent properties and broad range of applications. However, its excessive consumption and the difficulties associated with its disposal make it essential to explore effective removal strategies. In this work, the main objective has been to investigate its upcycling and valorization as an adsorbent material, specifically for the removal of bisphenol A. This compound is of particular concern due to its endocrine-disrupting effects and its widespread presence in aquatic environments due to is commonly used as a plastic additive.

PET samples were placed in a muffle furnace and activated under a nitrogen atmosphere. The treatment consisted of a heating ramp up to 400 °C (5 ºC/min) with a 1-hour hold, followed by a second ramp to 800 °C (5 ºC/min) maintained for an additional 2 hours. The resulting carbonaceous material was then used for the adsorption of bisphenol A (BPA), employing an initial contaminant concentration of 100 mg/L at 40 °C and varying the mass of adsorbent. For comparison, the same experiments were conducted under identical conditions using a commercial carbon. In both cases, the adsorption isotherms were fitted to the Langmuir model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m * K_L} \quad (1)$$

leading to the following linearized equations for the PET-derived carbon (2) and the commercial carbon (3)

$$\frac{C_e}{q_e} = 10.83 C_e + 56.072 \quad R^2 = 0.9948 \quad (2)$$

$$\frac{C_e}{q_e} = 5.33 C_e + 50.974 \quad R^2 = 0.9982 \quad (3)$$

The good values of R^2 in both fittings indicates that BPA adsorption occurs predominantly as a monolayer on a relatively homogeneous surface. Besides, As expected, the PET-derived carbon exhibits a lower qm (maximum adsorption capacity) than the commercial carbon; however, its performance remains significant, reaching approximately half of the adsorption capacity of the commercial material

Acknowledgement
This study forms part of the ThinkInAzul programme and was supported by MCIU with funding from European Union NextGenerationEU (PRTR-C17.I1) and by Comunidad Autónoma de la Región de Murcia - Fundación Séneca.

Evaluation of dry photo-oxidation with excimer lamps as a pretreatment to enhance biodegradability of commercial cellusose-based glitter

Salvadora Ortega-Requena[a], *, Marta Doval-Miñarro[b], María Claudia Montiel[a], Javier Bayo[b], María Gómez[a], Ramón Pamies[c], María Dolores Murcia[a], Cristian Sánchez-Rodríguez[c]

[a] *Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30100 Murcia, Spain*
[b] *Department of Chemical and Environmental Engineering, Technological University of Cartagena, Doctor Fleming s/n, 30202 Cartagena, Spain*
[c] *Materials Science and Metallurgical Engineering Research Group, Technological University of Cartagena, Doctor Fleming s/n, 30202 Cartagena, Spain*

E-mail: dortega@um.es

Due to their small particle size and polymer-based composition, mainly polyethylene terephthalate (PET), glitter particles are categorized as primary microplastics. Their extensive use across sectors such as arts and crafts, cosmetics, and textile production promotes their inadvertent release into various environmental compartments. Once emitted, these particles are efficiently transported through wastewater pathways, leading to their accumulation in freshwater and marine systems and contributing to the overall microplastic burden. Lately, glitters formulated mainly from modified regenerated cellulose have emerged as an alternative, labeled as "ecological" since they are presented as biodegradable in aquatic environments. However, this biodegradability still needs to be fully tested [1]. It is known that advanced oxidation processes (AOPs) enhance the biodegradability of microplastics and recently they are gaining importance as a pretreatment to improve the effectiveness of subsequent biological treatments.

In this sense, this study is focused on an advanced oxidation treatment of commercial cellulose-based glitter, to evaluate its efficiency as a pretreatment. A KrCl excimer lamp is used for the photo-oxidation of glitter samples in dry conditions. The samples are subjected to a characterization before and after the oxidation treatment, including Elemental Analysis, Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA), in order to determine the extent of physicochemical changes and their potential impact on biodegradability.

Acknowledgements: This work has been funded by University of Murcia and Technological University of Cartagena within the framework of “Proyectos Semilla” (Campus Mare Nostrum actions).

[1] M. Yurtsever, *J. Agric. Environ. Ethics.* **2019**, 32(3), 459–478.

Polyurethane degrading bacteria: isolation, identification and enzymatic activity

Marta Munoz-Martí [a*], ***María Virtudes Navarro-Bañón*** [b], ***Ainoa Candela Gil*** [b], ***María Àngeles Castillo*** [a], ***Jorge García-Hernández*** [a]

[a] *Advanced Center of Food Microbiology (CAMA), Universitat Politècnica de València, Camí de Vera, 46022 València, Spain*
[b] *Technology Centre of Furniture and Wood of the Region of Murcia (CETEM), Perales, 30510 Yecla, Spain*

E-mail: m.munoz@cetem.es

Polyurethane (PU) is a versatile synthetic polymer widely used in everyday products and industrial applications. However, the **absence of sustainable end-of-life management strategies**, particularly for flexible PU foams, represents a significant environmental challenge. For instance, discarded mattresses are commonly incinerated or disposed of in landfills. In recent decades, increasing attention has been directed toward the development of innovative and environmentally friendly approaches for PU degradation and valorisation. Among these, the **isolation of novel degradative microorganisms** from waste-associate environments has emerged as a promising strategy. The present study aimed to **isolate and identify new PU-degrading bacterial strains** from waste accumulation sites and to **characterize their enzymatic activity** with potential application in PU waste valorization.

A selective enrichment procedure was designed to isolate bacteria with the capacity to degrade PU [1]. **Soil samples and PU foam residues** were collected from **four waste accumulation sites**. The samples were incubated in a **saline mineral medium supplemented with a commercial aqueous PU dispersion** (**MM-PU**) to isolate PU-degrading bacteria, that were identified using MALDI-TOF and 16S rRNA gene sequencing. Their degradation capacity was evaluated using a **spectrophotometric assay based on the decrease in turbidity of the PU** dispersion, which becomes progressively transparent upon polymer breakdown [1]. Enzymatic activities, including **esterase, urease, and protease**, were assessed using plate-based assays with selective culture media [2].

A total of **31 bacterial isolates showing** evidence of PU biodegradation were obtained and classified into 12 phylogenetic groups. **Sixteen isolates showed significant degradation capacity in liquid MM-PU medium,** achieving up to 70%, while four strains reached values close to 90%. Protease was the most prevalent enzymatic activity, detected in 25 isolates, whereas esterase activity was less frequently observed, being present in only nine strains.

[1] J. Alvarez-Barragan, L. Dominguez-Malfavon, M. Vargas-Suarez, R. Gonzalez-Hernandez, G. Aguilar-Osorio, H. Loza-Tavera, *Appl. Environ. Microbiol.,* **2016**, *82*, 5225–5235.
[2] A. Oceguera-Cervantes, A. Carrillo-Garcia, N. Lopez, S. Bolanos-Nunez, M.J. Cruz-Gomez, C. Wacher, H. Loza-Tavera, *Appl. Environ. Microbiol.,* **2007**, *73*, 6214–6223.

Sustainable Hydrolytic Depolymerization of Polyurethane Foam enabled by Ionic Liquids and Superbases

Maite Nuño,[a] Rocio Villa,[a,*] Francisco Velasco,[a] Rebeca Salas,[a] Maria Macia,[b] Jairton Dupont,[a] Eduardo Garcia-Verdugo,[b] Pedro Lozano[a,*]

[a] Department of Biochemistry and Molecular Biology B and Immunology, Faculty of Chemistry, University of Murcia, Campus de Espinardo, E-30100 Murcia, Spain.
[b] Department of Inorganic and Organic Chemistry, University Jaume I, Campus del Riu Sec, E-12071 Castellon, Spain.

E-mail: maite.n.s@um.es

Flexible polyurethane foams (PUFs) are extensively used materials whose crosslinked chemical structure complicates conventional recycling pathways, contributing to challenging end-of-life management.[1,2] This study examines a hydrolytic depolymerization approach under mild reaction conditions for flexible polyurethane foam waste (PUFW) using an aqueous depolymerization medium (DM) based on the water-miscible ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) combined with the organic superbase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (see **Figure 1**). Operated at atmospheric pressure and 95–98 °C for 4 h, the system enabled efficient depolymerization of several representative industrial PUFW formulations at 25 wt% PUFW loading and a fixed [Bmim][Cl]:DBU:H_2O composition of 62:13:25 wt%.[3]

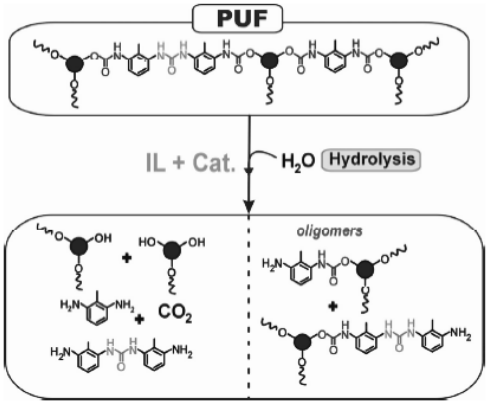


Figure 5. Schematic representation of PUFW hydrolytic depolymerization. The top section illustrates the representative chemical structure of a conventional PUF, featuring urethane (-NH-CO-O-) and urea (-NH-CO-NH-) bonds, while the bottom section shows the main products formed after hydrolysis.

A simple separation protocol was performed by directly adding water, which induced phase separation. A white solid recycled polyol (RP) precipitated, whereas the DM remained in the aqueous phase and was subsequently concentrated and reused. FTIR showed marked attenuation or disappearance of the urethane carbonyl band (~1720 cm^{-1}) in the RP, consistent with depolymerization. Scalability from gram to kilogram scale was demonstrated, with efficient recovery and reuse of both RP and DM. Physicochemical characterization confirmed RP suitability for reintegration. Moreover, re-foaming with 5 wt% RP yielded foams comparable to virgin polyol and superior to a commercial recycled polyol, supporting a mild, efficient and practically closed-loop recycling route for PUFW.

Acknowledgements
This work has been partially supported by MICINN-FEDERAEI 10.13039/501100011033 (PID2024−159264OBC21/C22
and CPP2023−010883) and Fundación SENECA (21884/PI/22 and 22518/PDC/24).

[1] F. Velasco, R. Villa, R. Salas, F. J. Ruiz, S. Nieto, J. Dupont, E. Garcia-Verdugo, P. Lozano, ACS Sustain. Chem. Eng. 2026, 14, 3758–3777.
[2] F.M. de Souza, P.K. Kahol, R.K. Gupta, *J. Am. Chem. Soc*. **2021**, *1380*, 1-24.
[3] R. Salas, R. Villa, S. Cano, S. Nieto, E. Garcia-Verdugo, P. Lozano, *Catal. Today*. **2024**, *430*, 114516.

Selective Glycolysis of Polyurethane Foam Wastes through Ionic Liquids Technology

Francisco Velasco,[a] Rocio Villa,[a] Maite Nuño,[a] Carlos Sotillo,[a] Susana Nieto,[a] Eduardo Garcia-Verdugo,[b] Jairton Dupont [a] and Pedro Lozano. [a]

[a] Department of Biochemistry and Molecular Biology B and Immunology, Faculty of Chemistry, University of Murcia, Murcia, Spain
[b] Department of Organic and Inorganic Chemistry, Faculty of Chemistry, University Jaime I, Castellón, Spain
E-mail: francisco.velascod@um.es

Polyurethane foams (PUFs) represent the sixth most produced plastic globally, yet over 80% of their waste (PUFW) is still disposed of *via* incineration or landfilling.[1] Current chemical recycling through glycolysis is limited by harsh reaction conditions (170-250 ºC), lack of selectivity, and the formation of toxic aromatic amines.[2] Herein, we report a sustainable and scalable strategy for the chemical depolymerization of PUFW by employing the ionic liquids 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-n-butyl-3-methylimidazolium acetate ([Bmim][OAc]) as a dual-function system.[3]

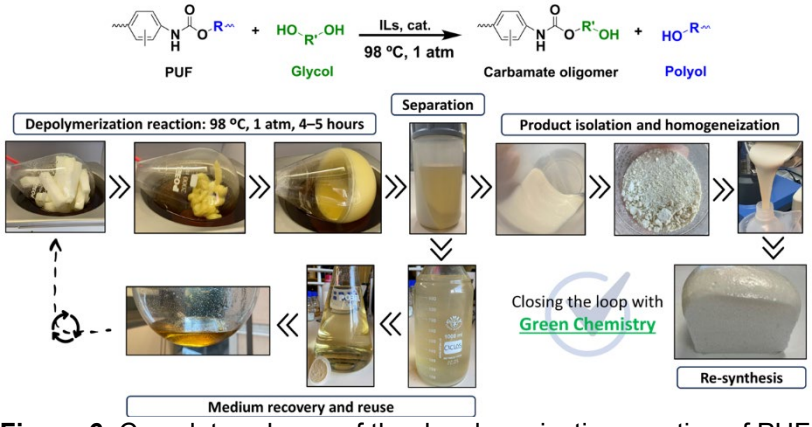


Figure 6. Complete scheme of the depolymerization reaction of PUF through glycolysis and the subsequent washing-centrifugation cycle to obtain the pure recycled products (*e.g.*, polyol and urethane/urea oligomers).

In this process, [Bmim][Cl] facilitates the physical swelling of the polymer matrix while the acetate anion of [Bmim][OAc] acts as an efficient catalyst for the selective glycolysis of urethane bonds using ethylene glycol (EG) as the nucleophile. Full depolymerization is achieved under mild conditions (<100 ºC, 1 atm) within 4–5 hours, minimizing side reactions and maintaining a residual monomeric aromatic amine content of only 0.05 w%. The addition of water to the reaction medium enables the direct precipitation of the recycled polyol and the efficient recovery of the water-miscible ILs, which were reused for six consecutive cycles without loss of catalytic efficiency. The recycled products were characterized by iKOH, NMR, and ATR-FTIR, confirming their suitability for synthesizing new flexible foams with identical physico-chemical and mechanical properties to the original materials. This methodology was successfully scaled up to 100 g and extended to recalcitrant rigid polyisocyanurate (PIR) foams, demonstrating its robustness and potential for industrial-scale application in a circular economy framework.

Acknowledgements
This work has been partially supported by MICINN-FEDERAEI 10.13039/501100011033 (PID2024−159264OBC21/C22 and CPP2023−010883) and Fundación SENECA (21884/PI/22 and 22518/PDC/24).

[1] EUROPUR. The End-of-Life of flexible polyurethane foam from mattresses and furniture brochure. **2020**. https://europur.org/flexible-pufoam/sustainability/
[2] H. W. He, H. Hu, K. M. Du, M. Lu, F. Yang, L. X. Cui, M. Ma, Y. L. Zhu, Y. Q. Shi, S. Chen, X. Wang, *Green Chem*. **2025**, *27*, 8467-8491.
[3] F. Velasco, R. Villa, N. Alonso, R. Salas, J. Dupont, E. Garcia-Verdugo, P. Lozano, *Green Chem*., **2025**, *27*, 13235.

Modulating PET Hydrolase Activity via Rational Loop Grafting

Norbert Graefe,[a] Georg Künze,[a]

[a] *Institute for Drug Discovery, Medical Faculty, Leipzig University, Germany*

E-mail: norbert.graefe@medizin.uni-leipzig.de

The hydrolysis of post-consumer plastics by polyester hydrolases represents a promising strategy for the closed-loop recycling of polyethylene terephthalate (PET). Within polyester hydrolases, the β8–α6 loop plays a critical role in catalysis, as it contains the catalytic histidine and regulates access to the active site. A key structural distinction between type I and type II PET hydrolases lies in this region: type I enzymes possess a loop that is typically two to three residues shorter, resulting in a more rigid conformation and a well-defined active-site geometry. In contrast, type II PET hydrolases compensate for increased loop flexibility through a disulfide bridge connecting the β8–α6 loop to the β7–α5 loop, which harbors the catalytic aspartate, thereby maintaining active-site integrity [1].

In this study, we investigated the role of the β8–α6 loop in engineered enzyme variants R4M10 (PHL7) [2], TurboPETase [3], and Kubu-PM12 [4] by replacing this region with loop sequences derived from a diverse set of type I polyester hydrolases. The goal was to identify loop architectures that enhance PET degradation efficiency.

Loop sequences from type I polyester hydrolases were extracted from the PAZy database, clustered based on sequence similarity, and selected according to AlphaFold 3 [5] pLDDT confidence scores. Selected loops were grafted into the scaffold enzymes, expressed, and purified. Enzymatic activity was evaluated using electrochemical impedance spectroscopy[6], while thermal stability was assessed via nanoDSF. We observed that β8–α6 loop variants are differentially tolerated within the scaffold enzymes, with several substitutions leading to improved performance.

These results demonstrate that β8–α6 loop composition is a key determinant of PET hydrolase performance and provide a foundation for future structure-guided enzyme engineering, offering a pathway toward sustainable enzymatic plastic recycling.

References:

1. T. Fecker, P. Galaz-Davison, F. Engelberger, *Biophys. J.* **2018** 114 (6), 1302-1312.
2. about to be published
3. Y. Cui, Y. Chen, J. Sun, *Nat. Commu.* **2024** *15* (1), 1417.
4. H. Seo, H. Hong, J. Park, *Science* **2025** 387 (6729).
5. J. Abramson, J. Adler, J. Dunger, *Nature*, **2024** 630 (8016), 493-500.
6. R. Frank, D. Krinke, C. Sonnendecker, *ACS Catal.* **2021** 12 (1), 25-35.

Transforming Plastic Waste into Antiviral Glycodendrimers: A Sustainable Glycochemistry Strategy

María J. Hernáiz, Carlos Martínez, Alejandro Merchán, Ainhoa Martín, Pedro Ramirez, Almudena Perona

Department of Chemistry in Pharmaceutical Sciences, Faculty of Pharmacy, Complutense University of Madrid, Plz. Ramón y Cajal s/n, Madrid, C.P. 28040, Spain

E-mail: mjhernai@ucm.es

The increasing accumulation of plastic waste represents a critical environmental issue, aggravated by the fact that less than 12% is effectively recycled worldwide. In particular, polymers such as polyethylene terephthalate (PET) present significant challenges for conventional recycling processes. Consequently, the valorization of plastic waste into high-value functional materials has emerged as a key objective in sustainable chemistry.[1]

Chemical depolymerization of PET provides accessible intermediates such as bis(2-hydroxyethyl) terephthalate (BHET) and terephthalic acid (TPA), which can be repurposed as versatile building blocks. In this context, we report an alternative approach to exploit these monomers for the preparation of biologically active systems. [1]

Specifically, we have developed antiviral glycodendrimers using BHET- and TPA-derived scaffolds, contributing to the advancement of circular glycochemistry. These multivalent architectures, functionalized with carbohydrate units, are capable of mimicking natural glycans and interacting selectively with viral surface proteins.

The synthetic strategy relies on the conjugation of mannose[2] and glucuronic acid[3,4] azides onto the aromatic cores via CuAAC click chemistry, performed under energy-efficient and environmentally friendly conditions. The resulting compounds were evaluated for their interaction with envelope proteins from Dengue virus and HIV-1.

Binding studies using surface plasmon resonance, supported by molecular modeling, demonstrated selective recognition, underscoring the potential of these glycodendrimers as antiviral agents. Overall, this work highlights the feasibility of transforming plastic waste into high-value glycomaterials with biomedical relevance.

[1] J. M. Garcia, M. L. Robertson, *Science,* **2017,** 358, 870-872.
[2] C. Martínez, A. Merchán, A. Perona, P. Ramírez-López, J. R. Suárez, M. J. Hernáiz, *Catal. Today.* **2024**. 429, 114493.
[3] A. Merchán, P. Ramírez-López, C. Martínez, J. R. Suárez, A. Perona, M. J. Hernaiz, *Bioconjugate Chem.* **2024**, 35, 34–422.
[4] P. Ramírez-López, C. Martínez, A. Merchán, A. Perona, M. J. Hernaiz, *Bioorganic Chem.* **2023**, 141, 106913.

Valorisation of Polyester Textile Waste into Activated Carbons for High-Performance Supercapacitor Electrodes

María Alexandre-Franco[a], Laura Mendoza-Cerezo[b,c], Jesús Píriz[a], Antonio Macías-García[d], José Manuel Rodríguez-Rego[d]

[a] *Department of Organic and Inorganic Chemistry, University of Extremadura, Avda. de Elvas s/n, 06006 Badajoz, Spain*
[b] *Department of Graphic Expression, School of Industrial Engineering, University of Extremadura, 06006 Badajoz, Spain*
[c] *Department of Biochemistry and Molecular Biology and Genetics, Faculty of Sciences, University of Extremadura, 06006 Badajoz, Spain*
[d] *Department of Mechanical, Energetic and Materials Engineering, School of Industrial Engineering, University of Extremadura, 06006 Badajoz, Spain*

E-mail: malexandre@unex.es

The exponential growth of fast-fashion consumption has transformed polyester textile waste into a critical environmental challenge, demanding innovative valorization strategies within a circular economy framework [1,2]. In this work, polyester textile residues were successfully converted into high-performance activated carbons (ACs) for energy storage applications.

The waste materials were carbonized (600–900 °C) and subsequently activated via steam and KOH treatments. The resulting carbons were characterized by N_2 adsorption (BET), FT-IR spectroscopy and electrical conductivity measurements. Chemical activation with KOH produced ultrahigh surface areas (SBET > 1700 m^2/g) and a hierarchical micro–mesoporous structure, which is known to be crucial for adsorption and electrochemical performance [3]. FT-IR analysis revealed the formation of oxygen-containing functional groups, enhancing surface wettability and electrode–electrolyte interactions.

Electrical conductivity increased significantly after carbonization (0.02 to ~600 S/m) and remained high after activation (~100 S/m) in KOH-treated samples, indicating preservation of conductive graphitic domains. Electrochemical evaluation showed quasi-rectangular cyclic voltammetry curves characteristic of electric double-layer capacitor (EDLC) behavior [4].

The TPL-K900 sample exhibited the highest current response and excellent rate capability up to 100 $mV \cdot s^{-1}$. Capacitance values reached 115 $F \cdot g^{-1}$ with retention above 94% after 1000 cycles, demonstrating outstanding stability and competitiveness with recently reported systems [5].

These findings highlight the synergistic role of porosity and surface chemistry in charge storage and confirm the potential of polyester waste as a sustainable precursor for advanced energy materials.

[1] W. Wang et al., Crit. Rev. Environ. Sci. Technol. 2021, 52, 3921–3942.
[2] W. Chen et al., Environ. Sci. Pollut. Res. 2017, 24, 22602–22612.
[3] A. Bogeat, Crit. Rev. Solid State Mater. Sci. 2019, 46, 1–37.
[4] A. G. Pandolfo, A. F. Hollenkamp, J. Power Sources 2006, 157, 11–27.
[5] R. Bennie et al., J. Power Sources 2025, 235649.

Low-Temperature Alkaline Depolymerization of Polyethylene Terephthalate (PET) as a Chemical Recycling Strategy for Textile Waste

María Alexandre-Franco[a], Manoli Rodríguez[a], Juan Manuel Rodríguez Zoido[a]
[a] *Department of Organic and Inorganic Chemistry, University of Extremadura, Avda. de Elvas s/n, 06006 Badajoz, Spain*

E-mail: malexandre@unex.es

The increasing generation of textile waste derived from polyethylene terephthalate (PET) represents a major environmental challenge due to its persistence and the limitations associated with conventional mechanical recycling. In this context, chemical recycling has emerged as a promising alternative, enabling the recovery of high-value monomers and supporting circular economy strategies [1,2].

This work addresses the chemical depolymerization of PET textile waste through an alkaline hydrolysis process conducted at low temperatures. The methodology involves the use of sodium hydroxide (NaOH) and potassium hydroxide (KOH) in a mixed organic solvent system composed of ethanol and dichloromethane. This approach offers significant advantages over traditional recycling methods, including reduced energy consumption and improved purity of the recovered products [3].

To optimize the depolymerization process, a central composite, orthogonal, and rotatable factorial design (FCCOR) was implemented, comprising 23 experimental runs. The main independent variables studied were NaOH concentration and solvent composition, while the response variable was the amount of terephthalic acid (TPA) recovered. The results demonstrate a strong dependence of process efficiency on these variables, enabling the identification of optimal conditions that maximize TPA yield.

Furthermore, recent advances highlight the feasibility of closed-loop recycling approaches for polyester-based textile waste, reinforcing the industrial relevance of such strategies [4,5]. Overall, alkaline depolymerization at low temperatures is presented as an efficient and sustainable pathway for PET textile recycling with promising scalability.

[1] Jehanno C, Pérez-Madrigal MM, Demarteau J, Sardon H, Dove AP. Critical advances and future opportunities in upcycling commodity polymers. *Nature*. 2022; 603:803–814.
[2] Rahimi A, García JM. Chemical recycling of waste plastics for new materials production. *Nat Rev Chem*. 2017; 1:0046.
[3] Wang S, Wang Y, Li Y, Zhang X. Alkaline hydrolysis of PET for terephthalic acid recovery under mild conditions. *Green Chem*. 2020; 22:123–134.
[4] Ügdüler S, Van Geem KM, Denolf R, Roosen M, Mys N, Ragaert K, et al. Towards closed-loop recycling of multilayer and textile polyester waste. *ACS Sustain Chem Eng*. 2020; 8:8586–8594.
[5] De Smet N, Billen P, Ragaert K, Dewulf J. Chemical recycling of PET: State-of-the-art and future perspectives. *Chem Eng J*. 2021; 403:126346. W. Wang et al., Crit. Rev. Environ. Sci. Technol. 2021, 52, 3921–3942.

The structural and optical properties of N and rGO-doped TiO_2 films deposited on glass substrates by spin coating

Maria Begoña Asenjo,[a,*] Maria Paz Alcacera [a] and Roberto Rubio[b]

[a] Avda Complutense 40, Madrid, Spain, CIEMAT.
[b] C. de Francos Rodríguez 106, Madrid, Spain, IES Virgen de la Paloma.

E-mail mbegona.asenjo@ciemat.es

Photovoltaic power generation systems are one of the best solutions for renewable energy utilization. TiO_2 is an abundant material on Earth, essential for the sustainable and cost-effective development of various technologies, with anatase being the most effective polymorph for photocatalytic [1] and photovoltaic applications [2].

In this work, a study of materials for photovoltaic applications based on TiO_2, doped with nitrogen (N) and with reduced graphene oxide (rGO) has been carried out to increase the performance in such devices. The rGO dopant used is commercial and two different types of precursors have been used as a nitrogen source to see how it influences the properties of the material.

The films were synthesized by sol gel method and deposited on glass using the spin coating technique.

The progress of the synthesis reaction over time was studied using FT-IR spectrum spectroscopy.
Ultraviolet–visible spectroscopy is used to disclose the absorption region and to calculate the energy gap (Eg) for the films and Raman spectroscopy, revealed the incorporation of nitrogen and rGO into the TiO_2 structure.

Doping TiO_2 reduces the band gap, allowing it to absorb and utilize visible light more efficiently, since undoped TiO_2 is active in ultraviolet light in DSSC cells, which are the future cells that will be prepared with these materials.

It was observed that doping with rGO modifies the electronic structure of TiO_2 more profoundly than doping with nitrogen, due to the structure of carbon, its high conductivity, and its ability to generate new intermediate states that reduce the band gap.

This preliminary study demonstrates that rGO and nitrogen are good alternatives for doping the TiO_2 used as a photoanode in DSSCs.

[1] L. Collado, M. García-Tecedor, M. Gomez-Mendoza, *CatalysisToday.* **2023**, *423*, 114279.
[2] P.R. Jubu, Z.S. Mbalaha, E.V. Tikyaa, *Next Materials.* **2025**, *9*, 101166.

Preparation of In-ZnO thin films with reduced graphene oxide (IZO/rGO) using the sol-gel method.

Maria Begoña Asenjo,[a,*] Maria Paz Alcacera [a] and Ignacio Sánchez [b]

[a] Avda Complutense 40, Madrid, Spain, CIEMAT.
[b] Universidad Complutense de Madrid, Pl. de las Ciencias 1, Madrid, Spain.

E-mail mbegona.asenjo@ciemat.es

In the field of thin-film, transparent conductive oxides (TCOs), have been used as electrodes in various applications such as solar cells, organic light-emitting diodes, etc. The most commonly used transparent conductive oxide in photovoltaic solar cells is indium tin oxide (ITO) [1]. The deposition process for this compound is its main drawback, as the most widely used method is by magnetron sputtering, which is very expensive due to the extremely high temperatures required.
An alternative to ITO is In-doped Zn oxide (IZO). This material has properties such as resistivity, photoconductivity, transmittance, and energy gap (Eg) that make it suitable for use as a TCO in solar cells [2].

The objective of this work is to obtain thin layers of doped and undoped IZO with reduced graphene oxide (rGO) using chemical methods, in order to reduce synthesis costs.

The films were synthesized by sol gel method and deposited on glass using the spin coating technique.

A thorough characterization of the solutions and samples obtained has been carried out, discussing the most influential parameters and optimal operating conditions for obtaining fine, homogeneous layers of IZO and IZO/rGO.
The progress of the synthesis reaction over time was studied using Ft-IR spectrum spectroscopy. Optical characterization was performed using spectroscopy UV-vis spectroscopy and the electrical measurements were obtained using the 4-point technique.

Reduced graphene oxide was added to the In-ZnO solution to reduce defects and increase conductivity in thin films. The conductivity of the films improved due to its excellent conductivity. The energy levels of the films varied depending on the synthesis conditions; the incorporation of rGO decreases the Eg from 3.55 eV to 2.92 eV

[1] P. Lippens y U. Muehlfeld, Handbook of Visual Display Technology **2012**, 779-794. doi: 10.1007/978-3-540-79567-4_54.
[2] L. C. K. Liau y J. S. Huang, Mater Res Bull, **2018**, 97, 6-12

Engineering Amorphous MOFs as Batteries Electrodes

Carmen Martín,[a*] Jouma Katati,[a] Elena García[a] and David Ávila[a*]

[a]Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid. Avda. Complutense s/n. 28040-Madrid.

E-mail: mariad80@ucm.es

Portable electronic devices, depending on energy storage technology, have become a ubiquitous in our modern society. Consequently, advances in new materials for more efficient energy storage devices have become an important research area.

Recently, metal-organic frameworks (MOFs) have emerged as an important type of electrodes for electrochemical energy storage.[1] MOFs are crystalline porous networks formed *via* coordination bonding between nodes (metal ions or ionic metal clusters) and ligands (organic molecules). However, their high ordering degree can restrain the charge carriers and ions mobility through the MOFs pore, limiting their electrochemical performance. A more recent strategy to improve the performance of electrode materials is the incorporation of amorphous materials due to their unique properties (e.g., abundant active sites, structural flexibility and fast ion diffusion). Thus, for example, the crystalline carboxylate MOF-74 (Co), with 2,5-dihydroxybenzene-1,4-dicarboxylic acid (H_4DOBDC) as ligand, has shown a reversible capacity of 50 mAh/g at C/10 (intercalation of 0.65 Li per formula unit).[2] Interestingly, when this material was transformed into the amorphous phase, the reversible capacity was increased three times (up to 150 mAh/g).

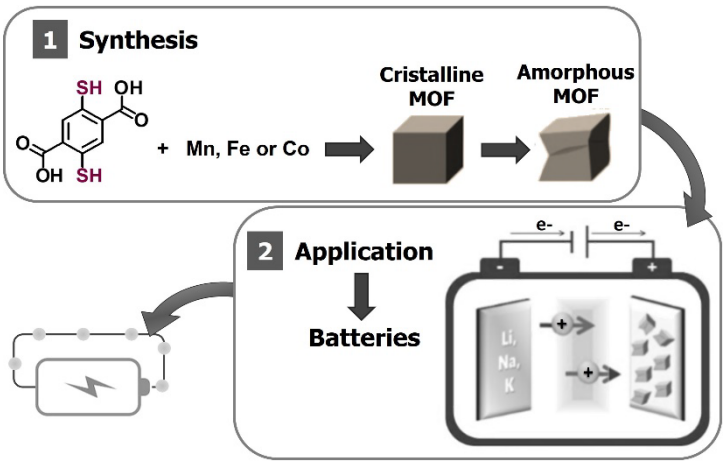


Figure 1. Synthesis and application of amorphous MOFs.

In this contribution, we will present the electrochemical performance of electrodes based on amorphous MOFs within a sulphur-based ligand in the structure, the 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid (H_4DSBDC), in Li batteries.

[1] G. Song, Y. Shi, S. Jiang, H. Pang, *Adv. Funct. Mater.* **2023**, *33 (42)*, 2303121.
[2] E. Garcia-Chamocho, R. Loredana-Vasile, J. Carretero-Gonzalez, E. Castillo-Martinez, D. Ávila-Brande, *Inorg. Chem.* **2025**, *64,* 21379-21386.

Deep eutectic solvent functionalized polymeric membranes as microbial fuel cell separators

María José Salar-García[a,*], Kateřina Hamalová[b], Víctor Manuel Ortiz-Martínez[c,*], Pedro Antonio García-Soto[c], Sergio Sánchez Segado[c], Luis Javier Lozano-Blanco[c]

[a] *Department of Chemical and Environmental Engineering, Technical University of Cartagena (UPCT) member of European University of Technology EUT+, Campus Alfonso XIII, Aulario C, 30203, Cartagena, Spain*
[b] *Centre for Nanomaterials and Biotechnology, Faculty of Science, Jan Evangelista Purkyně University in Ústí nad Labem, 400 96, Ústí nad Labem, Czech Republic.*
[c] *Department of Chemical and Environmental Engineering, Technical University of Cartagena (UPCT) member of European University of Technology EUT+, Campus Muralla Del Mar, 30202, Cartagena, Spain*

E-mail: victor.ortiz@upct.es ; mariajose.salar@upct.es

Deep eutectic solvents (DES) are emerging green solvents formed by mixtures of hydrogen-bond donor and acceptors, known for their high ionic conductivity, tunable physicochemical properties, low cost, and simple preparation methods [1]. In this work, DES based on Aliquat-336 and menthol were incorporated into a polyvinyl chloride (PVC) matrix to produce functionalized polymeric membranes for use as separators in microbial fuel cells (MFCs) for wastewater treatment. This type of separator is also of interest for related bioelectrochemical systems such as microbial electrolysis cells (MECs), in which the membrane plays a similar role.

Membranes containing varying DES loading were fabricated via solution casting and characterized in terms of morphology and ion-transport prior to evaluation in MFC operation. The optimal configurations showed a favorable balance between structural integrity and ionic conductivity, achieving power densities of nearly 300 $mW \cdot m^{-3}$ and high chemical oxygen demand (COD) removal efficiencies exceeding 78%, thereby clearly outperforming pristine PVC membranes.

These results demonstrate that DES-functionalized membranes provide a sustainable, low-cost alternative to conventional MFC separators [2], enhancing both electrochemical performance and wastewater treatment efficiency.

Acknowledgments

This work is supported by project PID2023-1510000A-I00 funded by MICIU/AEI/10.13039/501100011033 and by FEDER, EU.

[1] B. B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, E. J. Maginn, A. Ragauskas, *Chem. Rev.* **2021**, 121, 1232-1285.
[2] M. Shabani, H. Younesi, M. Pontié, A. Rahimpour, M. Rahimnejad, A. A. Zinatizadeh, *J. Clean. Prod.* **2020**, 264, 121446.

Economic and operational evaluation of the production of solketal tert-butyl ether (STBE) for use as an oxygenated additive in diesel/STBE blends.

Clara Hernández, Rafael Estévez*, Ana Granados, Vicente Montes, F.M. Bautista

Departamento de Química Orgánica, Instituto Químico para la Energía y el Medioambiente (IQUEMA), Universidad de Córdoba, Campus de Excelencia Internacional Agroalimentario CeiA3, Edificio Marie Curie, E-14014, Córdoba, España
E-mail: q02heluc@uco.es

Solketal, also known as 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane, is the main product of the ketalization reaction between glycerol and acetone. This compound can be used as a fuel additive; however, it cannot be blended with diesel in proportions higher than 5% due to physicochemical limitations [1].

An alternative approach is its alkylation to produce solketal tert-butyl ether (STBE) [2], a compound that is not commercially available and for which, limited information is found in the literature, but which can be used as an oxygenated fuel additive due to its higher physicochemical affinity with diesel.

This work focuses on optimizing STBE synthesis. The conventional route (1) involves ketalization of 1-mono glycerol tert-butyl ether (1-m-GTBE) with acetone followed by isolation of STBE through Column Chromatography, a complex process with high solvent consumption. To reduce the number of steps, two alternative routes were studied: (2) synthesis from a mixture of MTBGs and h-GTBEs, avoiding chromatographic separation after glycerol etherification with tert-butanol; and (3) direct reaction between glycerol, tert-butanol, and acetone with unreacted glycerol removed by liquid-liquid extraction. All three processes were economically evaluated considering reagent, solvent, and energy consumption.

The fractions obtained from the three routes were blended with diesel at 5% v/v and their physicochemical properties were analyzed, confirming compliance with fuel standards (UNE-EN 590:2022). Their performance was evaluated in a diesel engine coupled to an AYERBE generator (5 kVA, 230 V), and the different parameters measured are collected in Table 1.

Table 1. Measured parameters: GP: generated power; emissions of NO_x, CO, and CO_2; OP: opacity, which measures soot emissions; and BSFC: Brake Specific Fuel Consumption, which measures fuel consumption. D5_1, D5_2, and D5_3 refer to diesel blends, tested at a power output of 3 kW.

		ENGINE PERFORMANCE AT INTERMEDIATE POWER (3kW)					
Route	**Cost per mL of additive (€)**	**GP (kW)**	**NOx (ppm)**	**CO (ppm)**	**CO_2 (%)**	**OP (Bosch)**	**BSFC (g/h·kW)**
DIESEL	0.0014	1.9	156.0	97	1.40	0.72	562
D5_1	2.54	2.1	90.3	104	1.55	0.12	573
D5_2	0.88	1.6	85.3	89	1.39	0.21	311
D5_3	0.89	1.9	138.3	87	1.31	0.43	327

Results showed that all three routes reduced pollutant emissions, in some cases substantially, compared to conventional diesel, without significantly affecting engine power output. The economic study indicated that routes 2 (0.88 €/mL) and 3 (0.89 €/mL) substantially lowered costs relative to route 1 (2.54 €/mL). Although product purity decreased, no significant differences were observed in engine performance.

Acknowledgements. Research granted by Project PID2022-142275OB-I00 (MCIU/AEI/10.13039/501100011033 y FEDER, UE)

[1] A. Cornejo, I. et al. Renew. Sustain. Energy Rev. (2016) 79 1400–1413.
[2] V.O. Samoilov,et al., Fuel (2017) 172 310–319.

Glycerol derivatives as oxygenated additives for diesel fuel reformulation: Effect on performance and exhaust emissions of a diesel engine

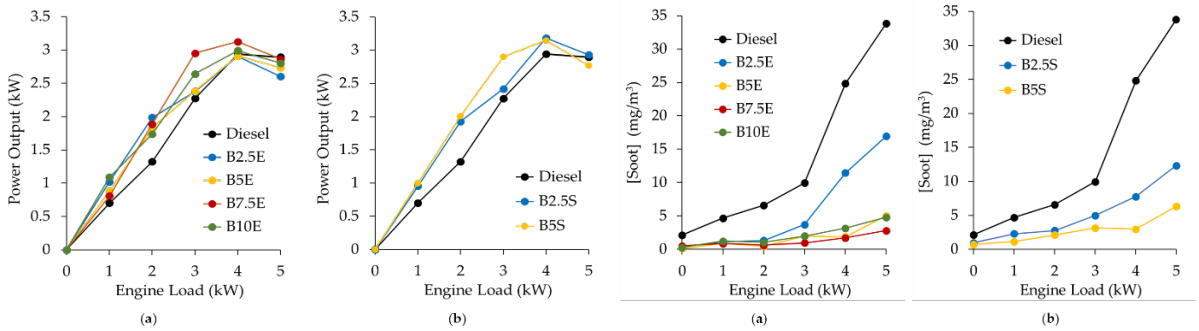
Laura Aguado-Deblas, Vicente Montes, Rafael Estévez*, Diego Luna, Felipa M. Bautista

Departamento de Química Orgánica, Instituto Químico para la Energía y el Medio Ambiente, Universidad de Córdoba, Campus de Excelencia Internacional Agroalimentario CeiA3 Edificio Marie Curie, E14014 Córdoba, Spain.

E-mail: q22mojiv@uco.es

The substantial increase in global biodiesel production has resulted in a notable surplus of glycerol, which can be upgraded into high-value compounds like oxygenated fuel additives [1]. In this study, solketal (S) and high ethers (h-GTBE) were evaluated as bio-additives in a commercial diesel.

h-GTBE was synthesized via etherification of glycerol with tert-butyl alcohol and successfully isolated using liquid-liquid extraction with glycerol or column chromatography. Diesel was then blended with X% v/v of h-GTBE (BXE, X= 2.5, 5, 7.5, 10) or solketal (BXS, X= 2.5, 5) and their physicochemical properties were analyzed, confirming compliance with fuel standards (UNE-EN 590:2022). The addition of both glycerol derivatives slightly increased kinematic viscosity and density, but successfully reduced cloud point and pour point temperatures, improving cold flow properties [2]. Engine tests carried out on a 4-stroke, single-cylinder diesel engine revealed that the blends improved power output compared to pure diesel, mainly at low and medium loads, due to the high oxygen content, Figure 1. Moreover, the brake specific fuel consumption (BSFC) decreased, indicating more efficient combustion.



Remarkably, exhaust emissions of soot (Figure 1), CO, and NOx were significantly reduced (data not shown due to the lack of space). The B10E blend exhibited the best performance, showing an 83%, 31%, and 21% reduction in soot, CO, and NOx, respectively, along with a 15% increase in power output. Similarly, the B5S blend demonstrated excellent results with BSFC, soot, and CO reductions of 22%, 75%, and 4%, respectively, while increasing power output by 25%. These results confirm the potential of h-GTBE and solketal as eco-friendly alternatives to conventional diesel additives.

[1] A. Çakmak, H. Özcan, *Fuel.* **2022**, 315, 123200.
[2] E. Alptekin, M. Canakci, *Appl. Therm. Eng*. **2017**, 124, 504-509.

Acknowledgements
Researches granted by Projects TED2021-132224B-I00 (MCIU/AEI/10.13039/501100011033 and European Union "NextGenerationEU/PRTR") and PID2022-142275OB-I00 (MCIU/AEI/10.13039/501100011033 y FEDER, UE)

High-Efficiency Metal-Oxide Ionanofluids: A Dual Experimental-Simulation Strategy for Solar-Thermal Heat Transfer

Jesús León-García, José Javier Delgado-Marín, Imane Moulefera, Ignacio Carnerero-Hinojosa, Alberto Cascales, Mercedes G. Montalbán, Gloria Víllora*

Chemical Engineering Department, Faculty of Chemistry, CEIR Campus Mare Nostrum (CMN), University of Murcia, 30071 Murcia, Spain.
Email: jesus.leong@um.es

The development of next-generation heat-transfer media is essential for improving the efficiency and reliability of advanced solar-thermal technologies. In this work, two ionanofluids (INFs) formulated with metal oxide (CuO and ZnO) nanoparticles dispersed in an ionic liquid are investigated as promising candidates for high-performance heat-transfer applications. Both systems exhibited excellent stability and significant enhancements in key thermophysical properties, notably thermal conductivity (Figure 1) and heat capacity, compared with the corresponding base fluid. These improvements directly influence their heat-transport capability, positioning these INFs as advantageous working fluids for solar-thermal collectors.

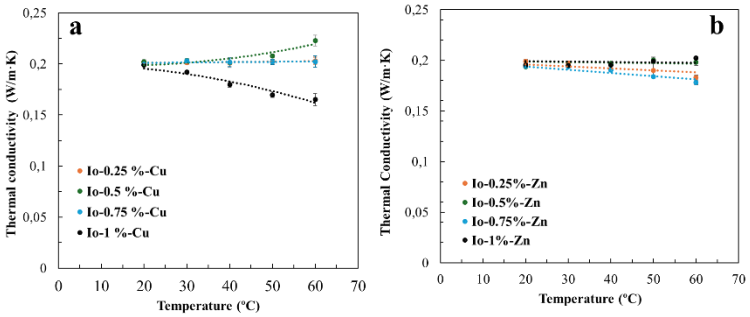


Figure 1. Thermal conductivity of the INFs as a function of temperature. a) INFs prepared at different concentrations of CuO; b) INFs prepared at different concentrations of ZnO.

Beyond experimental characterization, this study incorporates advanced simulation tools [1] to predict the behavior of the fluids under diverse operating conditions. Two complementary simulation approaches are employed: one dedicated to forecasting the performance of a full solar-collector experiment, and another aimed at reproducing the internal thermal and hydrodynamic behavior of the fluid within the collector plate. These predictive models enable a more detailed understanding of the system's response to variations in flow rate, irradiation, and geometric configuration, while providing a framework for optimizing operational parameters prior to experimental validation. This work reinforces the relevance of INFs as emerging alternatives to conventional heat-transfer fluids and demonstrates the value of integrated simulation-assisted methodologies for accelerating the design and assessment of advanced solar-thermal materials.

Funding: This work is part of the following research projects: Ref. PID2023-150761OB-C21 funded by MICIU/AEI/10.13039/501100011033 and by FEDER, UE and Ref. 22129-PI-22 funded by the research support program of the Seneca Foundation of Science and Technology of Murcia, Spain. J.J. Delgado-Marín and J. León-García acknowledge support from the Juan de la Cierva contract (Ref. JDC2023-052774-I) and FPI contract (Ref. PID2023-150761OB-C21), respectively, funded by MICIU/AEI /10.13039/501100011033 and the FSE+.

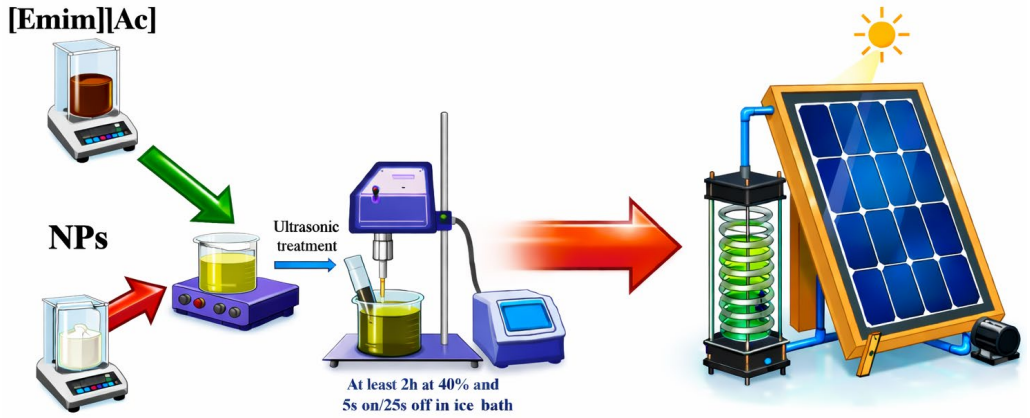
[1] M. Seco-Nicolás, M.A., García, A. P. Ramallo González, J. P. Luna Abad et al. *Results Eng.*, **(2023)**, 17, 100983.

Thermophysical Performance of Al_2O_3–ZnO/[Emim][AC] Hybrid Ionanofluids for Advanced Solar Collectors

Jesús León-García, José Javier Delgado-Marín, Imane Moulefera, A. Aguayo, Ignacio Carnerero-Hinojosa, Alberto Cascales, Mercedes G. Montalbán, Gloria Víllora*

Chemical Engineering Department, Faculty of Chemistry, CEIR Campus Mare Nostrum (CMN), University of Murcia, 30071 Murcia, Spain.
Email: jesus.leong@um.es

Nanofluids further enhance thermal conductivity and stability by combining different nanoparticles [1]. Recently, ionic liquids have emerged as promising base fluids, enabling the development of highly stable ionanofluids with improved thermal performance for solar-thermal applications. In this work, hybrid ionanofluids (H-INFs) based on alumina (Al_2O_3) and zinc oxide (ZnO) nanoparticles dispersed in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim][AC]) were prepared by ultrasonication (see Scheme 1) and evaluated with the aim of enhancing the thermal properties required for solar-thermal applications. Four hybrid compositions were prepared using the concentrations shown in the reference matrix (Al_2O_3: 0.25–0.5 wt%; ZnO: 0.25–0.75 wt%). The H-INFs were systematically characterized in terms of particle size distribution, colloidal stability, density, thermal conductivity, and specific heat capacity to assess the combined influence of nanoparticle ratio and ionic-liquid interactions. The H-INF (0.5% Al_2O-0.25% ZnO) demonstrated the best performance, combining strong thermal-conductivity enhancement with high dispersion stability and acceptable heat capacity. These results confirm that Al_2O_3–ZnO/[Emim][AC] H-INF are promising candidates for stable, high-efficiency working fluids in future solar-thermal systems.



Scheme 1. H-INF preparation method.

Funding: This work is part of the following research projects: Ref. PID2023-150761OB-C21 funded by MICIU/AEI/10.13039/501100011033 and by FEDER, UE and Ref. 22129-PI-22 funded by the research support program of the Seneca Foundation of Science and Technology of Murcia, Spain. J.J. Delgado-Marín and J. León-García acknowledge support from the Juan de la Cierva contract (Ref. JDC2023-052774-I) and FPI contract (Ref. PID2023-150761OB-C21), respectively, funded by MICIU/AEI /10.13039/501100011033 and the FSE+.

[1] A. Zacarías, M. de Vega, N. García-Hernando, M. Venegas, *Appl. Sci.* ***(2024),*** *14*(8), 3225.

Computational Acceleration of Sustainable Natural/Bioactive Compound Discovery through Large Language Models

Horacio Pérez-Sánchez[a] and Carlos Martínez-Cortés[a]

[a] *Structural Bioinformatics and High Performance Computing Research Group (BIO-HPC), Universidad Católica San Antonio de Murcia (UCAM), 30107 Guadalupe, Spain*

E-mail: hperez@ucam.edu

Green chemistry promotes the development of environmentally responsible processes and compounds with improved efficiency, safety, and circularity. Computational methodologies support these objectives by reducing experimental burden and resource consumption in early-stage discovery. Beyond conventional structure-based and ligand-based virtual screening (SBVS/LBVS), Large Language Models (LLMs) introduce new possibilities for knowledge-integrated, data-driven molecular design [1].

We propose integrating LLM-driven molecular discovery within established screening pipelines to enhance the exploration of sustainable natural and bioactive chemical space. LLMs function as generative and reasoning systems capable of learning chemical representations and structure–property relationships from large-scale corpora enriched with green chemistry and bioactivity data. By combining chemical, biological, and bibliographic knowledge, these models enable hypothesis-driven compound generation and prioritization. When coupled with SBVS and LBVS workflows, LLMs refine candidate selection and direct screening efforts toward chemically feasible, sustainability-oriented proposals [2].

The framework is implemented within the BIO-HPC ecosystem, incorporating automated literature mining, structured knowledge extraction, and similarity-aware reasoning under biological constraints. Current research evaluates LLM-guided strategies for identifying natural bioactive compounds with potential applications in nutraceutical, pharmacological, and agro-biotechnological contexts, emphasizing reduced toxicity, circular economy alignment, and valorization of bioresources and industrial byproducts [3]. Scalability and integration into sustainable chemistry workflows are under active assessment.

A multi-model consensus strategy integrates diverse LLM architectures, including open-source and proprietary systems, using cross-model agreement to increase robustness and reduce bias in molecular prioritization. Overall, this LLM-augmented framework aims to minimize experimental waste, optimize resource use, and enable more efficient exploration of sustainable bioactive chemical space, contributing to greener discovery paradigms aligned with sustainable and (bio)catalytic innovation [4].

[1] M. Caldas Ramos, C. J. Collison, A. D. White, *A review of large language models and autonomous agents in chemistry*, Chem. Sci., 2025, 16, 2514–2572.
[2] L. Jiang et al., *Chem3DLLM: 3D Multimodal Large Language Models for Chemistry*, arXiv:2508.10696 (2025).
[3] S. Yadav et al., *Role of Artificial Intelligence and Data Science in Green and Sustainable Chemistry*, Discover Chemical Engineering, 2026, 6(1).
[4] ChatChemTS: *Large language model-powered molecule design*, J. Cheminformatics, 2025, DOI:10.1186/s13321-025-00984-8.

Computational chemistry for fast and cost-effective bioactive compound discovery and revalorization

Jose Francisco Costa-Rubio,[a] Jorge Ricardo Alonso-Fernández,[a] Alejandro Rodríguez-Martínez,[a] Carlos Martínez-Cortés[a] and Horacio Pérez-Sánchez[a,*]

[a] *Structural Bioinformatics and High Performance Computing Research Group (BIO-HPC), Universidad Católica San Antonio de Murcia (UCAM), 30107 Guadalupe, Spain*

E-mail: jfcosta8@ucam.edu

Green chemistry proposes a framework for innovation in environmentally sustainable processes and compounds, from their design to their disposal. In this context, computational chemistry accelerates and cuts costs of molecular design and screening, providing green solutions to numerous challenges in green chemistry. These include the search for natural alternatives to synthetic nutritional, cosmetic and pharmaceutical compounds, as well as the revalorization of industrial waste by-products for reuse within a circular economy.

Metascreener (https://github.com/bio-hpc/metascreener) is a software developed by the BIO-HPC group that integrates docking, similarity search, and molecular dynamics functionalities. Another tool, OBE-DB, provides a user-friendly interface for obesity-related virtual screening (VS). Many other methods employ machine learning models to accelerate VS in ultra-large chemical spaces and, in recent years, active learning is being incorporated to retrain models with experimental evidence feedback, enhancing predictive performance.

Numerous studies and interdisciplinary collaborations from our group illustrate the potential of VS for sustainable innovation. For instance, in the context of diabetes, multiple plant-derived compounds with antidiabetic activity were identified from plants present in Mediterranean diet and flora [1], guava leaves [2], and common herbs and spices [3]. In the brewing process, screening molecules present in spent hop waste enabled their revalorization in cosmetic formulations after identifying elastase inhibitory activity [4].

The next step proposed here is further optimization of VS through the implementation of iterative multi-cycle active learning, leveraging experimental results on ranked compounds to progressively improve predictive performance, with updated predictions again subjected to experimental validation. In addition, this project incorporates interpretability: the model must not only achieve high predictive accuracy but also explicitly report the importance of atomic-level features, molecular interactions, and consensus among different predictive models. Overall, this approach represents a substantial advance in the exploration of novel bioactive compounds with reduced toxicity and environmental impact.

[1] V. Goulas, A. J. Banegas-Luna, A. Constantinou, *Plants*, **2022**, *11*, 1637, https://doi.org/10.3390/plants11131637
[2] E. Díaz-de-Cerio, F. Girón, A. Pérez-Garrido, *Int. J. Mol. Sci.*, **2023**, *24*, 5761, https://doi.org/10.3390/ijms24065761
[3] A. S. P. Pereira, A. J. Banegas-Luna, J. Peña-García, *Molecules*, **2019**, *24*, 4030, https://doi.org/10.3390/molecules24224030
[4] M. Paredes-Ramos, E. Conde-Piñeiro, J. M. Lopez-Vilariño, *Sci. Rep.*, **2022**, *12*, 2274, https://doi.org/10.1038/s41598-022-26149-3

Consensus Virtual Screening for Sustainable Ligand Discovery

Jorge Ricardo Alonso Fernández [a], **Horacio Pérez Sánchez** [a,*]

[a] *Structural Bioinformatics and High-Performance Computing (BIO-HPC), Campus de los Jerónimos, Universidad Católica de Murcia (UCAM), Guadalupe, Murcia, España (Spain)*

E-mail: jralonso7@ucam.edu

Green and sustainable chemistry aims to minimize reliance on hazardous chemicals and resources by promoting environmentally friendly alternatives, including bio-based pharmaceuticals and catalysts, and by advancing methods that support efficient, low-impact chemical discovery and transformation. In this context it's possible to apply consensus virtual screening (which consists on integrating several predictive computational methods) to offer a robust in silico framework to accelerate various stages of investigation (like the identification of promising bio-derived ligands or the search for potential biocatalyst targets) while reducing resource-intensive experimental screening.

Our group integrates several ligand-based, structure-based and molecular dynamics techniques with a consensus approach[1]. Ligand-based techniques are based on feature, electrostatic or pharmacophorical comparison and search for diverse molecules that have similar characteristics, providing alternative compounds with similar interactions. Structure-based techniques are based on docking with several engines or pharmacophorical matching and help predict new ligands for given proteins or complexes. Molecular dynamics simulations can refine the predictions and provide more insight on the interactions and their stability. Below we explore some potential aplications regarding the congress topics.

Within the bio-based pharmaceuticals and cosmetics topic, a consensus virtual screening can be applied in various ways. One example is to find bio-molcule alternatives to some chemicals, by applying ligand-based consensus against natural compound databases, providing compounds that may have similar effects. Another application example is to find novel ligands for target proteins, by applying the structure-based techniques with the protein structure to the same libraries and potentially complementing with ligand-based techniques with known ligands for them. This latter application has already been explored and validated extensively. One recent application includes the search for novel EP3 agonists[2].

Within the exploration for new enzymes, target phishing can be performed with structure-based (against predicted structures for new molecules) or ligand-based (against ligands in databases that probide target interaction information) techniques, identifying potential targets of selected compounds. We are currently collaborating in the REDALIM project, where we explore potential targets for compounds present in plant extracts. Finally, within the directed evolution for new enzymes, iterative molecular docking simulations with different variants or mutations of a protein can provide key insights. It could be even possible to explore a range of potential modifications in-silico, at the expense of computational resources.

[1] Nelen, J.; Carmena-Bargueño, M.; Martínez-Cortés, C.; Rodríguez-Martínez, A.; Villalgordo-Soto, J.M.; Pérez-Sánchez, H. *J. Chem. Inf. Model*. **2024**, 64, 160 DOI: 10.1021/acs.jcim.3c01982
[2] Alonso-Fernández, J.R.; Montoro-García, S.; Cruz, A.F.; Ponce-Valencia, A.; Carmena-Bargueño, M.; Pérez-Sánchez, H. *Int. J. Mol. Sci.* **2025**, 26, 4879 DOI: 10.3390/ijms26104879

Therapeutic deep eutectic solvents as green carriers for transdermal delivery of lidocaine and prilocaine

Beatriz Giner*, Estela Sanguesa, Alvaro Werner, M. Pilar Garralaga, Estefania Zuriaga, Laura Lomba

Universidad San Jorge, Facultad de Ciencias de la Salud. Campus Universitario, Autovía Mudéjar, km. 299, A-23, 50830 Villanueva de Gállego, Zaragoza

E-mail: bginer@usj.es

Transdermal drug delivery offers a non-invasive route for localized therapy, minimizing systemic exposure and reducing environmental impact compared to conventional administration methods [1]. Therapeutic Deep Eutectic Solvents (THEDES), biodegradable and non-volatile liquids formed through hydrogen-bond interactions between generally safe components, represent a sustainable platform for enhancing transdermal transport [2]. In particular, THEDES composed of lidocaine and prilocaine, widely used local anesthetics with established efficacy and rapid onset of action and commonly applied in topical formulations for cutaneous anesthesia combine efficient drug solubilization and membrane penetration with eco-friendly formulation, avoiding toxic organic solvents and supporting green chemistry principles.

In this study, we evaluated the diffusion of lidocaine-prilocaine THEDES in 1:1 (LID-PRI 11) and 1:2 (LID-PRI 12) molar ratios using Franz diffusion cells with Strat-M™ membranes as a human-skin surrogate [3]. Samples were collected hourly over 8 hours and analysed by HPLC. Nonlinear regression of experimental data Q/A (mg/cm^2) and t (s), $Q = \frac{A \cdot t^n}{(t^n + t50^n)}$, was used to calculate key diffusion parameters.

The diffusion of lidocaine-prilocaine THEDES was evaluated for two molar ratios (1:1, LID-PRI 11, and 1:2, LID-PRI 12). For LID-PRI 11, lidocaine exhibited a diffusion coefficient (D) of $9.64 \cdot 10^{-8}$ cm²/s, a maximum permeated amount A = 0,035 mg/cm², a t50 of 8161 s, and n = 1.993. Prilocaine in the same formulation showed D = $2.30 \cdot 10^{-7}$ cm²/s, A = 0,047 mg/cm², t50 = 5647 s, and n = 1.693. In comparison, LID-PRI 12 demonstrated lower cumulative permeation for lidocaine (D = $4.68 \cdot 10^{-6}$ cm²/s, A =0,004 mg/cm², t50 = 3248 s, n = 1.179) and for prilocaine (D = $4.70 \cdot 10^{-7}$ cm²/s, A = 0,011 mg/cm², t50 = 1339 s, n = 2.193. These results demonstrate that eco-friendly lidocaine-prilocaine THEDES can achieve transdermal delivery while adhering to green chemistry principles by avoiding harmful solvents and maximizing sustainability.

[1] M.R. Prausnitz, R. Langer, *Nat Biotechnol*. **2008**, 26, 1261–1268.
[2] H. Wang, G. Gurau, J. Shamshina, O. A. Cojocaru, J. Janikowski, D.R. MacFarlane, J. H. Davis, R. D. Rogers, *Chem. Sci.* **2014**, 5, 3449-3456**.**
[3] H. Kichou, F. Bonnier, Y. Dancik, J. Bakar, R. Michael-Jubeli, A.C. Caritá, X. Perse, M. Soucé, L. Rapetti, A. Tfayli, I. Chourpa, E. Munnier, *Int J Pharm*. **2023,** 647, 123488.

Levoglucosenone: a versatile platform molecule for the preparation of high-boiling solvents and building blocks for polymer synthesis

Alessandro Pellis,[a,*] Francesco Maria Raboni[a], Maria Jose Calandri[a], Cicely May Warne,[b] Con Robert McElroy,[c]

[a] University of Genova, Department of Chemistry and Industrial Chemistry, via Dodecaneso 31, 16146, Genova (GE), Italy
[b] BOKU University, Department of Agricultural Sciences, Institute of Environmental Biotechnology, Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria.
[c] University of Lincoln, School of Chemistry, LN6 7DL, Lincoln, UK

E-mail: alessandro.pellis@unige.it

Most commercial solvents and polymers are synthesized from the seven base chemicals derived from the petrochemical industry via the distillation of crude oil. In recent years there has been a strong drive to move away from non-renewable feedstock and to develop chemicals, solvents and materials derived from renewable resources using more sustainable synthetic procedures and considering the end of life of these products.

One promising platform molecule is levoglucosenone (LGO), a chiral compound that can be easily obtained via pyrolysis of materials containing cellulose, such as wood chips and bagasse. The chirality at C1 and C5 in LGO gives it advantages in stereoselective synthesis when compared to achiral biomass derivatives while the reduced number of chiral centers simplifies its use when compared to monosaccharides. Enantio-, stereo-, regio- and chemo selective reactions have been executed around the core ring-system, leading to the controlled synthesis of a multitude of biologically active structures. Moreover, the reactivity of the ketone and enone functionalities is influenced by the 1,6-anhydro bridge, which strongly biases reaction to occur from the less hindered exo-face of the molecule [1].

In this work, LGO was explored as the starting point for the green and scalable synthesis of a series of novel high boiling solvents having varying polarity called Cygnets. These solvents were then used for polymer chemistry applications such as the production of membranes [2] and the enzymatic synthesis of aliphatic and aromatic polyesters allowing both the synthesis and the work up of the obtained polymers to be performed without the use of halogenated and/or toxic solvents [3, 4].

[1] J. E. Camp, B. W. Greatrex, *Front. Chem.* **2022**, *10*, https://doi.org/10.3389/fchem.2022.902239. DOI: 10.3389/fchem.2022.902239
[2] R. A. Milescu et al., *ChemSusChem.* **2021**, *14*, 3367-3381. DOI: 10.1002/cssc.202101125
[3] C. M. Warne et al. *Green Chem. Lett. Rev.* **2023**, *16*, 2154573. DOI: 10.1080/17518253.2022.2154573
[4] C. M. Warne et al., *ChemSusChem*. **2024**, *17*, e202301841. DOI: 10.1002/cssc.202301841

Hydrophobic Deep Eutectic Solvents as Green Media to Assess Activity and Stability of Halohydrin Dehalogenase HheC

Petra Švaco,[a] Doroteja Mutak,[a] Irena Dokli,[a] and Maja Majerić Elenkov[a,*]

[a] *Bijenička cesta 54, Zagreb, Croatia, Ruđer Bošković Institute*

E-mail: Petra.Svaco@irb.hr

Hydrophobic deep eutectic solvents (hDES) represent a versatile class of alternative media that can improve substrate solubility and modulate the microenvironment of biocatalytic systems, thereby offering new opportunities for epoxide transformations and stabilization of labile intermediates [1]. In this work, we evaluated a panel of menthol- and thymol-based hDESs in biphasic and aqueous-organic systems for the hydrolytic stability and biocatalytic conversion of aromatic epoxides using halohydrin dehalogenase HheC in both crude cell-free extract and whole-cell form.

Halohydrin dehalogenases (HHDHs, EC 4.5.1.-) represent a group of industrially relevant enzymes that catalyze the reversible dehalogenation of vicinal haloalcohols with formation of the corresponding epoxides. In the reverse reaction, these enzymes also accept negatively charged nucleophiles such as azide, cyanide, nitrite, cyanate, or formate to open the epoxide ring [2].

Despite the considerable biocatalytic potential of HHDHs, their application in industrial processes faces several limitations related to conventional aqueous reaction media. One major concern is the hydrolytic instability of epoxide substrates in aqueous media. Epoxides undergo spontaneous hydrolysis to form vicinal diols, which represents an undesired competing reaction that reduces the yield of the enzyme-catalyzed transformation [2].

Hydrolytic half-lives of selected epoxides were significantly extended in the presence of 20% (v/v) hDES compared to buffer, with styrene oxide showing an apparent $t_{1/2}$ increase from 9.1 h in buffer to approximately 128 h in hDES. HheC retained substantial activity after incubation in 20% (v/v) hDES and catalyzed efficient azidolysis of both hydrolytically stable and unstable epoxides in 1,4-tetradecanol:menthol-containing systems. The same hDES-based system outperformed an *n*-heptane biphasic setup under otherwise identical conditions. Substrate availability, enzyme performance, and suppression of non-enzymatic hydrolysis can be balanced by tuning the volume fraction of selected hDES, enabling azidolysis of hydrolytically sensitive epoxides even at low HheC loadings.

[1] D. J. G. P. van Osch, C. H. J. T. Dietz, J. van Spronsen, M. C. Kroon, F. Gallucini, M. van Sint Annaland, R. Tuinier, *ACS Sustainable Chem. Eng.* **2019**, *7*, 2933–2942.
[2] N. Milčić, M. Sudar, I. Dokli, M. M. Elenkov, Z. Findrik Blažević, *React. Chem. Eng.*, **2023**, *8*, 673-686.

2-in-1 Menthol based Deep Eutectic Solvents for "Solvent-Free" Enzymatic Esterification

Estelle Schwarz,[a,*] Kiran Hidayat,[b] Dr. Daniel Ohde,[b] Prof. Dr. Andreas Liese,[b] and Prof. Dr. Dirk Holtmann[a,*]

[a] *Author affiliation: Fritz-Haber-Weg 4 76131, Karlsruhe, Germany, Process Engineering in Life Sciences 2 – Electro Biotechnology, Karlsruhe Institute of Technology*
[b] *Author affiliation: Denickestr. 15 21073 Hamburg, Germany, Institute of Technical Biocatalysis, Hamburg University of Technology*

E-mail: estelle.schwarz@kit.edu

Enzymatic reactions are commonly performed by dissolving the substrates and the enzymes in suitable solvents such as buffers or deep eutectic solvents (DESs). The solubility of the substrates, particularly those in a solid state, is essential as it determines the potential productivity of the reaction. The integration of the substrates within a 2-in-1 DES has been shown to increase their availability within the reaction. In addition, a solvent-free process and a greener reaction can be performed, as fewer waste products and a higher atom efficiency are achieved. This concept has been previously demonstrated in the work of Pätzold *et al*. [1], who examined the esterification of fatty acids with (–)-menthol by the *Candida rugosa* lipase. Commercially, (–)-menthol is a relevant aroma compound due to its mint flavor and its refreshing cooling effect. Therefore, the chiral resolution between (–)-menthol and its enantiomer (+)-menthol is needed.

The esterification of fatty acids is applied to the chiral resolution of menthol, as shown in **Figure 1** with dodecanoic acid as representative acyl donor. To shift the reaction equilibrium towards the esterification, the reaction is setup in a water activity-controlled system. Thus, the produced water can be removed from the reaction medium, thereby further shifting the equilibrium in favor of the desired ester formation. Furthermore, a water-activity controlled environment is beneficial as enzymes require an optimal amount of water activity to function effectively. [2] Considering, the influence of different substrate molar ratios within the DES, as well as the use of various acyl donors, is investigated to assess their impact on reaction performance.

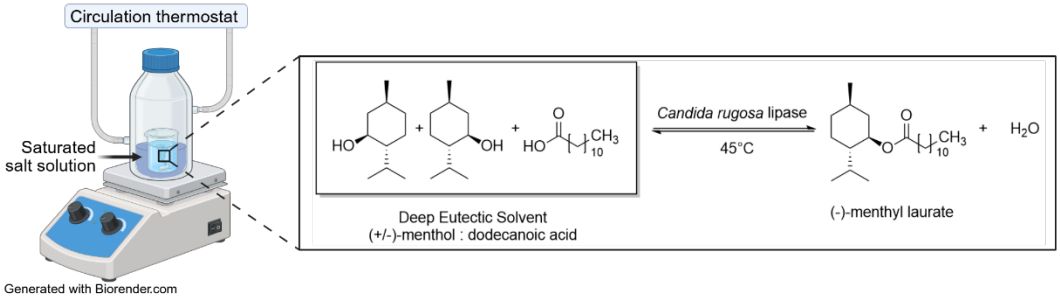


Figure 1. Experimental setup (left) and reaction scheme (right) of the chiral resolution of menthol based on the esterification of the 2-in-1 deep eutectic solvent.

[1] M. Pätzold, A. Weimer, A. Liese, D. Holtmann, *Biotechnology Reports* **2019**, *e00333*.
[2] L. Ma, M. Persson, P. Adlercreutz, *Enzyme Microb. Technol*. **2002**, *31 (7)*, 1024-1029.

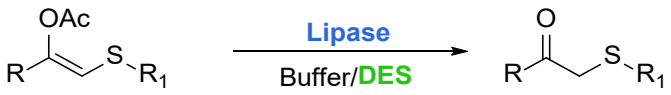
Lipase-catalyzed hydrolysis of β-alkylsulfide enol esters in presence of Deep Eutectic Solvents

C.Falcini, R. Fernández, G. de Gonzalo*

Department of Organic Chemistry, Universidad de Sevilla
c/ Profesor García González 1, 41012, Sevilla, Spain

E-mail:gdegonzalo@us.es

β-Ketosulfides are valuable molecules found in natural products and pharmaceutical active intermediates [1], and can be efficiently accessed through the lipase-catalyzed hydrolysis of enol ester. However, such biotransformations typically require mixture of buffer containing different percentages of classical organic solvents [2].
Deep eutectic solvents (DESs) have emerged in recent years as an attractive alternative to conventional organic solvents, owing to their favorable environmental properties and the ease of preparation by simply combining a hydrogen bond donor with a hydrogen bond acceptor in a defined stoichiometric ratio [3].
Herein, some choline chloride-based Deep Eutectic Solvents have been evaluated as cosolvents in the lipase-catalyzed hydrolysis of a set of alkylsulfide enol esters for the synthesis of β-ketosulfides. (**Scheme 1**).
The solvent analysis revealed that 30% v/v DES led to the optimal conversions. Increasing the DES content resulted in gradual enzyme deactivation under micro-aqueous conditions. Nevertheless, the biocatalyst demonstrated remarkable tolerance to high DES concentrations, retaining measurable activity even in media containing up to 90% v/v DES. Optimized conditions were extended to a series of substituted alkylsulfide enol esters, demonstrating the applicability of DES media in enzymatic hydrolysis processes.



Scheme 1. Lipase-catalyzed hydrolisis of *β*-alkylsulfide enol esters in buffer/DES media.

[1] C. Falcini, J.Carvajal-Bárcena, L. V. Urban, J. P. Colomer, F.R. Bisogno, R. Fernández, G. de Gonzalo, *ChemCatChem.* **2026**, *18*, e202501617.
[2] A. A. Heredia, M. G. López-Vidal, M. Kurina-Sanz, F. R. Bisogno, A. B. Peñéñory, *Beilstein J. Org. Chem*. **2019**, *15*, 378–387.
[3] P. A. Shah, V. Chavda, D. Hirpara, V. S. Sharma, P. S. Shrivastav, S. Kumar, *J. Mol. Liq.* **2023**, *390*, 123171.

Investigation of *in situ*-product crystallisation from deep eutectic solvents and its reuse potential

Quirin Mollweide[a] and Jan von Langermann[a]*

[a] *Universitätsplatz 2, 39106 Magdeburg, Germany, Otto-von-Guericke-University Magdeburg*

E-mail jan.langermann@ovgu.de

In situ-product crystallisation (ISPC) is a is a straight-forward process-approach for removing the product directly from the respective reaction solution and converting it into a solid phase [1]. This technique facilitates a direct access to the product and improves overall conversion due to an apparent shift of the reaction equilibrium via *in situ*-product removal. This also minimizes the risk of product inhibition as only a low product concentration is present in the remaining reaction solution [2,3]. Most importantly, ISPC allows a direct re-use of the remaining product-depleted reaction solution without any additional purification steps [4]. In this study Deep Eutectic Solvents (DESs) were used as the main solvent system since DESs have emerged as a promising alternative to conventional aqueous and organic solvents in biocatalysis, and have shown positive effects on the activity and stability of various enzymes [5]. We investigated the application of an ISPC for the transaminase-catalysed synthesis of chiral amines in tailor-made choline-based DESs and their reuse potential in repetitive batch reaction (Figure 1). This approach involves the accumulation of the solid product salt, the isolation and eventually re-use of the mother liquor in the following reaction cycle, without discarding the entire DES reaction solution. For this purpose, the solubility of the product salt in the choline-based DESs is crucial, which needs to be carefully adjusted.

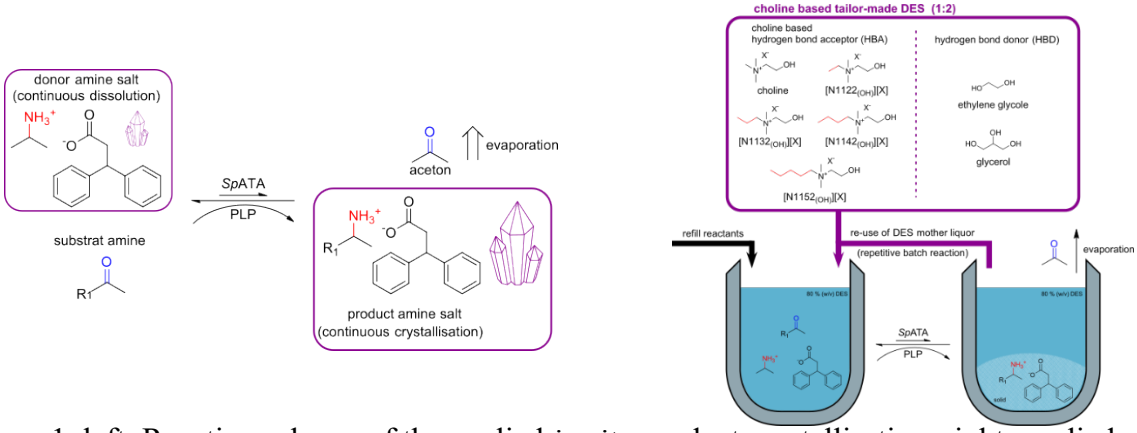


Figure 1, left: Reaction scheme of the applied *in situ*-product crystallisation, right: applied tailor-made choline-based deep eutectic solvents within a repetitive batch reaction.

[1] M. A. McDonald, H. Salami, P. R. Harris, C. E. Lagerman, X. Yang, A. S. Bommarius, M. A. Grover, R. W. Rousseau, React. Chem. Eng. 2021, 6, 364.
[2] D. Hülsewede, L.-E. Meyer, J. von Langermann, Chem. Eur. J. 2019, 25, 4871–4884.
[3] J. M. Woodley, M. Bisschops, A. J. J. Straathof, M. Ottens, J. Chem. Technol. Biotechnol. 2008, 83, 121–123.
[4] S. Tiedemann, J. E. Neuburger, A. Gazizova, J. von Langermann, *Eur. J. Org. Chem.* 2024, 27.
[5] N. Zhang, P. Domínguez de María, S. Kara, *Catalysts* **2024**, *14*, 1-29.

Substrate-Integrated Natural Deep Eutectic Solvents (NaDES) for Lipase-Catalyzed Esterification Monitored by FTIR

Kiran Hidayat, [a,*] **Estelle Schwarz,** [b] **Dr. Daniel Ohde,** [b] **Prof. Dr. Dirk Holtmann,** [b] **Prof. Dr. Andreas Liese** [a,*]

[a] *Author affiliation: Denickestr. 15 21073 Hamburg, Germany, Institute of Technical Biocatalysis (V-6) Hamburg University of Technology*
[b] *Author affiliation: Fritz-Haber-Weg 4 76131, Karlsruhe, Germany, Process Engineering in Life Sciences 2 – Electro Biotechnology, Karlsruhe Institute of Technology*
E-mail: kiran.hidayat@tuhh.de

Scalable, solvent-efficient biocatalysis remains a key industrial challenge. Traditional esterification is hindered by the environmental and energy costs of volatile solvents, whereas hydrophobic '2-in-1' NaDES offer a sustainable alternative by using substrates as the reaction medium [1,2]. While this approach improves atom efficiency and streamlines product recovery, high viscosity and mass-transfer limitations currently restrict industrial application.

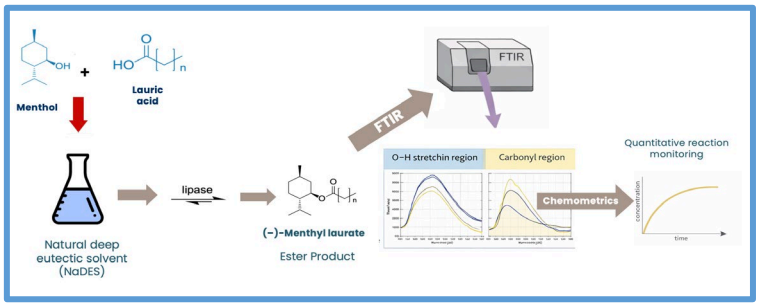


Figure 7: Schematic representation of solvent-free, lipase-catalyzed esterification of L-menthol and lauric acid in a natural deep eutectic solvent (NaDES) with FTIR-based monitoring.

Substrate-integrated NaDES composed of L-menthol and lauric acid were developed as both the hydrogen-bond donor/acceptor system and the reactive substrates in a solvent-free, biocatalytic esterification system [2]. A stable eutectic phase formed at a 3:1 molar ratio (L-menthol: lauric acid), and FTIR spectroscopy confirmed strong intermolecular hydrogen bonding via characteristic OH and C=O shifts. Using *Candida rugosa* lipase (CRL) at 40 °C, enzymatic esterification was performed directly in (L-menthol: lauric acid)-based NaDES.

In situ FTIR monitoring verified conversion through the emergence of an ester carbonyl band at 1735 cm^{-1} and a concurrent decrease in hydroxyl and carboxyl signals, while enzyme-free controls showed no spectral changes, confirming both enzymatic activity and chemical stability of the eutectic system. Building on established spectroscopic approaches [3,4], PEAXACT-based chemometric models enabled real-time quantification of reaction kinetics and water formation. This integrated methodology supports sustainable, solvent-free process monitoring and optimization, with implications for scalable green biocatalysis.

[1] A. Paiva,et al., ACS Sustainable Chemistry & Engineering 2014, 2, 1063–1071.
[2] M. Pätzold, et al. Trends in Biotechnology 2019, 37, 943–959.
[3] J. Müller, eta l., Analytical Chemistry 2011, 83, 9321–9327.
[4] R. Hiessl, et al., Analytical Methods 2020, 12, 3137–3144.

Solid/Gas Biocatalysis with CalB-CLEA for Green Aroma Ester Synthesis

Cruz-Martínez Yahir Alejandro,[a,b] Velasco-Lozano Susana,[b*] Huerta-Ochoa Sergio,[a*]

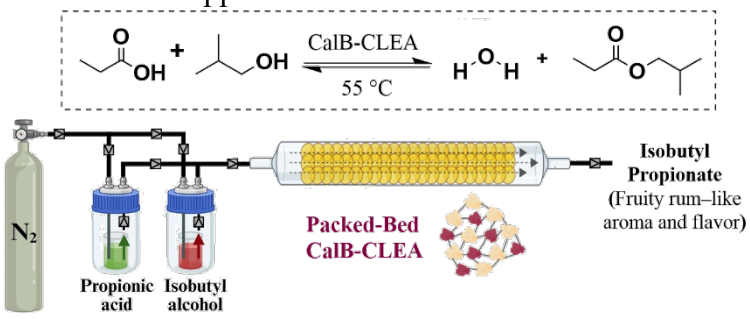
[a] *Department of Biotechnology, Universidad Autónoma Metropolitana-Iztapalapa, Ciudad de México 09340, México;*
[b] *Instituto de Síntesis Química y Catálisis Homogénea, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009, Spain*

E-mail: yacm95@xanum.uam.mx; svelasco@unizar.es

This work presents an efficient and sustainable strategy for the synthesis of natural aroma compounds, particularly isobutyl propionate (IsoPro), through a solid/gas (S/G) phase esterification. The method employs cross-linked enzyme aggregates of *Candida antarctica* lipase B (CalB-CLEA) as a robust and effective biocatalyst. S/G bioreactor are proposed as an innovative alternative to conventional liquid-phase (solvent-based or solvent-free) systems, as they overcome key limitations related to efficiency and scalability [1]. Additionally, the study addresses unresolved challenges in enzyme immobilization and reactor design, demonstrating that CalB-CLEA exhibits high catalytic activity, operational stability, and reusability in continuous-flow systems.

A CalB-CLEA formulation containing 10 mg mL^{-1} BSA and 3% glutaraldehyde was selected due to its high activity in *n*-heptane and enhanced thermal and operational stability. Under solid/gas conditions, 600 mg of this biocatalyst achieved an isoPro yield of 91.71% at a water activity of 0.52, with a nitrogen flow rate of 62 mL min^{-1}, an acid/alcohol molar ratio of 1:4, at 55 °C and 585 mmHg. The catalytic performance in the S/G platform was compared with the commercial biocatalyst CalB ImmoPlus. Although 1.0 g of this product achieved a higher yield (98.9%), its total turnover number and specific space–time yield under steady-state conditions were 6- and 4-fold lower, respectively, than those of the formulated CalB-CLEA. Furthermore, the use of CalB-CLEA eliminates resin disposal costs and enables comparable yields with lower enzyme loadings while maintaining similar productivity [2].

Overall, the S/G system using CalB-CLEA outperforms both CalB ImmoPlus (in S/G) and CalB-CLEA (in *n*-heptane) in terms of sustainability and mass-based efficiency, highlighting its strong potential for industrial application.



Scheme 1. IsoPro synthesis catalyzed by CalB-CLEA in a S/G packed-bed bioreactor.

[1] I. N. Cordero-Soto, C. O. Castillo-Araiza, L. E. García-Martínez, A. Prado-Barragán, S. Huerta-Ochoa, *Biochem. Eng. J.* **2020**, *164,* 107767.
[2] Y. A. Cruz-Martínez, C. O. Castillo-Araiza, E. Castillo-Rosales, S. Velasco-Lozano, S. Huerta-Ochoa, *ACS Omega* **2025**, *10*, 59692–59705.

In Situ Product Recovery of Bio-Based Lactic Acid with Deep Eutectic Solvents: Biocompatibility Assessment

Fernando Ródenas Pérez-Cuadrado,[a] Víctor Manuel Ortiz Martínez,[a] Carlos Godínez Seoane,[a] María José Salar García,[*a] and Sergio Sánchez-Segado,[*a]

[a] *Department of Chemical and Environmental Engineering, Polytechnic University of Cartagena, C/ Dr. Flemming s/n, 30202 Cartagena, Spain.*

E-mail: sergio.segado@upct.es

The development of sustainable bioprocesses for lactic acid production requires the integration of efficient biomass valorization strategies and environmentally friendly extraction systems. Deep eutectic solvents (DES) have emerged as green alternatives for biomass processing; however, their compatibility with microbial fermentation systems remains a critical challenge. This study evaluates the biocompatibility of selected DES´s with the microorganism *Lactobacillus delbrueckii* during the lactic fermentation of carob pod aqueous extracts[1].

Selected DES´s were firstly screened to assess their ability to recover lactic acid from aqueous model solutions. The effects of DES type on *Lactobacillus delbrueckii* metabolic activity, were assessed through batch fermentation assays in an orbital incubator.

Results indicate that while aqueous extracts supported robust growth and efficient lactic acid production, certain DES formulations exhibited inhibitory effects on *L. delbrueckii*. However, partial biocompatibility has been demonstrated, maintaining metabolic activity and acceptable lactic acid yields. These findings highlight the importance of solvent selection and process integration to ensure microbial performance.

This work provides valuable insights into the compatibility between green extraction technologies and microbial fermentation processes, contributing to the development of integrated and sustainable platforms for lactic acid production within a circular bioeconomy framework[2].

Acknowledgements

The authors wish to acknowledge the Fundación Séneca financial support under the action FSRM/10.13039/100007801(22620/PI/24). Spain.

[1] N. Vidal, M. Ventura, F. Martínez, J.A. Melero, *Sep. Purif. Technol.,* **2024**, 346, 127540

[2] H. Kebaili, A. Pérez de los Ríos, M.J. Salar-García, V.M. Ortiz-Martínez, M. Kameche, J. Hernández-Fernández, F.J. Hernández-Fernández, *Front. Mater.*, **2020**, 7.

Solid-phase modification of immobilized lipases with glutaraldehyde. Roles of the enzymatic loading and enzyme chemical amination on the efficiency of intermolecular crosslinkings and biocatalyst stability.

Pedro Abellanas-Perez[1] & Roberto Fernández-Lafuente[1]

1 Departamento de Biocatálisis. ICP-CSIC, C/Marie Curie 2, Campus UAM-CSIC Cantoblanco, 28049 Madrid.

Email: m.a.p@icp.csic.es

Lipase B from *Candida antartica* (CALB) and the lipase from *Thermomyces lanuginosus* (TLL) were immobilized on cross-linked 4% agarose beads modified with octyl groups, at two different enzymatic loadings. One lowly loaded, for the enzyme to be distributed, throughout the support pore, but enough to still give a measurable activity value (1 mg of enzyme per gram of support). And one highly loaded, exceeding the maximum support capacity, ensuring the enzymes are closer to each other and the support pores are full of enzyme molecules (24 mg of enzyme per gram of support) [1].

First, these four biocatalysts were chemically modified following three different methodologies. Either, 1% (v/v) glutaraldehyde modification, carbodiimide/ethylenediamine amination or the combination of amination and glutaraldehyde modification. Once modified, their stability was studied by carrying out thermal inactivation in different buffers (sodium phosphate, Tris-HCl and HEPES) at pH 7 [1].

The modification just with glutaraldehyde allowed the enzyme stabilization (depending on the buffer) of both highly loaded biocatalysts, CALB and TLL, but not to the lowly loaded biocatalysts. This stabilization could be very likely due to the generation of intermolecular crosslinking. This effect could be hard to achieve in the lowly loaded biocatalysts, where the distance between the enzymes may be too big to generate this type of crosslinking, using a small molecule such as glutaraldehyde [1]. This was confirmed by SDS-PAGE experiments.

In the case of TLL, when combining amination and glutaraldehyde modification, the intramolecular crosslinking increased enzyme stability of the lowly loaded biocatalysts, an effect that was further increased for the highly loaded biocatalysts due to intermolecular crosslinking. Using CALB, the stabilization was lower, very likely because the intramolecular crosslinking was less intense, even though the intermolecular crosslinking was quite intense for the highly loaded biocatalyst as revealed by SDS-PAGE [1].

The stabilization factor detected depended on the inactivation buffer. The interactions between enzyme loading and inactivating buffer on the effects of the chemical modifications suggest that the modification and inactivation studies must be performed under the target biocatalysts and conditions [1].

[1] P. Abellanas-Perez, D. Carballares, R. Fernandez-Lafuente, J. Rocha-Martin, Glutaraldehyde modification of lipases immobilized on octyl agarose beads: Roles of the support enzyme loading and chemical amination of the enzyme on the final enzyme features, Int. J. Biol. Macromol. 248 (2023) 125853. https://doi.org/10.1016/j.ijbiomac.2023.125853.

Beyond choline chloride and betaine: sarcosine as an understudied hydrogen bond acceptor for designing enzyme-stabilizing deep eutectic solvents

Nina Yilmaz[a], Katerina Margariti[a], Francesco Napoletano[a], Qirin Mollweide[b], Ningning Zhang [a], Jan von Langermann[b], Pablo Domínguez de María[c], Selin Kara[a,d*], Marina Cvjetko Bubalo[e*]

[a] Callinstr. 5, 30167 Hannover, Germany, Leibniz University Hanover
[b] Universitätsplatz 2, 39106 Magdeburg, Germany, Otto-von-Guericke-University Magdeburg
[c] Av. Ansite 3, 4-6, Las Palmas de Gran Canaria, Spain, Sustainable Momentum, SL.
[d] Gustav Wieds Vej 10, 8000 Aarhus, Denmark, Aarhus University
[e] Pierottijeva 6, 10000 Zagreb, Croatia, University of Zagreb

E-mail marina.cvjetko.bubalo@pbf.unizg.hr

Over the past decade, Deep Eutectic Solvents (DESs) have emerged as promising alternatives to conventional aqueous and organic media for sustainable biocatalysis [1]. While enzyme behavior in choline- and betaine-based DESs is well studied, alternative hydrogen bond acceptors (HBAs) remain underexplored. Sarcosine (*N*-methylglycine) is a naturally occurring osmolyte and compatible solute that protects proteins from environmental stress by modulating solvent-protein interactions and counteracting unfolding, motivating its recent incorporation into DES formulations [2]. Recent studies indicate that sarcosine-based DESs can act as effective enzyme stabilizers [3,4].

In this study, we investigated the stabilizing effects of sarcosine-based DESs for seven enzymes: horse liver alcohol dehydrogenase (HLADH), *Lactobacillus brevis* alcohol dehydrogenase (*Lb*ADH), unspecific peroxygenase mutant PaDa-I, *Thermocrispum minicipale* cyclohexanone monooxygenase (*Tm*CHMO), *Ruegeria pomeroyi* amine transaminase (*Rp*ATA), *Bacillus subtilis* phenolic acid decarboxylase (*Bs*PAD), and *Chlorella variabilis* fatty acid photodecarboxylase (*Cv*FAP). Enzyme melting temperatures (T_m) were determined and compared across sarcosine-, choline chloride-, and betaine-based DESs.

Overall, DESs stabilized the selected model enzymes more than the corresponding buffers, with sarcosine-based DESs producing a stronger T_m increase for six of seven enzymes compared to choline chloride- and betaine-based systems, while showing a comparable effect to betaine-based DESs for HLADH. Notably, in a sarcosine-glycerol mixture (1:2) containing 20 wt% water, the T_m values of *Lb*ADH, *Cv*FAP, and *Sp*ATA increased by more than 25 °C relative to the reference buffer. In addition, the sustainability of sarcosine-based DESs was assessed from a cradle-to-grave perspective, considering the (bio)synthesis of the components, and their potential fate through dilution in wastewater treatment plants. Overall, this study identifies sarcosine as a promising HBA for DES design and highlights its potential to enhance enzyme stability in biocatalytic applications.

[1] N. Zhang, P. Domínguez de María, S. Kara, *Catalysts* **2024**, *14*, 1-29.
[2] M. Cvjetko Bubalo, T. Andreou, M. Panić, M. Radović, K. Radošević, I. Radojčić Redovniković, *Green Chem*. **2023**, *25*, 3398–3417.
[3] A. Damjanović, M. Logarušić, A. Jurinjak Tušek, M. Radović, N. Ukalović, T. Weitner, T. Andreou, M. Cvjetko Bubalo, I. Radojčić Redovniković, *J. Mol. Liq*. **2025**, *436*, 128259.
[4] N. Zhang, E. Schwarz, J. P. Bittner, S. Jakobtorweihen, I. Smirnova, P. Domínguez de María, S. Kara, *ChemCatChem*, **2025**, *17*, e00986.

General design principles for enzyme tolerance in non-aqueous media

Yannik Brack,[a] and Ulrich Schwaneberg[a,*]

[a] *Lehrstuhl für Biotechnologie, RWTH Aachen University, D-52074 Aachen, Germany*

E-mail: y.brack@biotec.rwth-aachen.de

Enzymes naturally operate in aqueous media, but water is often impractical for industrial synthesis, for example through its low solubility of many industrially important hydrophobic compounds (e.g. steroids, fatty acids, alkanes as well as some synthetic polymers). Therefore, organic solvents are employed in many industrial chemical processes. Since some of the most often used organic solvents are not biodegradable and/or their use in catalytic processes has an unfavorable CO_2 footprint, alternative solutions are needed. One promising alternative to organic solvents are, for instance, ionic liquids (ILs).

To enable the use of enzymes in ionic liquids general principles that govern IL-resistance in enzymes and the use of these principles to generate enzyme variants with improved IL-tolerance were investigated. For this a *Bacillus subtilis* Lipase A (BSLA) library that contains all the natural diversity of BSLA with one amino acid exchange (3620 variants) was constructed.[1] The screening of the library against four [BMIM]-based ILs as co-solvents revealed important principles for IL-resistance. In total, substitutions on 50-69 % of all amino acids led to an improved IL-resistance of BSLA and 6-13 % of the 3620 BSLA variants (217 to 470 variants) were found to have improved IL-resistance.[1] Following, a molecular dynamics simulation revealed that the improved variants had a higher probability of forming a catalytically important hydrogen bond between S77 and H156. Also, polar substitutions on the surface showed a notable effect on keeping the water network tighter bound to BSLA and thereby maintain its flexibility and activity in ILs.[2] Further studies revealed that the ILs can bind to the BSLA surface also through hydrophobic or π–π interactions, and thereby remove critical water molecules from the BSLA surface.[3] Through a combination of *in silico* variant generation, thermodynamics stability analysis and molecular dynamics simulations, the hydration shell integrity was confirmed as a crucial factor for IL-resistance of BSLA.[4,5]

Building on the insights gained into design principles for enhancing enzyme stability in ionic liquids, ongoing research is now focused on extending these strategies to other solvent systems to further advance the field. To systematically understand how individual components influence enzyme tolerance, we are currently screening the BSLA library against a range of non-conventional solvent systems.

[1] V. J. Frauenkron-Machedjou, A. Fulton, L. Zhu, C. Anker, M. Bocola, K.-E. Jaeger, U. Schwaneberg, *ChemBioChem*. **2015**, *16*, 937–945
[2] J. Zhao, V. J. Frauenkron-Machedjou, A. Fulton, L. L. Zhu, M. D. Davari, K. E. Jaeger, U. Schwaneberg, M. Bocola, *Phys. Chem. Chem. Phys.* **2018**, *20*, 9600–9609.
[3] S. Pramanik, G. V. Dhoke, K. E. Jaeger, U. Schwaneberg, M. D. Davari, *ACS Sustain. Chem. Eng*. **2019**, *7*, 11293–11302.
[4] H. Cui, L. L. Zhang, C. B. Yildiz, L. Eltoukhy, L. Y. Cheng, K. E. Jaeger, U. Schwaneberg, M. D. Davari, *ACS Sustain. Chem. Eng*. **2022**, *10*, 15104–15114.
[5] H. Cui, S. Pramanik, K. E. Jaeger, M. D. Davari, U. Schwaneberg, *Green Chem*. **2021**, *23*, 3474–3486.

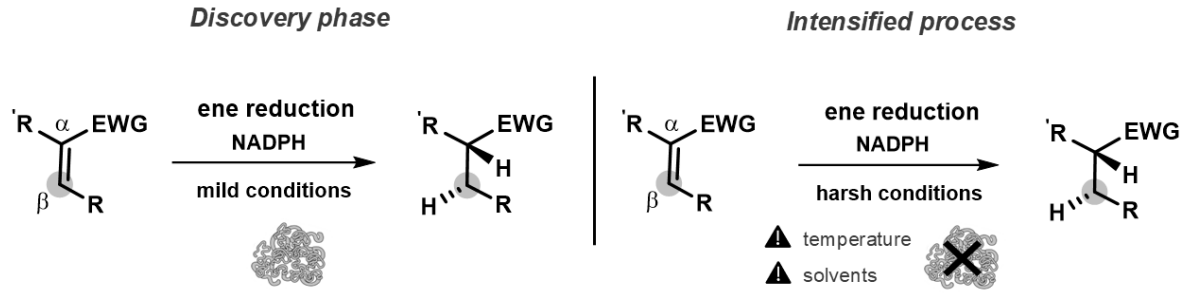
Influence of water-miscible organic cosolvents on enzyme stability

Frieda Sorgenfrei[a], Nathalia Vargas-Valverde[a, c], Stefan Seemayer[b], Florian Weißensteiner[c], Marco Zechner[c], Doreen Schachtschabel[b], Michael Breuer[b], Isabel Oroz-Guinea[c], Wolfgang Kroutil*[,c]

[a] acib - Austrian Centre of Industrial Biotechnology, Krenngasse 37, A-8010 Graz
[b] BASF SE, Group Research, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany
[c] University of Graz, Institute of Chemistry, Heinrichstraße 28, 8010 Graz, Austria

E-mail: nathalia.vvargas@acib.at

Preparative scale biotransformations frequently rely on organic cosolvents to improve substrate solubility or simplify downstream processing.[1] However, solvent exposure can compromise enzyme activity or even result in their complete inactivation. The molecular basis underlying the varying tolerance of enzymes toward different cosolvents is still not fully understood. Here, we aim to unravel the solvent resistance of different ene-reductases and identify significant enzyme and solvent features that determine their stability in non-conventional reaction media.



Scheme 1. Process intensification may impact biocatalyst stability in non-native conditions.

To address this, a diverse set of ene-reductases was selected based on phylogeny and sequence identity [2] to generate a reliable dataset for solvent stability analysis. Thermostability was evaluated in the presence of various cosolvents, together with their effects on initial enzymatic activity. [3] In all cases, the addition of organic solvents resulted in a decrease in melting temperature. The extent of destabilization depended on both solvent type and concentration. In contrast, initial activity responses varied significantly, as certain cosolvents enhanced initial activity for some ene-reductases, whereas others caused activity losses depending on the enzyme–solvent combination. These observations will be further investigated using molecular dynamics (MD) simulations.

[1] U. T. Bornscheuer, G. W. Huisman, R. J. Kazlauskas, S. Lutz, J. C. Moore, K. Robins, *Nature.* **2012**, *485*, 185- 194.
[2] C. Peters, D. Frasson, M. Sievers, R. Buller, *ChemBioChem.* **2019**, *20*, 1569-1577.
[3] F. A. Sorgenfrei, J. J. Sloan, F. Weissensteiner, M. Zechner, N. A. Mehner, T. L. Ellinghaus, D. Schachtschabel, S. Seemayer, W. Kroutil, *Nat. Commun.* **2024**, *15*.

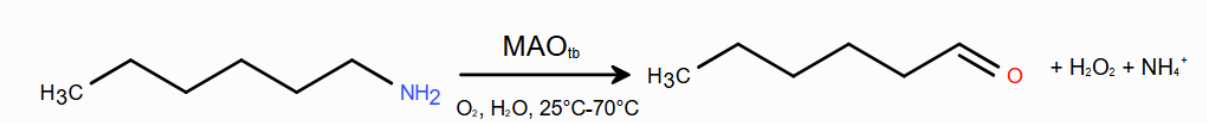
Discovery of a thermostable bacterial monoamine oxidase

Claudia Binda,[a,*] Lorenzo Basile,[a] Chiara Poli,[a] Lars L. Santema[b], Răzvan C. Lesenciuc[b], Marco W. Fraaije[b,*]

[a] Department of Biology and Biotechnology, University of Pavia, via Ferrata 9, 27100 Pavia, Italy
[b] Molecular Enzymology, University of Groningen, Nijenborgh 3, 9747AG Groningen, The Netherlands

E-mail: claudia.binda@unipv.it

Monoamine oxidases (MAOs) are membrane flavoenzymes dedicated to regulate the levels of aromatic neurotransmitters in mammals, while microbial water-soluble MAOs proved valuable biocatalytic tools for enantioselective synthesis of active pharmaceutical ingredients (APIs) [1]. MAO enzymes were discovered also in bacteria [2] and we recently identified a MAO from the thermophile Thermoanaerobacterales bacterium (MAO_{Tb}) [3]. MAO_{Tb} showed melting temperatures of about 70 ºC in different buffers and organic solvents and can be expressed at high yields in *E. coli*. MAO_{Tb} preferentially oxidizes *n*-alkyl monoamines (Scheme 1) but is active also on polyamines and aromatic monoamines. The crystal structure of MAO_{Tb} determined at 1.5 Å showed a high similarity with mammalian monoamine oxidases in the core of the catalytic site in front of the FAD cofactor, while the enzyme features a much more open active site cavity in proximity of the protein surface. Structural studies on MAO_{Tb} in complex with putrescine, benzylamine, spermidine and *n*-heptylamine provided clues on ligand binding mode and fostered site-directed mutagenesis to modulate substrate specificity [4].



Scheme 1. MAO_{Tb}-catalyzed reaction. The enzyme is active on several *n*-alkyl monoamines in a number of buffer conditions including organic solvents.

[1] D. Ghislieri, D, A.P. Green, M. Pontini, S.C. Willies, I. Rowles, A. Frank, G. Grogan, N.J. Turner, *J. Am. Chem. Soc.* **2013,** *135*, 10863-9.

[2] S.N. Muellers, M.A. Tararina, U. Kuzmanovic, J.E. Galagan, K.N. Allen, *Biochemistry* **2023**, *62*, 851-862.

[3] L.L. Santema, L. Basile, C. Binda, M.W. Fraaije, *FEBS J.*, **2024**, *291*, 849-864.

[4] L. Basile, C. Poli, L.L. Santema, R.C. Lesenciuc, M.W. Fraaije, C. Binda, *Arch. Biochem. Biophys.* **2025**, *764*, 110276.

Assessing protein stability in novel alginate eutectogels formulated with osmolyte-based deep eutectic solvents

Anja Damjanović[a], Maria-Anna Karadendrou[b], Georgios Sagias[b], Vasiliki Nianiara[b], Ioannis Papaioannou[b], Georgios D. Stefanidis[b], Ivana Radojčić Redovniković[a], Anastasia Detsi[b], Marina Cvjetko Bubalo[a]

[a] *Pierottijeva 6, 10000 Zagreb, Croatia, University of Zagreb*
[b] *Iroon Polytechniou 9, 15780 Athens, Greece, National Technical University of Athens*

e-mail marina.cvjetko.bubalo@pbf.unizg.hr

Eutectogels, polymer networks structured with deep eutectic solvents (DESs), merge the advantages of DESs with hydrogel integrity and show promise in biosensors, batteries, and drug delivery [1]. While their biomedical potential has been investigated for stabilization and delivery of bioactive compounds, their potential for immobilization and stabilization of proteins remains unexplored.

This study examines the development of novel crosslinker-free alginate eutectogels as platforms for stabilization of structurally and functionally distinct proteins, specifically the enzymes lipase, laccase, and lysozyme. Initially, seven DES formulations based on naturally occurring osmolytes were prepared [2] and screened for their ability to stabilize the three enzymes, over the course of 30 days at 4 °C, 25 °C, and 50 °C to reflect common storage conditions and protein thermostability within these solvents. The results identified DES formulations that effectively preserved enzyme activity, informing the rational selection of candidates for gel incorporation. The selected DESs were then integrated into polymer networks to form alginate eutectogels, prepared for the first time without the use of $CaCl_2$ or other crosslinkers, which were characterized in terms of key rheological properties, confirming their gel-like nature. The incorporation process resulted in homogenous enzyme-loaded eutectogels that were studied for their ability to retain enzymatic activity at 4 °C and 25 °C. The study revealed high stabilizing ability of the eutectogels, outperforming the stabilizing effect of the DES liquid formulations in most of the studied cases.

Overall, this work demonstrates that eutectogels can serve as effective protein-stabilizing platforms, offering potential applications in biomedical and biotechnological fields.

[1] P.A. Mercadal, A. González, A. Beloqui, L.C. Tomé, D. Mecerreyes, M. Calderón, M.L. Picchio, *JACS Au* **2024**, 4, 3744–3758.
[2] M. Cvjetko Bubalo, T. Andreou, M. Panić, M. Radović, K. Radošević, I. Radojčić Redovniković, *Green Chem*. **2023**, *25*, 3398–3417.

Decoupling Cytochrome P450 from Ferredoxin and Ferredoxin Reductase: A Fast Approach to Substrate Scope Screening

Fatemeh Aziziyan,[a] Francesca Paradisi[a,*]

[a] *Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3 3012 Bern, Switzerland*

E-mail: fatemeh.aziziyan@unibe.ch, francesca.paradisi@unibe.ch

Cytochrome P450s (CYPs) are promising biocatalysts for selective C–H hydroxylation [1]. In natural systems, they require the redox partners (RP) to achieve efficient electron transfer [2]. In recombinant systems, the entire operon, including CYPs and their RPs, is cloned, and activity is assessed using whole-cell systems [3]. However, engineering microorganisms for this purpose faces challenges, including the metabolic burden in host cells and the difficulty of balancing cell survival with production yield [4]. Furthermore, the application of CYPs in whole-cell systems was significantly hindered by their dependence on compatible electron-transport chains, inefficient electron utilization, and low enzyme efficiency [5]. Therefore, designing efficient systems for biotransformation has become an important focus.

In this study, we designed two separate constructs to decouple the RPs from CYP153A homologues, aiming to improve electron transfer and coupling efficiencies. A single redox fusion was found to efficiently support diverse CYP153A homologues while enabling distinct substrate-selectivity profiles. This approach establishes a modular and efficient platform for the reconstitution and optimization of CYP153A enzymes, thereby expanding their potential in biocatalysis and synthetic biology. The design enhances process control and scalability, facilitates pathway reassembly, and simplifies the cloning of new biocatalysts by enabling the use of a common RP with different CYP homologues. Furthermore, exploration of substrate scope demonstrated the potential of this system as an efficient biocatalytic platform to produce high-value pharmaceutical compounds.

[1] C. A. Martinez, S. G. Rupasinghe, *Current Topics in Medicinal Chemistry* **2013**, *13*, 1470–1490.
[2] X. Zhang, Y. Peng, J. Zhao, Q. Li, X. Yu, C. G. Acevedo-Rocha, A. Li, *Bioresources and Bioprocessing* **2020**, *7*, 1–18.
[3] S. Cornelissen, M. K. Julsing, J. Volmer, O. Riechert, A. Schmid, B. Bühler, *Biotechnology and Bioengineering* **2013**, *110*, 1282–1292.
[4] C. Yang, Y. Liu, W. Q. Liu, C. Wu, J. Li, *Frontiers in Bioengineering and Biotechnology* **2021**, *9*, DOI 10.3389/FBIOE.2021.730663/FULL.
[5] P. Cannazza, M. Rabuffetti, S. Donzella, V. De Vitis, M. L. Contente, M. da C. F. de Oliveira, M. C. de Mattos, F. G. Barbosa, R. P. de Souza Oliveira, A. Pinto, F. Molinari, D. Romano, *AMB Express* **2022**, *12*, 48.

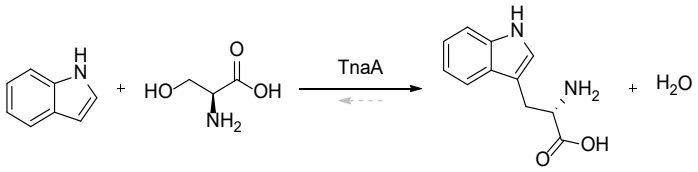
Mining for Novel Tryptophanase A: extremophilic organisms *Ardenticatena maritima* and *Haloarcula japonica* as alternative to *E. Coli* in the synthesis of tryptophan analogues

Evelyn Sgroi[a], Fatemeh Aziziyan[a], Francesca Paradisi[a*]

[a] *Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3 3012 Bern, Switzerland*

E-mail: evelyn.sgroi@unibe.ch, fatemeh.aziziyan@unibe.ch, francesca.paradisi@unibe.ch

L-Tryptophan is a key amino acid with significant roles in both biological systems and pharmaceutical industries. Beyond its natural role in cellular metabolism, L-tryptophan derivatives and other non-canonical amino acids (ncAAs) are increasingly valued in medicinal chemistry and synthetic biology, contributing to the design of chemical probes and pharmaceutical scaffolds [1,2]. The biosynthesis of L-tryptophan is classically mediated by the heterodimeric tryptophan synthase (TrpS) [3], however, in *Escherichia coli* strains, it has also been well-documented that L-tryptophan can be synthesized under high concentrations of L-serine via tryptophanase A (*Ec*TnaA), an enzyme typically involved in L-tryptophan catabolism (Figure 1) [4].



Scheme 1. Biosynthesis of L-tryptophan from indole and L-serine.

This research focuses on the characterization of two novel TnaA enzymes: *Am*TnaA from the thermophilic organism *Ardenticatena maritima* [5] and *Hj*TnaA from the halophilic organism *Haloarcula japonica* [6]. Owing to their resilience under harsh physicochemical conditions, these enzymes represent promising biocatalytic tools for challenging synthetic applications, and the exploration of their substrate scope further highlights their potential for sustainable production of tryptophan derivatives and pharmaceuticals.

[1] D. K. Romney, J. Murciano-Calles, J. E. Wehrmüller and F. H. Arnold, *J. Am. Chem. Soc.*, 2017, **139**, 10769–10776.
[2] S. Xiao, Z. Wang, B. Wang, B. Hou, J. Cheng, T. Bai, Y. Zhang, W. Wang, L. Yan and J. Zhang, *Front. Microbiol.*, 2023, **14**, 1099098.
[3] A. R. Buller, S. Brinkmann-Chen, D. K. Romney, M. Herger, J. Murciano-Calles and F. H. Arnold, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 14599–14604.
[4] W. A. NEWTON and E. E. SNELL, *Proc. Natl. Acad. Sci. United States*, 1964, **51**, 382–389.
[5] S. Kawaichi, N. Ito, R. Kamikawa, T. Sugawara, T. Yoshida and Y. Sako, *Int. J. Syst. Evol. Microbiol.*, 2013, **63**, 2992–3002.
[6] K. Horikoshi, R. Aono and S. Nakamura, *Experientia*, 1993, **49**, 497–502.

A Novel Plant Myrosinases: Efficient Recombinant Production and Its Preventive Anticarcinogenic Potential

Petrovičová T[1], Mikušková M[1,2], Vojtilla R[1], Marčeková Z[1], Rebroš M[1]

[1] *Faculty of Chemical and Food Technology, Slovak University of Technology , Bratislava, Slovakia*
[2] *Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Praha, Czech Republic*

Myrosinases are enzymes found in plants of the Brassicaceae family, responsible for the hydrolytic cleavage of glucosinolate substrates into D-glucose and bioactive compounds, such as isothiocyanates. These metabolites, which are toxic to pathogens, herbivores, and other threats, serve as a plant defence mechanism. Many isothiocyanates exhibit antimicrobial and anti-inflammatory properties and show promise in cancer prevention. Although the regular dietary intake of cruciferous vegetables benefits human health, its effectiveness is limited due to the low concentrations of both the enzyme and its substrate. To enhance the glucosinolate-myrosinase system, large-scale production of these components separately is a viable approach. Recombinant production enables high-yield myrosinase expression with significant enzymatic activity when an optimal production system is used. In this study, *Pichia pastoris* was selected as the host system for expressing various enzymes with potential myrosinase activity. Additionally, the impact of deleting the native signal sequence on myrosinase activity was investigated.

This work was co-funded by the Agency for supporting research and Development, according to Agreement No. APVV-22-0383, project Horizon Europe WIDEnzymes No. 101159534 and by
EU NextGenerationEU through the Recovery and Resilience Plan of the Slovak Republic under project No. 09I03-03-V04-00537

.

WORKSHOP ORGANIZED BY

UNIVERSIDAD DE MURCIA

Universidad Politécnica de Cartagena

GEQV
Grupo Especializado Química Verde
Green Chemistry Division

RSEQ
Real Sociedad Española de Química

Centro de Referencia Nacional de Química de Cartagena

Sef
Servicio Regional
DE EMPLEO y FORMACIÓN

ESAB
European Society of Applied Biocatalysis

MINISTERIO
DE EDUCACIÓN, FORMACIÓN PROFESIONAL
Y DEPORTES

TECHNICAL SECRETARIAT

VÉRTICESUR

DIAMOND SPONSORS

DESTILERÍAS
MUÑOZ GÁLVEZ S.A.


Derivados
Químicos


olon


CÁTEDRA
olon
UMU
Química Sostenible


Tahe
BEAUTIFYING YOUR LIFE
WE TURN ADVANCES IN GREEN CHEMISTRY
INTO REAL-WORLD COSMETIC SOLUTIONS
MARKET
ETHICS
ACCOUNTABILITY
GOALS
IMPACT
RESOURCES
TRANSPARENCY
SUSTAINABILITY
CO2
CARBON FOOTPRINT
We are committed to responsible innovation, incorporating the principles of green chemistry into our formulation, production and distribution processes.
Sustainable, science-based cosmetics
www.tahecosmetics.com
GREEN CHEMISTRY

GOLD SPONSOR

Scharlab
THE LAB SOURCING GROUP

50 1976 - 2026 deltalab
member of SCGP

Thieme

GREEN SCIENCES FOR SUSTAINABLE DEVELOPMENT FOUNDATION

Chemistry Europe
European Chemical Societies Publishing

Chem Cat Chem | Chem Sus Chem | Chemistry Europe

Sustainability & Circularity NOW

Green Chemistry

Oficina de Congresos Cartagena

AMC GLOBAL Feeding the future

CAMPUS MARE NOSTRUM
de Excelencia Internacional

UNIVERSIDAD DE MURCIA

Universidad Politécnica de Cartagena

GEQV Grupo Especializado Química Verde Green Chemistry Division RSEQ

RSEQ Real Sociedad Española de Química

ESAB

CAMPUS MARE NOSTRUM de Excelencia Internacional

Sef Servicio Regional DE EMPLEO y FORMACIÓN

Centro de Referencia Nacional de Química de Cartagena

GOBIERNO DE ESPAÑA MINISTERIO DE EDUCACIÓN, FORMACIÓN PROFESIONAL Y DEPORTES

DMG DESTILERÍAS MUÑOZ GÁLVEZ S.A.

Derivados Químicos

olon

CÁTEDRA olon UMU Química Sostenible

Tahe BEAUTIFYING YOUR LIFE

Scharlab THE LAB SOURCING GROUP

deltalab

Thieme

GREEN SCIENCES FOR SUSTAINABLE DEVELOPMENT FOUNDATION

GREEN CHEMISTRY POSTGRADUATE SUMMER SCHOOL 2026

Chemistry Europe

CATALYSIS TODAY

Green Chemistry

Sustainability & Circularity NOW

Oficina de Congresos Cartagena