EMERALD ISLE
CONFERENCE
ON SUSTAINABLE
CHEMISTRY &
ENGINEERING

9-11 April 2025
Belfast

QUEEN'S UNIVERSITY BELFAST

Conference Programme
and
Book of Abstracts

Sponsored by

QUEEN'S UNIVERSITY BELFAST

GORDON AND BETTY MOORE FOUNDATION

Institute of Chemistry of Ireland

ACS Publications
Most Trusted. Most Cited. Most Read.

ACS Green Chemistry Institute
Chemistry for Life®

ROYAL SOCIETY OF CHEMISTRY | SURFACE REACTIVITY AND CATALYSIS GROUP

RSC LOCAL SECTION NORTHERN IRELAND

Asynt

ALMAC
Partnering to Advance Human Health

Conference Programme

Day One – 9th April 2025

11:00	Registration
13:00	Welcome and Introduction Panagiotis Manesiotis, Haresh Manyar, Andrew Marr, Patricia Marr
13:20	Global Thought Leaders Panel Discussion Chairs - Andrew Marr, Patricia Marr
15:20	*The 40 Shades of Green Chemistry* Paul Anastas Yale University Chair - Andrew Marr
16:00	Coffee Break
16:30	*TBC* Julie Zimmerman Yale University Chair - Patricia Marr
17:10	Delegate Information Session Haresh Manyar
17:20	Reception - Poster Session and Exhibitors Sponsored by Almac
19:00	Day One - Close
20:00	Conference Delegate Banquet

Day Two – 10th April 2025

08:50	Welcome and Introduction
	Session Chair - Patricia Marr
09:00	*Teaching Green Chemistry in a Changing World* Martyn Poliakoff University of Nottingham
09:40	*Bio-Based Platform Chemicals from Local Plant Oils by Selective Semi-Hydrogenation and Homogeneous Catalysis* Thomas Seidensticker TU Dortmund
10:00	*Accelerating Development of Green Chemistry Technologies Through Cross-Sector Collaboration* Adelina Voutchkova ACS Green Chemistry Institute
10:40	Coffee Break
	Session Chair - Andrew Marr
11:00	*From Flexible to Adaptive: Dynamic Systems to Control the Performance of Catalysts* Walter Leitner Max Planck Institute for Chemical Energy Conversion
11:40	*Sustainable Chemistry & Engineering for Education, Outreach and Recruitment* Kevin Morgan Queen’s University Belfast
12:00	*Electrochemical Biomass Depolymerization: Will Complex Catalysts Trigger High Product Selectivity?* Adam Slabon Bergische Universität Wuppertal

12:20	Flash Session One James Metcalf Philippa Jacob Víctor Sans Sangorrín	 *Atmospheric Degradation of New “Green” Solvents* *Machine Learning for Polymer Biodegradability* *Digital Synthetic Platforms for the Efficient Capture and Valorisation of Carbon Dioxide into Added Valued Chemicals*
12:50	*Sustainable Monomers and Polymers* Steve Howdle University of Nottingham	
13:10	Lunch Session Chair - Gosia Swadźba-Kwaśny	
14:00	*Sustainability: Who Gives a Cr*p?* Mike George University of Nottingham	
14:40	*Small but Feisty: How Singapore Turns CO2 Problems into Greener Solutions* Bella Institute of Sustainability for Chemicals, Energy and Environment (ISCE^2)	
15:00	*New Ways of Building Carbon Chains - From Fischer Tropsch to New Synthetic Routes* Andreas J. Vorholt Max Planck Institute for Chemical Energy Conversion	
15:20	*Genes to GMP: How API Manufacture is ’Going Green’ with Engineered Enzymes* Stefan Mix Almac	
15:40	Coffee Break	
16:00	*Biobased Reversible Photo-Responsive Polymers for Useful Applications* Antonio Patti Monash University	

16:20	*Ionic Liquids Technology for Polyurethane Foam Waste Depolymerization* Pedro Lozano Rodriguez University of Murcia Session Chair - Haresh Manyar	
16:40	Flash Session Two	
	Jane Mueller	*IN Silico Informed metaGenomic Harvesting Technology - (INSIGHT) - How a Smart Platform Can Accelerate the Timelines of Genes-to-GMP*
	Thomas Freese	*Photochemical Production of Bio-Based Building Blocks as Acrylate Replacements*
	Shanika Yadav	*Inspiring Innovation in Green Chemistry - Startup Support Network KOALA*
17:10	*Crude Glycerol – Microbial Substrate for Production of Intermediates and Recombinant Enzymes* Martin Rebroš Slovak University of Technology	
17:30	*Green Catalytic Chemistry for the Energy Transition* Johannes A. Lercher TU München	
18:10	Poster Session and Exhibitors Sponsored by Institute of Chemistry of Ireland	
19:30	Day Two - Close	

Day Three – 11th April 2025

08:50	Welcome and Introduction	
	Session Chair – Gary Sheldrake	
09:00	*Hotspot Driven Research in Green and Sustainable Chemistry* Philip Jessop Queen's University at Kingston	
09:40	Flash Session Three	
	Elisa Isabel García-López	*Carbon Nitride Based Composites Photocatalysts Prepared with Materials Arising from Spent Li-Batteries for the Photoreforming of Biomass Residues*
	Sarmad Ahmad Qamar	*Bioplastics from ‘Annurca’ Apple Cellulose Doped with Polyphenolic Compounds for ‘Active’ Food Packaging Applications*
	Neil Robinson	*Measuring Nuclear Spin Dynamics in Sustainable Engineering Systems*
10:10	*Recent Developments in Asymmetric Synthesis and Catalysis* Pat Guiry University College Dublin	
10:50	Coffee Break	

	Session Chairs – Adelina Voutchkova, Isamir Martinez
11:10	ACS GCI Pharmaceutical Roundtable Workshop *Green Chemistry Tools and Metrics to Design Sustainable Processes* Nathan McCormack – Ipsen David Entwistle – Codexis Isamir Martinez – ACS GCI Adelina Voutchkova – ACS GCI
13:10	Lunch
	Session Chair – Haresh Manyar
14:00	*Mechanochemistry and Aging-Based Methods as Novel Tools to Transform Biopolymers into High Value Materials* Audrey H. Moores McGill University
14:40	*The Journey from Lab to Industry – A Sustainable Recycling Technology for Rare Earth Magnets* Peter Nockemann Queen's University Belfast
15:00	*Catalysis and Sustainability from Atom to Planetary Scale* Javier Pérez-Ramírez ETH Zurich
	Session Chair – Panagiotis Manesiotis
15:40	Poster and Flash Prizes Sponsored by Royal Society of Chemistry and ACS Publications
16:00	Conference Close Chris Johnson Department for Science, Innovation and Technology

Keynote, Oral and Flash Presentations

Teaching Green Chemistry in a Changing World

Martyn Poliakoff
School of Chemistry, University of Nottingham, Nottingham, NG7 2RD UK
E-mail: martyn.poliakoff@nottingham.ac.uk

Keywords: Education, SDGs, Africa

I am part of a team (Mike George, James Bennett, Pete Licence and myself) which teaches Green & Sustainable Chemistry across the different years of our undergraduate chemistry courses. I am not going to focus on what we teach currently apart from mentioning that we try to avoid setting what have been called “guess what I’m thinking” questions”. [1]. Instead, I will highlight the recent RSC Report, *Future Workforce and Educational Pathways* [2], which recommends among other points that we should “*Frame chemical sciences in further and higher education with a lens of green chemistry and sustainability where appropriate, so students understand the centrality of chemistry to net zero and sustainability efforts*.” In this context, I will discuss how, perhaps, we can help our students to think rather than memorise. I will also briefly discuss taking Green Chemistry to Africa. [3].

I am extremely grateful to Mike George, James Bennett, Pete Licence for their innovative ideas and for letting me teach with them. I also thank Zacharias Amara and Ana Aguiar-Ricardo for their help with the new version of the 13 Principles.

[1] N. Postman, C. Weingartner, **1971**, Teaching as a Subversive Activity, Penguin Education Specials (available secondhand from Amazon).

[2] https://www.rsc.org/policy-evidence-campaigns/discovery-research-and-innovation/discovery-research-innovation-reports-surveys-campaigns/future-workforce-and-educational-pathways/ (accessed 25/02/2025)

[3] N. Asfaw, Y. Chebude, A Ejigu, B. B. Hurisso, P. Licence, R. L. Smith, S. L. Y. Tang, M. Poliakoff “The 13 Principles of Green Chemistry and Engineering for GREENER AFRICA” 2011,*Green Chem. 13*, 1059-1060.

Bio-Based Platform Chemicals from Local Plant Oils by Selective Semi-Hydrogenation and Homogeneous Catalysis

T. F. H. Roth, H. W. Wegener, M. L. Spiekermann, T. Seidensticker
TU Dortmund University, Dortmund, Germany
E-mail: thomas.seidensticker@tu-dortmund.de

Keywords: Homogeneous Catalysis; Continuous Processes; Mechanistic Insights; Start-up

Selective functionalization reactions (carbonylations, metathesis, oxidations, …) of unsaturated oleochemicals make bio-based platform chemicals as molecular building blocks accessible. However, with their high content of polyunsaturated compounds and varying degrees of unsaturation, technical-grade plant oils, such as rapeseed oil, cannot be used efficiently enough to allow economic processes. Although the hydrogenation of vegetable oils has been known for centuries,[1] a catalytic approach that combines **economic feasibility** with **high selectivity** to monounsaturated compounds is lacking. This technology urgently needs an update in the context of the defossilisation of the chemical industry.

We, therefore, initially studied the phenomenon of reduced catalytic performance by using mixtures of mono- and polyunsaturated fatty acid methyl esters commonly found in biodiesel. In all three selected model reactions—hydroformylation, isomerizing methoxycarbonylation, and ethenolysis—the performance was significantly improved by several orders of magnitude when substrates were pretreated to remove polyunsaturated fatty acids (PUFAs) through hydrogenation.[2] For hydroformylation[3] and methoxycarbonylation,[4] subsequent analyses revealed that this behavior is linked to the formation of conjugated linoleic acid species, leading to stable allyl complexes. These findings were also mechanistically validated, stressing the importance of PUFA-free substrates for efficient catalysis.

Finally, we developed a proprietary catalytic system for selective semi-hydrogenation that makes any plant oil, irrespective of its fatty acid profile, a bio-based substrate for (homogeneously) catalyzed reactions. In our start-up **simplyfined**,[5] we now scale our technology up to provide monounsaturated oleochemicals to the chemical industry.

[1] M. L. Spiekermann, T. Seidensticker, *Catal. Sci. Technol.*, **2024**, *14,* 4390-4419. [2] T. F. H. Roth, M. L. Spiekermann, A. Kühl, H. Wegener, T. Seidensticker, *ChemSusChem*, **2024**, *17*, 13, e202400036. [3] T. F. H. Roth, M. L. Spiekermann, D. Lütkenhaus, F. Niefer, D. Vogt, T. Seidensticker, *Cat. Sci. Technol.* **2024***, 14,* 5551-5558*.* [4] H. W. Wegener, R. Reichert, N. Brede, A. Gierse, M. L. Spiekermann, D. Vogt, T. Seidensticker, **2024**, in revision. [5] www.simplyfined.com

Sustainable Chemistry & Engineering for Education, Outreach and Recruitment

K. Morgan
Queen's University Belfast, Belfast, UK
E-mail: k.morgan@qub.ac.uk

Keywords: Education, Outreach, Recruitment

Sustainability is a growing theme of the UK Secondary level curriculum and the Chemistry A-level specification in Northern Ireland has considerations of chemistry on the environment. There are also various programmes for Schools across the UK that promote sustainability such as the Eco-Schools (Green Flag) Network.[1] Consequently, there are high levels of knowledge of and engagement with the United Nations Sustainable Development Goals (UN SDGs)[2] amongst students that are preparing for Tertiary education. It has been reported that since 2012 the total number of applicants for Chemistry in the UK has declined while other subjects have seen increased interest.[3] This trend for Chemistry has been observed (and mirrored for Chemical Engineering) at Queen's University Belfast (QUB). It is, therefore, important to embed sustainability and the SDGs as part of resources and interventions that aim to encourage students to continue their education with Chemistry and (Chemical) Engineering degrees in Higher Education and a QUB a number of interventions have been implemented and these have seen a 26% increase in enrolment in Chemistry and Chemical Engineering in 2023 and a further 30% increase in applications for 2024.

This programme of interventions involves standalone events as well as prolonged interactions throughout the course of the academic year such as a project-based learning experience (with a sustainability focus) known as Towards Greener Fragrances.[4]

This presentation will discuss the impacts of promoting sustainable chemistry and engineering in an educational context.

[1] https://www.transform-our-world.org/ukssn/about-ukssn
[2] https://sdgs.un.org/goals
[3] https://www.michaeloneill.org/blog-1/2022/3/26/ten-years-of-9k-fees-how-has-chemistry-fared
[4] S. McLaughlin, H. Amir, N. Garrido, C. Turnbull, A. Rouncefield-Swales, G. Swadźba-Kwaśny, K. Morgan, *Journal of Chemical Education*, **2024**, 101 (2), 537-546

Electrochemical Biomass Depolymerization: Will Complex Catalysts Trigger High Product Selectivity?

A. Slabon
Chair of Inorganic Chemistry, University of Wuppertal, Wuppertal, Germany
E-mail: slabon@uni-wuppertal.de

Keywords: electrocatalysis, biomass depolymerization, in operando XAS

The electrochemical conversion of biomass represents an approach to the production of valuable chemicals, yet most catalyst studies have primarily focused on bulk electrodes with limited structural and chemical diversity. For instance, these electrodes lack often the necessary selectivity, resulting in a complex mixture of depolymerization products. To overcome this challenge, the question is whether more sophisticated catalysts - those exhibiting enhanced structural and chemical diversity - could be the key to product selectivity? In this talk, I will discuss electrochemical reductive depolymerization of lignin on both bulk electrodes[1-4] and complex carbon-supported materials such as Fe-based single-atom-catalysts (SAC) and dual atom catalysts (DAC) (Figure 1). In particular, the focus will be the application of high energy density X-ray methods like *in operando* X-ray absorption spectroscopy (XAS) experiments to study the critical chemical features during electrochemical reductive depolymerization on Fe-based SAC and DAC.[5]

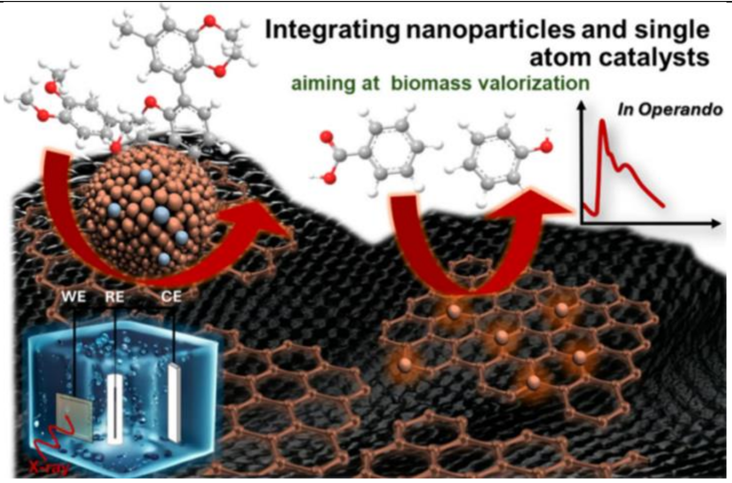


Figure 1. Nanoparticle and single-atom-catalyst systems for electrochemical reductive depolymerization (ERD) of biomass.

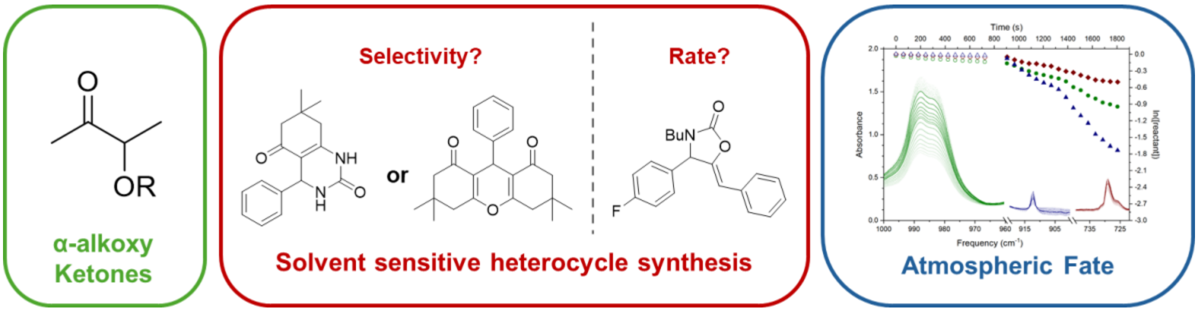
[1] L.M.Lindenbeck, B.V.M.Rodrigues, A.Slabon et al., *Chem. Mater.* **2024** accepted, https://doi.org/10.1021/acs.chemmater.4c02078
[2] M.G.A.da Cruz, B.V. M.Rodrigues, A.Slabon et al., *ChemSusChem* **2022**, 15, e202200718.
[3] .M. Lindenbeck, V.C. Barra, S. Dahlhaus, S. Brand, L.M. Wende, B.B.Beele, N.H.Schebb, B.V. M.Rodrigues, A.Slabon, *ChemSusChem* **2024**, e202301617
[4] L.M.Lindenbeck, A.Slabon, B.V. M.Rodrigues et al., *Green Chem. Lett. Rev.* **2024**, 17, 2390867.
[5] L.M.Lindenbeck, B.V. M.Rodrigues, A.Slabon, *in preparation.*

Atmospheric Degradation of new “Green” Solvents

J. D. D’Souza Metcalf[ab]*, C. Mapelli[ac], R. K. Winkless[b], C. Roman[d], I. G. Bejan[d],
C. R. McElroy[ae], J. R. Sherwood[a], T. J. Dillon[b]
[a] Green Chemistry Centre of Excellence, University of York, York, UK.
[b] Wolfson Atmospheric Chemistry Laboratories, University of York, York, UK.
[c] now Institute of Atmospheric Sciences and Climate, Lecce, Italy UK.
[d] CERNESIM, “Alexandru Ioan Cuza” University of Iasi, Iasi, Romania.
[e] now School of Chemistry, University of Lincoln, Lincoln, UK.
E-mail: jdm570@york.ac.uk

Keywords: Solvent, Atmosphere, Kinetics

Recent years have seen a rapid increase in the development and deployment of bio-derived and biodegradable “green” solvents. Design processes typically focus on performance, toxicity and renewability however the impact of these molecules on the atmosphere remains largely unexplored. As traditional sources of VOCs are increasingly regulated, solvents have emerged as the largest anthropogenic source of non-methane VOCs. It is therefore imperative that we understand more about the atmospheric fate of solvent emissions as they grow and diversify.



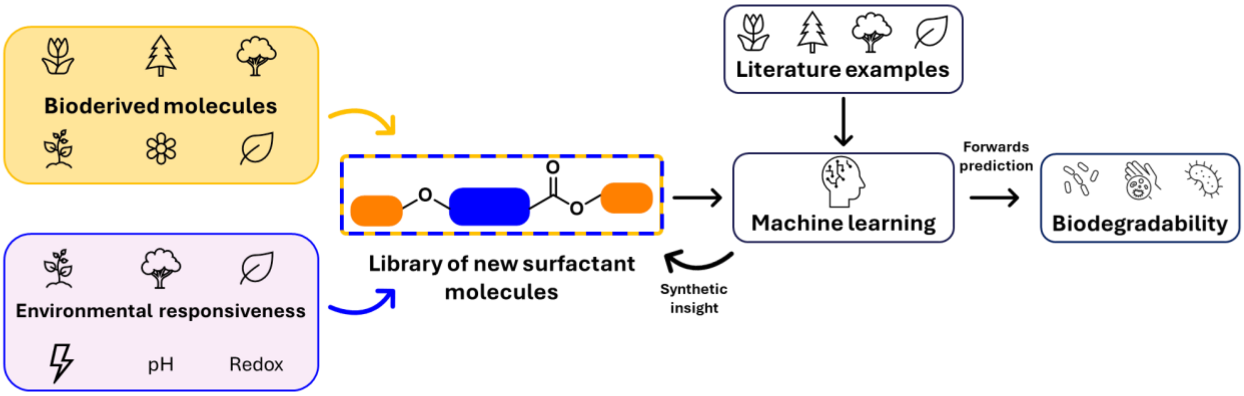
This work is a collaboration between green chemists and atmospheric scientists. Our interdisciplinary approach to solvent development involves rigorous experimental and *in silico* testing of both solvent performance and environmental impact. Here, two structurally distinctive, bio-derivable polar aprotic solvents were synthesised, characterised and evaluated as powerful reaction media for solvent sensitive multicomponent reactions. Investigations into the atmospherically relevant kinetics of these and other bio-based oxygenate solvent molecules were then carried out *via* laser-based (absolute) and chamber-based (relative) experiments, and by quasi-gas-phase UV/Vis spectroscopy, uncovering a range of unpredicted degradation rates, mechanisms, products and environmental impacts.

Machine Learning for Polymer Biodegradability

P. L. Jacob, M. Parker, D. J. Keddie, S. M. Howdle, V. Taresco and J. D. Hirst
University of Nottingham, Nottingham, United Kingdom
E-mail: pippy.jacob@nottingham.ac.uk

Keywords: Polymer chemistry, machine learning, biodegradability

Biodegradability is an important factor when considering the design and synthesis of new, functional polymers. With mounting consumer and legislative driving forces towards more degradable polymers, rapid assessment of the biodegradability of polymers of interest is becoming more crucial. We demonstrate the use of a rapid, high-throughput biodegradation assay to assess polymer biodegradability. These data, in combination with literature data[1], have been used in the development of a machine learning model for the prediction of polyester biodegradability from computed molecular descriptors. Insight from the machine learning model has been used to inform the rational design of novel, biobased, functional polyesters.



[1] K. A. Fransen, S. H. M. Av-Ron, T. R. Buchanan, D. J. Walsh, D. T. Rota, L. Van Note and B. D. Olsen, *Proc. Natl. Acad. Sci. USA*, **2023**, 120, e2220021120.

Digital synthetic platforms for the efficient capture and valorisation of carbon dioxide into added valued chemicals

Cristopher Tinajero,[a] Simone Marchetti,[a] Marcileia Zanatta,[a,b] Eduardo Garcia-Verdugo,[c] Victor Sans[a]
[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, Av. Sos Baynat s/n, 12071 Castelló de la Plana, Spain
[c] Departamento de Química Inorgánica y Orgánica, Grupo de Química Sostenible y Supramolecular Universidad Jaume I, E-12071 Castellón, Spain
E-mail: sans@uji.es

Keywords: electrochemistry, continuous-flow; carbon dioxide cycloaddition

The development of efficient and sustainable strategies for CO_2 valorization is crucial for decarbonizing the chemical industry. This study explores the integration of 3D printing (3DP) and additive manufacturing (AM) to fabricate high-resolution, functionalized reactors tailored for continuous-flow chemical transformations. We demonstrate the application of epoxy-functionalized acrylate-based resins for producing catalytic structures with immobilized ionic liquids (ILs), enabling precise control over surface functionality and catalytic activity.[1] These reactors exhibit superior resolution and process performance, significantly enhancing space-time yield (STY) in CO_2 cycloaddition reactions. Additionally, we present a seamless, two-step continuous-flow process combining electrooxidation of alkenes and subsequent CO_2 cycloaddition, eliminating intermediate purification steps.[2] The digitally designed 3DP reactors outperform traditional packed-bed and coil reactors, exhibiting increased productivity and extended operational stability (>300 h) while maintaining high catalytic efficiency.[3] This multi-scale approach, leveraging metal-free catalysts and polymer-supported ILs, highlights the transformative potential of AM in designing next-generation catalytic reactors for sustainable chemical manufacturing.

[1] S. Marchetti, C. Tinajero, G. Palmara, E. García-Verdugo, I. Roppolo, M. Zanatta, V. Sans *Additive Manufacturing* **2024,** (89), 104304.
[2] D. Iglesias, C. Tinajero, S. Marchetti, I. Roppolo, M. Zanatta, V. Sans, *Green Chemistry,* ***2023,*** (25) 9934-9940.
[3] D. Valverde, R. Porcar, M. Zanatta, S. Alcalde, B. Altava, V. Sans, E. Garcia-Verdugo, *Green Chemistry,* **2022***,* (24), 3300-3308.

Sustainable Monomers and Polymers

S.M. Howdle
School of Chemistry, University of Nottingham, UK
E-mail: steve.howdle@nottingham.ac.uk

Keywords: renewable, degradable, polymers

We will report on the development of new monomers and polymers derived from renewable resources. We have utilized a number of different sources to create a wide range of monomers and polymers. These sources include polyols and fatty acids that are derived directly from nature and could be applied commercially in household products that are based on polymer liquid formulations.

Our group has developed significant expertise in utilizing supercritical carbon dioxide (scCO$_2$). In particular, we have exploited the low viscosity and high diffusivity of scCO$_2$ to create a highly efficient and reversible plasticizer. This *in-situ* plasticization allows us to perform polymerisation reactions at temperatures as low as 40°C; much lower than is possible under conventional operating conditions. In some cases, these lower temperature operating conditions have opened up the opportunity to use enzymatic catalysts to yield new polymeric materials from renewable monomers.

1. Pin-Nó, M., Jacob, P. L., Taresco, V., Kastelijn, M., Nabuurs, T., Surti, C., Bilney, J., Daly, J., Keddie, D. J., Howdle, S. M., & Stockman, R. A. (2024). *RSC Sustainability*, *2*(9), 2515-2523. https://doi.org/10.1039/d4su00210e
2. Thomsett, M. R., Moore, J. C., Buchard, A., Stockman, R. A., & Howdle, S. M. (2019) *Green Chemistry*, *21*(1), 149-156. https://doi.org/10.1039/C8GC02957A
3. Baheti, P., Rheinberger, T., Gimello, O., Bouilhac, C., Wurm, F. R., Lacroix-Desmazes, P., & Howdle, S. M. (2020). *Green Chemistry*, *22*(10), 3248-3261. https://doi.org/10.1039/D0GC00819B
4. Gameiro, M. D., Jacob, P. L., Kortsen, K., Ward, T., Taresco, V., Stockman, R. A., Chebude, Y., & Howdle, S. M. (2022).. *Journal of Polymer Science*, *60*(24), 3354-3365. https://doi.org/10.1002/pol.20220050
5. Goddard, A. R., Apebende, E. A., Lentz, J. C., Carmichael, K., Taresco, V., Irvine, D. J., & Howdle, S. M. (2021). *Polymer Chemistry*, *12*, 2992-3003. https://doi.org/10.1039/D1PY00415H

Small but Feisty: How Singapore Turns CO_2 Problems into Greener Solutions

Bella, C.K. Poh, Z. Lili, Y.F. Lim, A. Amrute, L. Chen
*Institute of Sustainability for Chemicals, Energy and Environment (ISCE^2), A*STAR, Singapore*
E-mail: bella@isce2.a-star.edu.sg

Keywords: CO_2 conversion, emerging technologies, future energy carriers

Singapore is a small tropical country located in Southeast Asia, bare of natural resources, meaning we heavily rely on energy export to meet the demands of the country. Despite this major limitation, over the past 59 years after the declaration of independence, Singapore has been thriving as a nation and emerged as one of the most advanced countries in the world. This achievement could only be made possible by the continuous efforts and innovations developed by the brilliant minds across the country while holistically factoring in the availability of resources from neighbouring countries and international collaborations.

In this conference, we would like to share the advances developed in A*STAR together with other institutions and industries to reduce Singapore’s reliance on conventional fossil fuel, while also minimizing the environmental impact. Our efforts to align with the Sustainable Development Goals set in Singapore may include, but not limited to, CO_2 to aviation fuel (SAF), CO_2 to light olefins, decarbonisation by desalination of brine to form minerals, ammonia cracking, methane cracking, plastic valorisation, CO_2 methanation and many more [1]. Our research efforts are supported by our flagship joint innovation between three of A*STAR’s institutions, Accelerated Catalyst Development Platform (ACDP), which is essentially a combination of AI and automated high-throughput experimentations, shortening the deployment time by almost 5 times.

[1] https://www.a-star.edu.sg/isce2/key-research-areas/carbon-conversion-and-future-energy-carriers

New ways of building carbon chains - from Fischer Tropsch to new synthetic routes

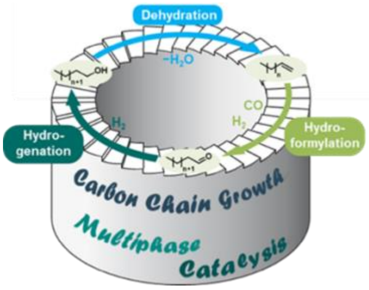
Andreas J. Vorholt
Max-Planck-Institute for chemical energy conversion, Mülheim, Germany
E-mail: andreas-j.vorholt@cec.mpg.de

Keywords: Catalysis, recycling, C1 building blocks

The Fischer-Tropsch process for the conversion of synthesis gas to hydrocarbons is currently estimated to exceed a production volume of about 30 million metric tonnes per year. So far, the Fischer-Tropsch reaction yields a broad spectrum of products from methane to long-chain waxes, paraffins, alcohols and olefins according to an Anderson-Schulz-Flory distribution. This makes Fischer-Tropsch particularly useful for large scale fuel applications but not for the synthesis of single specific compounds.[1-2]

In this work, we present a synthesis route that improves the selectivity of the hydrocarbon formation from synthesis gas and narrows down the product distribution to selective carbon chain lengths. By a combination of hydroformylation, hydrogenation and dehydration reactions, carbon chains can be elongated to specific value products. [3] The cycle can be ended at one of the desired products: olefins, aldehydes or alcohols. A key focus in the development of this system is the catalyst recycling in each of the three steps, making the process more sustainable and reducing waste to a minimum.

A dehydration based on a phosphoric acid catalyst was developed to convert alcohols to the corresponding olefins while recycling the acid catalyst.[4] To convert the resulting mixture of internal olefins, Rh/Biphephos has been applied in the isomerization hydroformylation reaction. The catalyst is recycled via a distillation and the aldehydes are converted in a hydrogenation over a heterogeneous Ru/carbon catalyst. The cycle of these reactions from hexene to decene provide a 27% yield of decenes.



[1] P. M. Maitlis, A. de Klerk, Greener Fischer-Tropsch Processes for Fuels and Feedstock, Wiley-VCH Verlag & Co. KGaA, Weinheim, 2013.
[2] F. Fischer, H. Tropsch, Brennst. Chem. 1923, 4, 276.
[3] P. W. N. M. van Leeuwen, N. D. Clément, M. J. L. Tschan, Coord. Chem. Rev. 2011, 255, 1499–1517.
[4] J. T. Vossen, A. J. Vorholt, W. Leitner, ACS Sustain. Chem. Eng. 2022, 10, 5922–5931.

Genes to GMP: How API manufacture is ’going green’ with engineered enzymes

Stefan Mix
Almac Group, Craigavon, UK/NI
E-mail: stefan.mix@almacgroup.com

Keywords: biocatalysis, enzyme optimization, metagenomics

The “greenness” advantages of biocatalysis over other chemical synthesis technologies are multiple: fewer synthetic steps producing less hazardous waste, higher chemo- and stereo-selectivity requiring reduced target compound purification effort, near-ambient reaction conditions requiring less energy for heating and cooling. Over the past two decades, these trends have mainly played out in a few ‘work horse’ enzyme classes like hydrolase and carbonyl reductase, attributable to abundance, diversity and robustness of these enzymes from natural sources. In contrast, other enzyme classes have been limited in their application scale by prevailing lack of thermal and solvent stability, as well as narrow substrate scope of known and characterised natural enzymes. The maturation of enzyme discovery and engineering technologies over the same period has brought with it new opportunities to mine process stable enzymes from metagenomes, and to address substrate interaction and enzyme stability deficiency via rational enzyme engineering. In turn, new enzyme classes have been added to the manufacturing technology tool kit. While following the question of what makes a good process enzyme, examples presented include recent novel applications of nitrilase, Bayer-Villiger monooxygenases (BVMO), and RNA-ligase enzyme classes [1, 2].

[1] S. Paul, D. Gray, J Caswell, J. Brooks, W. Ye, T. S. Moody, R. Radinov, L. Nechev, ACS Chemical Biology **2023**, 18(10), 2183-2187
[2] M. E. Scott, X. Wang, L. D. Humphreys, M. J. Geier, B. Kannan, J. Chan, G. Brown, D. F. A. R. Dourado, D. Gray, S. Mix, A. Pukin, Organic Process Research & Development **2022**, 26(3), 849-858

Biobased Reversible Photo-Responsive Polymers for Useful Applications

Pallabi Sinha Roy, Karteek Boga, Antonio F. Patti[1], Florent Allais[2], Gil Garnier, John Warner[1,3] and Kei Saito[4]
1. Monash University, Clayton 3800, Victoria, Australia
2. 2. AgroParisTech, Paris,.France 3. The Technology Greenhouse, Wilmington, Massachusetts, USA 4. Kyoto University, Kyoto, Japan
E-mail: tony.patti@monash.edu

Keywords: photo-responsive, polymer

In recent years, photo-responsive polymers have gained significant attention. The chemistry underpinning the behaviour of these materials is based on the [2+2] cycloaddition reaction, whereby reversible unsaturated double bonds are converted to a cyclobutane ring using UV light and the reverse reaction occurs when different higher energy UV light is applied [1]. The light source can be applied to form the polymers in the solid state, thus eliminating the usage of harmful solvents. The reversible material thus formed can be used multiple times only by irradiation using light stimulus. Coumarin and cinnamic acid moieties can be utilized to produce photo-responsive polymers for several value-added applications, such as self-healing, photoresist, liquid crystals and other smart materials.

This poster will feature the high atom economy and green synthesis and application of an α,β--unsaturated ester of p-hydroxycinnamic acid and coumarin modified soybean oil to demonstrate reversible adhesion switching[2,3], as well as other examples where this property can be applied.

1. Kaur, G.; Johnston, P.; Saito, K., Photo-reversible dimerisation reactions and their applications in polymeric systems. *Polymer Chemistry* **2014,** *5* (7), 2171-2186
2.Roy, P.S., Mention, M.M., Patti, A.F., Garnier, G., Allais, F. and Saito, K., 2023. Photo-responsive lignin fragment-based polymers as switchable adhesives. *Polymer Chemistry*, *14*(8), pp.913-924.
3. Boga, K., Patti, A.F., Warner, J.C., Simon, G.P. and Saito, K., 2023. Eco-Friendly Photoreversible Adhesives Derived from Coumarin-Functionalized Epoxy Soybean Oil. *ACS Applied Polymer Materials*, *5*(7), pp.4644-4653.

Ionic liquids technology for polyurethane foam waste depolymerization

Pedro Lozano,[1] Rocio Villa,[1] Rebeca Salas,[1] Francisco Velasco,[1] Maria Macia,[2] Susana Nieto, Belen Altava and Eduardo García-Verdugo[2]

[1] Department of Biochemistry, Faculty of Chemistry, University of Murcia, Spain.
[2] Department of Organic and Inorganic Chemistry, Faculty of Chemistry, University Jaime I, Spain

E-mail: plozanor@um.es

Flexible polyurethane foam (PUF) is one of the most widely produced synthetic polymers, with annual production exceeding 24 million tons, and is commonly used in mattresses, furniture and vehicles. The European association of PUF producers (EUROPUR) reports that 40 million mattresses are discarded yearly in the EU, forming a stack 904 times the height of Mount Everest. Most PUF waste is disposed of via landfilling (45%) or incineration (33%), significantly impacting the environment.[1] As a result of the absence of reuse procedures, a large amount of PUF waste from mattress has been thrown out by simple landfilling with dramatical impact on the environment. The full recycling of PUF waste through circular economy criteria has become an urgent and key environmental task, because of the recalcitrant nature of this plastic. [2,3] The combination of the ionic liquid technology and (bio)catalysis, has been shown as a suitable approach to carry out the easy and green depolymerization of PUF wastes under mild conditions (i.e. <100 ºC, 1bar, 6 h),[4] opposite to the classical glycolysis in reaction media based on a large excess in glycols (e.g. ethylene glycol, glycerol), which occurs under harsh operation conditions (up to 180-250 ºC, and pressures up to 50 bar), and long reaction times.[5] This new technology offers a versatile catalytic platform and enables the easy design and engineering of solutions for PUFW depolymerization and polyol recovery at industrial scale (Figure 1).

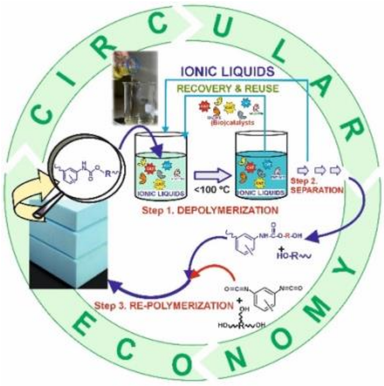


Figure 1. Schematic representation of the depolymerization process of polyurethane foam waste, including recovery and reuse of polyols.

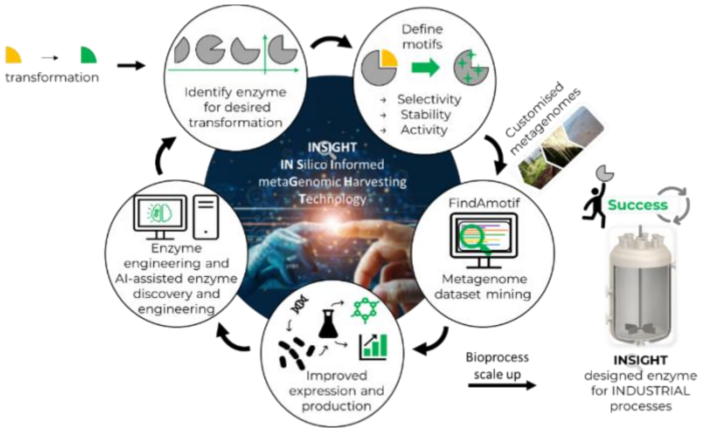
[1] EUROPUR. The End-of-Life of flexible polyurethane foam from mattresses and furniture brochure. **2020**. https://europur.org/flexible-pu-foam/sustainability/
[2] P. Lozano and E. Garcia-Verdugo. *Green Chem*. **2023**, 25, 7041-7057.
[3] F. G. Cirujano, R. Villa, R. Salas, M. Maireles, N. Martin, B. Altava, P. Lozano and E. Garcia-Verdugo. *RSC Sustain*., **2024**, 2, 2781-2804
[4] P. Lozano, R. Villa, R. Salas. E. Garcia-Verdugo, M. Macia. PCT/ES2023/070452. WO 2024/013423 A1. **2024**.
[5] a) G. Rossignolo, G. Malucelli, A. Lorenzetti, *Green Chem*. **2024**, 26, 1132-1152; b) Z. Y. Liu and Y. W. Ma, *ACS Eng. Au* **2024**, 4, 5, 432–449.

IN Silico Informed metaGenomic Harvesting Technology - (INSIGHT) - How a smart platform can accelerate the timelines of genes-to-GMP

Jane Mueller[1], Alexandra T.P. Carvalho[1], Christine Fleming[1], Lyndsey Bannon[1], Aliyu Ibrahim[2], Matthew Boyd[2], Xiangwen Wang[2], Derek Quinn[2], Tom Moody[1,3].
[1]Almac Sciences, 20 Seagoe Industrial Estate, Craigavon BT63 5QD, Northern Ireland, UK;
[2]Queen's University Belfast, University Road, Belfast BT7 1NN, Northern Ireland, UK.
[3]Arran Chemical Company Limited, Unit 1 Monksland Industrial Estate, Athlone, Co. Roscommon, Ireland.
E-mail: jane.mueller@almacgroup.com

Keywords: Biocatalysis, machine learning, enzyme engineering.

Biocatalysis is a key enabling technology towards more sustainable and efficient GMP manufacture of active pharmaceutical ingredients. The processes involved in traditional enzyme selection and screening can be resource heavy and limited to publicly available sequenced genomes. Almac's newly developed INSIGHT platform streamlines enzyme discovery, engineering and development by combining metagenomic and bioinformatic enzyme discovery, high throughput screening, *in silico* enzyme engineering and machine learning.



This poster will showcase a number of selected examples of the benefits of INSIGHT. It will highlight the stages of INSIGHT from the discovery of novel bulky-bulky Carbonyl Reductases (CREDs) from Almac's very own metagenomes with superior properties and take the audience through the accelerated engineering of cosubstrate stability in Transaminases that enabled reaction completion. It will also show examples how machine learning can work hand-in-hand with traditional enzyme engineering and discovery methods to further speed up the process. This accelerated timeline for enzyme discovery and engineering amplifies Biocatalysis as an attractive option for chemical processes even in late stage development, where timelines are short and pressure is high.

Photochemical production of bio-based building blocks as acrylate replacements

T. Freese, J.G. H. Hermens, M. L. Lepage, M. D. Edwards, M. Pratley, K. J. v.d. Berg,
R. V. Gemert, N. Elders, E. Keller, M. W. George, M. Poliakoff, B. L. Feringa

University of Groningen & Circolide, Groningen, Netherlands

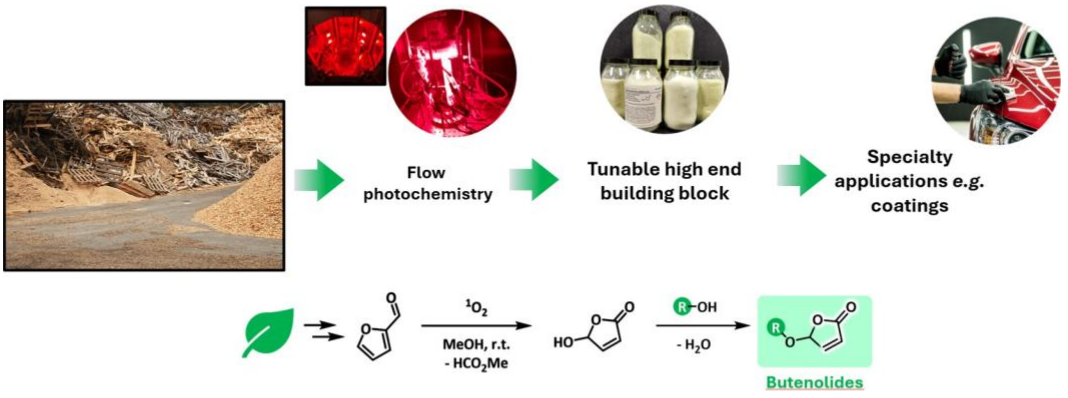
E-mail: t.freese@rug.nl ; t.freese@circolide.com

Keywords: biomass conversion, photochemistry, process intensification

The sustainable production of bio-derived alkoxybutenolide monomers presents a promising alternative to conventional acrylate-based coatings. Here, we report the optimization and scale-up of the synthesis of these monomers, leading to the development of a continuous-flow process with significantly improved efficiency. The first step involves the oxidation of furfural using photogenerated singlet oxygen, followed by a condensation reaction at ambient temperature to produce additional desired monomers.

This approach facilitated the scale-up of photo-oxidation to an 85% isolated yield, with a productivity of 1.3 kg day^{-1} and a space-time yield of 0.06 mol day^{-1} mL^{-1}. Further improvements demonstrated potential productivities of up to 4 to 10 kg day^{-1}.

Building upon these advancements, a startup has been established to further develop and commercialize this scalable synthesis platform for bio-based monomers. This work demonstrates how process intensification and flow chemistry innovations can drive sustainable chemical manufacturing, offering a viable pathway for the industrial adoption of renewable monomers.



[1] J. G. H., Hermens; T. Freese; K. J., van den Berg; R, van Gemert.; B. L. Feringa, *Sci. Adv.* **2020** (6) eabe0026

[2] M. D. Edwards et al., *Org. Process Res. Dev.* **2024** (28), 5, 1917–1928

Inspiring Innovation in Green Chemistry - Startup Support Network KOALA

Dr. Shanika Yadav[a], Dr. Sarah Schulz[a], René Hanke[b], Björn Johnen[b], Prof. Dr. Regina Palkovits[b], Prof. Dr. Walter Leitner[a]

[a]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany;
[b]RWTH Aachen University, Aachen, Germany

E-mail: shanika.yadav@cec.mpg.de; sarah.schulz@cec.mpg.de

Keywords: Research Transfer, Innovation, Network

Many groundbreaking Green Chemistry innovations fail to reach real-world application due to gaps in entrepreneurial training, industry collaboration, and funding. Project KOALA addresses this by providing a structured ecosystem that guides researchers from idea to impact. We encourage and enable researchers to develop their entrepreneurial skills to move beyond the lab, bridging the gap between scientific discovery, innovation, and industry needs. We foster a dynamic network that transcends academic and professional limits, reaching beyond boundaries to create real impact. KOALA also contributes to the Sustainable Development Goals by promoting Green Chemistry solutions that drive sustainable industrial transformations. We understand research trends and align them with industry and societal needs through:

- **Education & Training**: Workshops and mentoring to equip researchers with business and entrepreneurial skills.
- **Strategic Network**: Strong connections with industry leaders, experts, and funding bodies to drive technology transfer.
- **QuinCAT Incubator:** Free lab space and analytics to support innovation.

The QuinCAT incubator at the RWTH Aachen University provides free access to state-of-the-art labs, analytical equipment, and on-site mentoring, thus giving researchers the infrastructure they need to take their innovations further. Startups mentored within the KOALA program include Power2Polymers working on sustainable polymer production, SeCaRa working on plastic recycling, and ANISOTEC generating alternative systems for tissue engineering.

Thus, KOALA empowers early-career researchers with the skills, knowledge, and connections to transform discoveries into real-world solutions. Based in NRW, a key industrial hub, KOALA leverages cutting-edge research and infrastructure to drive a greener future. Through this dynamic and varied network, we are enabling the first steps in applying Green Chemistry principles beyond the lab, thereby creating sustainable economic impact and ensuring that Green Chemistry research benefits both society and the planet.

Crude glycerol – microbial substrate for production of intermediates and recombinant enzymes

M. Kočenda, P. Dobrovodský, Z. Hegyi, M. Rebroš
Institute of Biotechnology, Slovak University of Technology, Slovakia
E-mail: martin.rebros@stuba.sk

Keywords: glycerol, recombinant enzyme, circular bioeconomy

Crude glycerol, the main side product in biodiesel production is being produced at large quantities. There are a lot of native and even recombinant microorganisms, that can utilise it and use it as a carbon source for production of many kinds of products. These includes small platform molecules like 1,3-propanediol, butanol, butyric acid, but also large molecules like enzymes. Especially recombinant enzymes are esencial tools in biorefineries for the valorization of biomass. The combination of side stream valorization and production of added value products, which can be applied in biorefineries, makes this approach very attractive for the sustainable circular bioeconomy.

Acknowledgement:
This work was supported by NextGenerationEU funded project NewZymes contract No. 09I03-03-V04-00537.

Green Catalytic Chemistry for the Energy Transition

Johannes A. Lercher
Catalysis Research Center and School of Natural Science
Technische Universität München, Garching, Germany
E-mail: johannes.lercher@ch.tum.de

The marked decentralization of power harvesting, the storage of the harvested power in fuels and chemicals and the implementation of carbon recycling are the key elements for the energy transition. Catalysis will be the central element in this transition that will be characterized by a gradual evolution of today's petroleum and chemical processes and the necessity to develop conversion strategies that can be economically used at widely varying scale of implementation. Especially for decentralized concepts, Green Chemistry principles, low reaction temperatures and the presence of water will be mandatory for safe and reliable operation.

Realizing such a radical change from centralized specialized complexes, requires a fundamental understanding of the underlying interactions and transformations between catalysts and substrates. In addition to the primary conversion of electric power to hydrogen, hydrogen addition and removal as well as carbon-carbon bond manipulation are the critical elementary steps to reach eventually a carbon-balanced chemical and energy industry.

For both acid-base and metal catalyzed reactions, the lecture will show the links between underlying physicochemical causes for the observed changes in catalytic rates. The impact of water and protic solvents on oxide materials leads to a complex reaction environment in which catalysis takes place at relatively high ionic strength. It will be shown that in the extreme case of ionic liquids, C-C bonds can be manipulated close to ambient temperature and that even macromolecules can be converted to small molecules. Together, the fundamental insight helps enabling new strategies to foster a sustainable future in chemical transformations.

Hotspot Driven Research in Green and Sustainable Chemistry

Philip Jessop
Queen's University, Canada

Green chemistry researchers are motivated to use our research to benefit the environment, reduce harm, and help society become more sustainable. However, not all research projects are equally helpful to the environment. We should prioritize projects that should maximize the benefit. Improving a step, process or product that causes very little harm is not an effective use of the time and resources of a green chemistry lab. In particular, we should focus our efforts on life cycle or societal hotspots. A hotspot is a chemical or process step that causes more harm than the others. If we can identify hotspots, then we can use our energy, creativity, and lab time to find better alternatives. That's much more effective than spending time greening a part of the process that isn't a hotspot.

On the other hand, hotspot-driven research has some counter-intuitive features. For example, it is sometimes more effective to modify a step that is NOT a hotspot – and not by making it greener. Certain steps are indirect hotspots, meaning they cause little harm but they have an outsized influence on the total harm of a process. Bizarrely, it is sometimes better for the environment if we make such a step more harmful!

This presentation will explain direct and indirect hotspots, and describe how research chemists and chemical engineers can use these concepts to prioritize their research projects and maximize the resulting benefit to the environment. Examples will be given from the author's research into CO_2-switchable polymers for greener coatings and adhesives.

Carbon nitride based composites photocatalysts prepared with materials arising from spent Li-batteries for the photoreforming of biomass residues

E.I. García-López[1], N. Aoun[1], G. Marcì[1], G. Itri[2], E. Paone[2], F. Mauriello[2]
[1] *Dipartimento di Ingegneria, Università di Palermo, Italy*
[2] *Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, IT89123 Reggio Calabria, Italy*
elisaisabel.garcialopez@unipa.it

Keywords: Li-spent batteries, waste valorisation; photocatalysis; H_2

There is a justified enhanced interest in sustainable technologies that integrate renewable resources. In this context, the development of processes for the valorisation of spent lithium-ion batteries (s-LIB) is an urgent issue [1]. In the current work innovative materials, as graphitic carbon nitride (g-C_3N_4) enriched with a metal-based co-catalyst obtained from the mixture of anode and cathode powders (black mass (BM)) contained into the spent s-LIBs are prepared. The photoreforming technology is aimed to obtain H_2 from water and simultaneously oxidizing organic molecules to higher added-value substances in the presence of semiconductors as C_3N_4 [2]. Graphitic carbon nitride (g-C_3N_4) possesses optimal characteristics as a photocatalyst even under solar irradiation, and its coupling with various materials as graphene [3] or TiO_2 [4] improve the H_2 productivity by photoreforming. In this research, BM from s-LIB, containing mainly Co, was used pristine or activated and g-C_3N_4 was prepared by calcination of melamine, urea, thiourea or dicyanamide. Various sets of composites were prepared by different strategies to obtain g-C_3N_4/BM photocatalysts with an amount of BM enough to bring to the composite a content of Co in the range 0.5 to 2 % w/w. Additionally, hydrochar (HC) obtained from the hydrothermal combustion of orange peel waste was also used as a co-catalyst. The obtained materials were tested for H_2 production using aqueous solutions of ethanol, glycerol or triethanolamine irradiated with UV or natural solar light. Photoreactivity was performed in the absence or presence of 1% Pt. The best results were obtained with catalysts containing g-C_3N_4 with a 1% of Co from the BM that gave a H_2 productivity of 2.2 mmol h^{-1} g^{-1}. The further calcination of the composite doubled the H_2 productivity.

[1] E. Paone, M. Miceli, et al., ACS Sustain. Chem. Eng. 2022, 10 (7), 2275-2281.
[2] E.I. García-López, L. Palmisano, G. Marcì, ChemEng. 2023, 7, 11
[3] E.I. García-López, P. Lo Meo, A. Di Vincenzo, L. Palmisano, G. Marcì, Catal. Today 2023, 413-415, 113965
[4] E.I. García-López, A. Genco, V. Lagostina, M.C. Paganini, G. Marcì, Catal. Today 2023, 423, 114283.

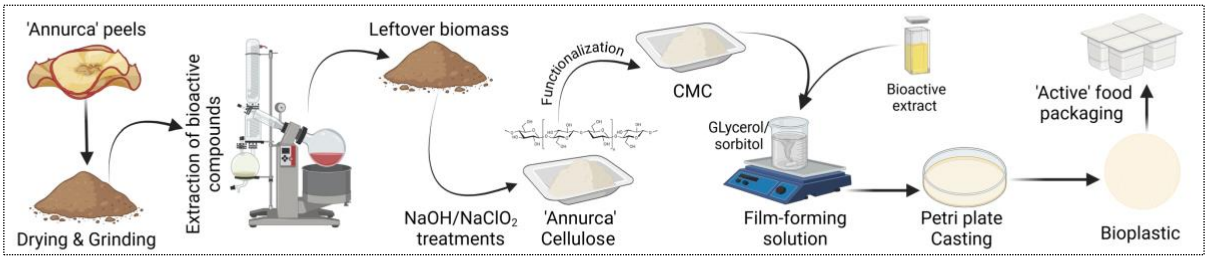
Bioplastics from ‘Annurca’ apple cellulose doped with polyphenolic compounds for ‘active’ food packaging applications

S. A. Qamar*****, A. Basharat, H. Mushtaq, S. Piccolella, S. Pacifico
DiSTABiF, University of Campania ‘Luigi Vanvitelli’, Via Vivaldi 43, 81100 Caserta, Italy.

E-mail: sarmad.qamar@unicampania.it

Keywords: Circular economy, Biodegradable materials, Waste valorisation.

The circular manufacturing of biodegradable and bioactive materials using agri-food byproducts is being promoted in bio-sector applications [1]. Herein, the use of ‘Annurca’ apple waste is considered for the first time to introduce cellulose-based films incorporated with polyphenolic compounds to improve bioactive functionality. The current strategy demonstrates ultrasound-assisted ethanolic extraction of bioactive compounds followed by the recovery of high-purity crystalline cellulose from leftover biomass. The conversion of ‘Annurca’ cellulose into carboxymethyl cellulose (CMC) was conducted and processed for the development of films using casting technique. For this purpose, a combination of plasticizer (both glycerol and sorbitol, with 30% (*w/w*) individual contents) was used. Different concentrations of ‘Annurca’ polyphenolic extract were used in the casting solution to improve the functional properties of resulting films. The films were analysed using different advanced instrumental techniques including FTIR, SEM/EDX, XRD, TGA/DSC, and mechanical analysis. The fabricated films showed reduced moisture content, solubility, and water vapor transmission rate (WVTR). Morphological analyses indicated crystalline nature of cellulose and resulting carboxymethyl cellulose (CMC), while the produced films were significantly transparent and smooth with a uniform distribution of polyphenolic compounds. FTIR findings further supported that extract was well dispersed in ‘Annurca’ CMC matrix, and no chemical reactions occurred during the film preparation. Further, the excellent biodegradability with high antioxidant and antimicrobial potentialities makes the films suitable for food packaging applications.



[1] M. Asgher, S.A. Qamar, M. Bilal, H.M. Iqbal. *Food Res. Int.* **2020**, 137, 109625.

Measuring nuclear spin dynamics in sustainable engineering systems

Neil Robinson
School of Chemistry and Chemical Engineering, Queen's University Belfast

E-mail: n.robinson@qub.ac.uk

Keywords: NMR; nuclear spin relaxation; porous materials; adsorption

While solid–fluid interactions underpin the efficacy of functional porous materials across a diverse array of chemical reaction and separation processes of direct relevance to UN Sustainable Development Goal 7, detailed characterisation of interfacial phenomena within such systems is often hampered by their optically opaque nature. Motivated by the need to bridge this capability gap, this talk will provide an introductory overview of the recent applications of low-field NMR relaxation measurements to such problems. Such measurements provide a versatile, non-invasive and chemically selective approach with which to characterise fluid interactions within porous solids, and may be implemented under operando pressure and temperature conditions of direct relevance to industrial chemical processes. Such measurements have been employed by the rock physics and hydrocarbon recovery community for over five decades, but their application to well-defined functional porous materials of relevance to sustainable chemical and engineering practices has been comparatively limited. Correspondingly, this talk will highlight recent applications of NMR relaxation to materials of relevance to catalysis, gas process engineering and construction.

[1] N. Robinson, C. Robertson, L. F. Gladden, S. J. Jenkins, C. D'Agostino, *ChemPhysChem* **2018**, 19 (19), 2472. https://doi.org/10.1002/cphc.201800513
[2] N. Robinson, E. F. May M. L. Johns, *ACS Appl. Mater. Interfaces* **2021**, 13 (45), 54476. https://doi.org/10.1021/acsami.1c13934
[3] S. Dong, L. Liu, N. N. A. Ling, E. F. May, M. L. Johns and N. Robinson, *Langmuir* **2024**, 40 (31), 16160. https://doi.org/10.1021/acs.langmuir.4c01245
[4] N. Robinson, R. Nasharuddin, E. O. Fridjonsson and M. L. Johns, *Phys. Rev. Lett.* **2023**, 130, 126204. https://doi.org/10.1103/PhysRevLett.130.126204

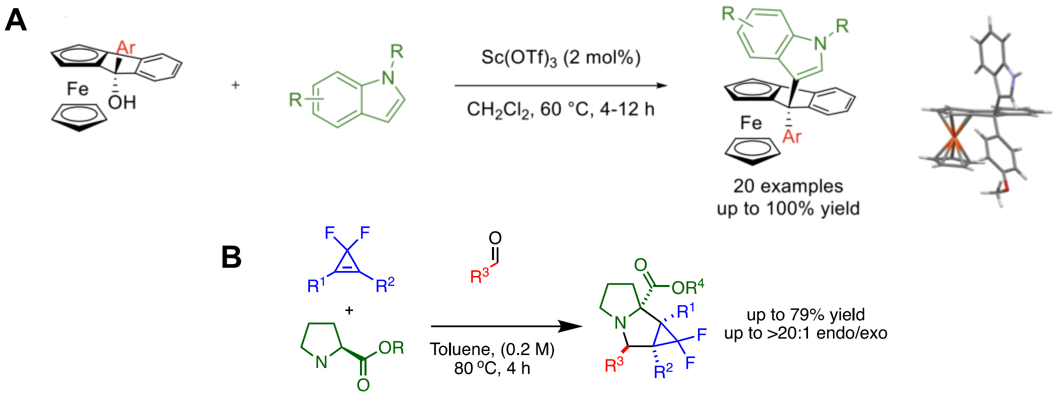
Recent Developments in Asymmetric Synthesis and Catalysis

Professor Pat Guiry
UCD School of Chemistry, University College Dublin, Ireland

E-mail: p.guiry@ucd.ie

Keywords: Ferrocene-containing Tetraarylmethanes; Enantioselective [3+2] Cycloadditions.

Gomberg reported the first synthesis of a tetraarylmethane (TAM),[1] but it was not until 2020 that the first enantioselective synthesis of chiral TAMs was reported by Sun.[2,3] Despite these significant advances, this area of asymmetric synthesis is still in its infancy. This presentation describes the first asymmetric synthesis of enantiopure α-ferrocenyl TAMs in up to 100% yield, with the absolute configuration confirmed using X-ray crystallography (Scheme 1 (A)). Azabicyclo[3.1.0]hexanes have emerged as promising bioisosteres for the replacement of pyridine and piperidine rings.[4,5] We will also describe our work on the first metal-catalysed enantioselective (3+2) cycloaddition of azomethine ylides and difluorocyclopropenes to give the corresponding densely functionalised fluorinated azabicyclo[3.1.0]hexanes in excellent yields, diastereoselectivities and enantioselectivities (Scheme 1 (B)).



Scheme 1.

[1] M. Gomberg, *Ber. Dtsch. Chem. Ges.* **1897**, *30* (2), 2043–2047.
[2)] X. Li, M. Duan, Z. Deng, Q. Shao, M. Chen, G. Zhu, K. N. Houk, J. Sun, J. *Nat. Catal.* **2020**, *3* (12), 1010–1019.
[3] X. Tan, Z. Deng, Q. Wang, S. Chen, G. Zhu, J. Sun, *Nat. Synth.* **2023**, *2* (3), 275–285.
[4] Y. Li, J. Feng, F. Huang, J. Baell, *Chem. Eur. J.* **2023,** *29* (48), e202301017.
[5] Y. Yuan, Z.-J. Zheng, F. Ye, J. H. Ma, Z. Xu, X. F. Bai, L. Li, L.-W. Xu, *Org. Chem. Front.* **2018**, *5*, 2759–2764**.**

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

Keywords: Catalyst design, Circular carbon, Green chemistry

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.[1] 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 CO_2 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.

[1] S. Mitchell, A.J. Martín, J. Pérez-Ramírez, *Nat. Chem. Eng.* **2024**, 1, 13-15.

Poster Presentations

Table of Poster Presentations

P1	A. Crowley	Where do I begin? Introducing Sustainable Practices to a Third Level Science Department
P2	A. Matei	Anti-Markovnikov Functionalisation of Olefins
P3	A. Jensma	Waterborne polymers and coatings from biobased butenolides
P4	A. Duggan	Interlaboratory Replicability of Flow Battery Cell Testing
P5	A. Windisch	Continuous Reductive Hydroformylation in Segmented Slug Flow Using a Single Catalyst Enabled via CO-Degassing
P6	B. J. Murray	Hydrophobic deep eutectic solvents for the recovery of gallium
P7	B. Hopkins	Closed-Loop Recycling of PET in Supercritical Carbon Dioxide
P8	C. Duffy Heath	The Lough Neagh Emergency: Development of New Hydrogen Peroxide based Treatments for Cyanobacterial Blooms and Toxins
P9	D. Goma-Jiménez	Selective CeO2-Based Materials with Controlled Morphology Doped with Zn, Zr and Ca for Glycerol Carbonation: Effect of Morphology and Surface Modifiers
P10	D. Molloy	Non-Thermal Plasma For The Degradation of Aqueous Microplastics
P11	E.I. García-López	Optimisation of 5-hydroxy methyfurfural (5-HMF) production from biomass through heterogeneous catalysis
P12	E. Rooney	Understanding the Applications of Mechanochemistry for Pharmaceutical and Agrochemical Synthesis
P13	E. B. McCrea	Advancing chemical recycling of polyethylene terephthalate (PET) using ionic liquids
P14	F. Zafar	CO2 hydrogenation on hollow tube MIL-68(FeIn)-catalysts for enhanced methanol production
P14	G. Saini	Direct Synthesis of Polyesterether from Ethylene glycol
P15	G. Irvine	Highly Entangled Hydrogels by Photoiniferter-Mediated Polymerization
P16	G. Cadman	Poly- substitution of polyfluoroarenes by SNAr mediated by KHMDS generated acetylides
P17	H. O. LeClerc	The CO_2 Tree: The Potential for Carbon Dioxide Utilization Pathways
P18	J. Luk	Exploiting decarbonylation and dehydrogenation of formamides for the synthesis of ureas, polyureas and polyureaurethanes
P19	J. T. Meijer	Functionalization of the butenolide scaffold – Towards responsive polymers and coatings
P20	J. Streets	Sustainable Paired Electrooxidation Using Recyclable Multifunctional Ionic Liquids
P21	J.J. Villora-Pico	Enhanced CO_2 Hydrogenation to Hydrocarbons via SIL-Modified Fe-Ru/Al_2O_3 Catalysts: Tailoring Activity and Selectivity Through Support Engineering
P22	J. Sinclair Janko	Catalytic Depolymerisation of Polyurethanes
P23	J. Liu	Lignin Oxidative Depolymerization on Graphitic Carbon Nitride - Explore the Cleavage of β-5 Linkage
P24	K. Hanek	The alliance of mechanochemistry and environment. Solvent-free protocol for β-sulfenylated compounds.
P25	K. Ralphs	Mechanochemically prepared photocatalysts
P26	K. E. Savage	Identifying the Catalytic Species in Indium Ionic Liquids for Sustainable Alkylation

P27	K. Al-Essa	Graphitic Carbon Nitride/CeO2 Nanocomposite for Photocatalytic Degradation of Methyl Red
P28	M. Fitzsimons	Sustainable Porous Liquids (SUPLI)
P29	M. Zanatta	Direct air capture and CO_2 transformation into added-value chemicals
P30	M. Kočenda	Recombinant xylanolytic enzymes production by Komagataella phaffii and their application in biorefineries
P31	M. C. O'Donnell	Recycling Lithium-ion Batteries using Dielectrophoretic Filtration
P32	M. A. Goss	Renewable Molecules of Relevance to Agriculture from Biomass Sources
P33	M. Sweeney	Ionic liquids for CO_2 capture from high temperature technical gas streams
P34	N. Garland	Designing Polysaccharide-Derived Mesoporous Carbon Materials (Starbon) for Selective Metal Recovery
P35	N. S. Anjos	Synthesis, Characterisation and Application of Polystyrene-supported BrØnsted-Acidic Ionic Liquid as an Efficient and Reusable Catalyst for Groebke-Blackburn-Bienaymé Multicomponent Reaction
P36	N. Bahari	The Effects of Salinity on Exo-polysaccharides Productivity Towards Algal Bioplastics
P37	P. Inrirai	Mechanochemically Engineered CaO-CeO_2 Catalysts for Solvent-Free Synthesis of Glycerol Carbonate
P38	P. A. Bailie	Seaweed Bioactives Supplemented Animal Feeds. Green Chemistry Methods of Seaweed Extraction
P39	E. M. Zahidi	Mechanistic Study of Chirality Transfer on a Catalyst Surface
P40	P. McNeice	Enzyme-Inspired Gel Materials: Tuneable, Bio-Based Gels for Catalysis
P41	R. Salotra	Extraction and Characterisation of Seaweed Polyphenols
P42	S. Gholami	Selective extraction of platinum group metals utilising novel non-ionic hydrophobic (deep) eutectic solvents
P43	S.U. Khan	Electrochemical dicarboxylation of 1,3-butadiene with CO_2 to 3-hexenedioic acid with non-sacrificial anode
P44	T. S. Lambert	Producing Monomers for Sustainable Coatings Using Photochemistry – Utilising Reactor Design and Process Analytical Chemistry for Scale-up
P45	V. Ganthimeri	Flow Biocatalysis: Application of Monolithic Porous Open Tubular Capillary Reactors
P46	J. W. Medlin	Understanding aldol condensation kinetics in complex feed streams

Where do I begin? Introducing Sustainable Practices to a Third Level Science Department

A. Crowley, J. O'Keefe, & P. Conroy
Atlantic Technological University, Galway, Ireland
E-mail: aisling.crowley@atu.ie

Keywords: Sustainability, Higher Education, Interdisciplinary

As part of the Climate Action Plan, Irish Higher Education Institutes (HEIs) are tasked with leading by example and reducing emissions by 51% by 2030[1]. HEIs are also committed to embedding and advancing the United Nations Sustainable Development Goals (SDGs) in their teaching, research, and campus operations[2].

However, making practical changes to meet these goals, especially within the sciences, can feel overwhelming. Laboratories are known to consume 5 to 10 times more energy and 4 times as much water as office spaces, and they generate up to 40% of the waste produced by universities[3].

This poster will document the journey of an interdisciplinary grassroots group of academics and technical staff at Atlantic Technological University, Galway, who have undertaken the monumental task of introducing and advancing sustainable practices within the School of Science & Computing. It will discuss the initial formation and subsequent formalization of the group, international certification, student engagement, local initiatives, limitations, and prospects, with the goal of educating and inspiring others who may not know where to begin.

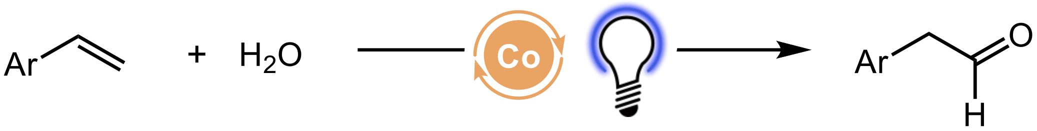
1. Irish Universities Association. (2024). *Climate Action Roadmap Delivery: Delivering on our 2030 Carbon Emission Targets*.
2. Department of the Environment, Climate and Communications (2023) *Ireland is Performing Well in Achieving the Sustainable Development Goals*. Available from: https://www.gov.ie/en/press-release/adcb3-ireland-is-performing-well-in-achieving-the-sustainable-development-goals/#education
3. Royal Society of Chemistry (2022) *Sustainable Laboratories: A Community-Wide Movement Towards Sustainable Laboratory Practices.*

Anti-Markovnikov Functionalisation of Olefins

Alexandra Matei, Sebastian B. Beil, Ben L. Feringa
University of Groningen, Stratingh Institute for Chemistry, Groningen, The Netherlands

E-mail: m.a.matei@rug.nl

Keywords: anti-Markovnikov, oxidations, photochemistry



Classical oxidations of terminal olefins generally follow Markovnikov selectivity, producing ketones. However, anti-Markovnikov oxidations of terminal alkenes are interesting for organic chemists, as they give direct access to aldehydes, which are versatile building blocks in numerous organic synthetic applications. While several Pd-catalysed methodologies for the regioselective oxidation of alkenes have been developed, the number of more sustainable direct oxidative protocols is limited.[1]-[5] A combination of metal-redox catalysis and photochemistry to achieve anti-Markovnikov oxidations of alkenes into aldehydes would present a highly desirable and sustainable alternative towards synthesising this important class of chemical intermediates. This project focuses on the development of new methodologies taking advantage of highly active catalysts to avoid the stoichiometric use of oxidants in order to achieve direct anti-Markovnikov oxidation of ideally unactivated terminal alkenes.

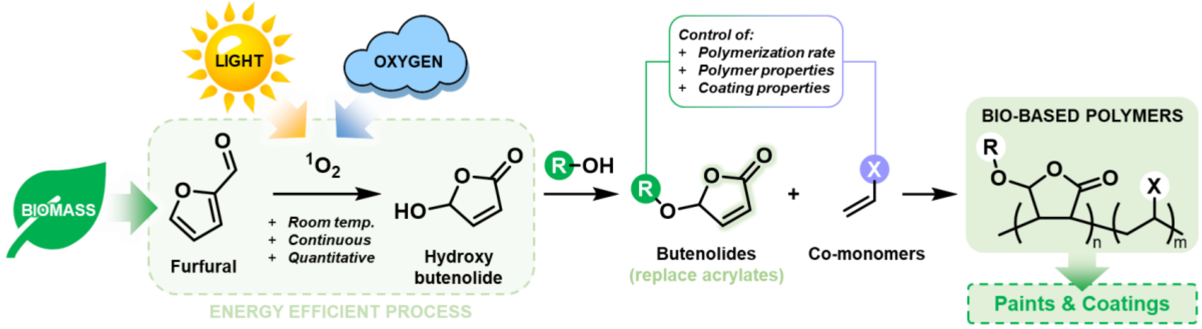
[1] B. Weiner, A. Baeza, T. Jerphagnon, B. L. Feringa, *J. Am. Chem. Soc.* **2009**, *131*, 9473–9474.
[2] Z. K. Wickens, B. Morandi, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2013**, *52*, 11257–11260.
[3] J. J. Dong, E. C Harvey, M. Fañanás-Mastral, W. R. Browne, B. L. Feringa, *J. Am. Chem. Soc.* **2014**, *136*, 17302–17307.
[4] Q. Huang, Y.-W. Li, X.-S. Ning, G.-Q. Jiang, X.-W. Zhang, J.-P. Qu, Y.-B. Kang, *Org. Lett.* **2020**, *22*, 965–969.
[5] G. Zhang, X. Hu, C.-W. Chiang, H. Yi, P. Pei, A. K. Singh, A. Lei, *J. Am. Chem. Soc.* **2016**, *138*, 12037–12040.

Waterborne polymers and coatings from biobased butenolides

A. Jensma, N. Elders, K.J. Van den Berg, B.L. Feringa
University of Groningen, Groningen, The Netherlands
E-mail: a.jensma@rug.nl

Keywords: biobased, polymers, coatings

In the ongoing energy, materials and feedstock transition, the development of sustainable resins, polymers and coatings with high percentages of biobased content is a highly desirable goal. Our group has shown that biobased butenolides are promising monomers for the paints and coatings industry.[1] The synthesis of this class of biobased monomers starts from the platform chemical furfural, which is derived from hemicellulosic biomass. Photo-oxidation of furfural with singlet oxygen affords hydroxy butenolide, with minimal waste in matter and energy. This efficient process can be performed both in batch and flow setups.[2] Hydroxy butenolide can be further derivatized through its acetal moiety, for instance by condensation with a variety of (potentially bio-based) alcohols. These substituted butenolides can be co-polymerized with electron-rich vinyl co-monomers, such as vinyl ethers, vinyl esters and vinyl lactams, under solventborne conditions. Here, we show the first step towards aqueous poly-butenolide dispersions using high molecular weight polyurethanes as colloidal stabilizing moiety.[3]



[1] J.G.H. Hermens, T. Freese, K.J. Van den Berg, R. Van Gemert, B.L. Feringa, *Sci. Adv.*, **2020**, 6, eabe0026.
[2] M.D. Edwards, M.T. Pratley, C.M. Gordon, R.I. Teixeira, H. Ali, I. Mahmood, R. Lester, A. Love, J.G.H. Hermens, T. Freese, B.L. Feringa, M. Poliakoff, M.W. George, *Org. Process. Res. Dev.*, **2024**, 28(5), 1917-1928.
[3] A. Jensma, N. Elders, K.J. Van den Berg, B.L. Feringa, *Green Chem.*, **2024**, 26, 9676-9681.

Interlaboratory Replicability of Flow Battery Cell Testing

Hugh O'Connor, Alexander Quinn, Fikile Brushett, Peter Nockemann, Josh Bailey, Aodhán Dugan
QUB, Belfast, Ireland

E-mail: adugan02@qub.ac.uk

Keywords: Flow batteries, renewable energy, storage

Flow batteries are emerging as a promising technology for long-duration energy storage. However, the lack of standardized cell designs and testing protocols makes it difficult to fairly compare different systems. Additionally, research on related but more established electrochemical technologies has revealed issues with transparency in methodology, as well as a failure to measure or report uncertainties. Comparing electrochemical flow cells across studies while accounting for variance can lead to more reliable conclusions than relying on single-point measurements. Therefore, studies that focus on quantifying variance in flow cell performance can help establish standards, protocols, and best practices. In this work, we define "replicability" as the variance observed in inter-team measurements conducted on the same system by different researchers. These participants followed the same instructions but had minimal interaction during data collection. To investigate interlaboratory replicability in flow cell performance, eight research groups from seven institutions collaborated to collect and analyze polarization, impedance, and charge-discharge cycling data. Each group used an identical flow cell in a symmetric configuration with a near-neutral pH ferri/ferrocyanide-based electrolyte. To guide the experimental design, participants were first surveyed about their available equipment. Based on these responses, a standardized experimental request was developed and shared, clearly specifying the cell setup while intentionally leaving certain aspects of the experiments flexible. This allowed researchers to incorporate elements of their typical experimental and analytical approaches. After data collection, a follow-up survey was conducted to capture variations in experimental practices and decision-making during analysis. Finally, anonymized data were processed by two independent researchers to assess variance across the datasets.

Continuous Reductive Hydroformylation in Segmented Slug Flow Using a Single Catalyst Enabled via CO-Degassing

A. Windisch, P. Pey, D. Vogt, T. Seidensticker
TU Dortmund University, Laboratory of Industrial Chemistry, Dortmund, Germany
E-mail: arno.windisch@tu-dortmund.de

Keywords: Flow Chemistry, Reductive Hydroformylation, Tandem Catalysis

Tandem catalytic systems offer significant advantages in energy and material efficiency by enabling multiple reaction steps within a single process. Assisted tandem catalytic systems enhance performance by allowing tailored conditions for each step, but continuous operation remains challenging.[1] Capillary flow reactors present a promising solution, offering a platform to investigate and fine-tune reaction conditions while maintaining a continuous process.

As a case study, we explored reductive hydroformylation, where CO required for hydroformylation inhibits subsequent aldehyde reduction.[2] We therefore developed a degassing unit to continuously remove CO between the reaction steps, allowing catalyst switching and optimized conditions, significantly boosting overall process efficiency in continuous operation.

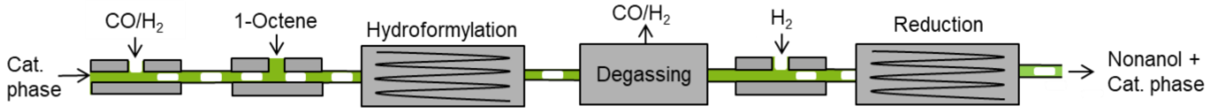


Figure 1: Schematic illustration of the continuous flow set-up.

Using this approach, the reductive hydroformylation of 1-octene was successfully realised, which marked the first continuous system with integrated CO removal, achieving an overall alcohol yield of 83% and a linear-to-branched ratio above 10. The aldehyde reduction alone showed 98% selectivity to alcohols.

Although small-scale and unoptimized, these results demonstrate feasibility at lower temperatures and pressures than industrial processes. The method is less material- and energy-intensive and highlights the switchability of the catalyst between hydroformylation and reduction, enhancing its sustainability and versatility.

[1] D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.*, **2004**, 248, 2365–2379

[2] O. Diebolt, C. Müller, D. Vogt, *Catal. Sci. Technol.*, **2012**, 2, 773–777

Hydrophobic deep eutectic solvents for the recovery of gallium

B. J. Murray, E.L. Byrne, J.D. Holbrey and M. Swadźba-Kwaśny
The QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University Belfast, UK

E-mail: bmurray22@qub.ac.uk

Keywords: gallium extraction, deep eutectic solvents (DESs), metals

Global demand for gallium has surged over the past two decades due to its use in electronic devices. Supply challenges arise from the lack of gallium ore, as it is mainly recovered as a secondary element from aluminium mine tailings, with potential recovery from zinc tailings.[1] Currently, geopolitical factors threaten supply for UK and EU, with China providing 80% of global gallium.[2] This work focuses on the separation of gallium from the zinc manufacturing industry, specifically from zinc leachate solution. This route of recovery is of great interest, on account of Europe's zinc mining industry.[3] Our strategy relies on the use of hydrophobic deep eutectics solvents (DESs) as cost effective, bifunctional solvents for the extraction of gallium. We have developed a family of DESs based on trioctylphosphine oxide (TOPO), which is already used as a metal extractant in the industry, benefitting from long alkyl chains which promote hydrophobicity.[4] TOPO has been combined with a selection of benign and inexpensive small organic molecules, that can act as cooperative complexing agents and/or reducing agents. These mixtures have been effective for the extraction of gallium from a simulated zinc leachate solution, where small (36 ppm) quantities of gallium are present, accompanied by very large quantities of other metals.[5] No mineral acids or hazardous solvents are needed for the process.

[1] F. Lu, T. Xiao, J. Lin, Z. Ning, Q. Long, L. Xiao, F. Huang, W. Wang, Q. Xiao, X. Lan and H. Chen, *Hydrometallurgy*, **2017**, 174, 105-115.

[2] E. Commission, *Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability,* **2020**, EU Brussels

[3] E. L. Byrne, R. O'Donnell, M. Gilmore, N. Artioli, J. D. Holbrey and M. Swadźba-Kwaśny,, *Phys. Chem. Chem. Phys.*, **2020**, 22, 24744-24763

[4] M. Gilmore, L. M. Moura, A. H. Turner, M. Swadźba-Kwaśny, S. K. Callear, J. A. McCune, O. A. Scherman and J. D. Holbrey, *J. Chem. Phys.*, **2018**, 148, 193823

[5] T. Kinoshita, Y. Ishigaki, N. Shibata, K. Yamaguchi, S. Akita, S. Kitagawa, H. Kondou and S. Nii, *Sep. Purif. Technol.,* **2011**, 78, 181-188.

Closed-Loop Recycling of PET in Supercritical Carbon Dioxide

B. Hopkins, D.J. Keddie, D. Irvine and S.M. Howdle
University of Nottingham, United Kingdom

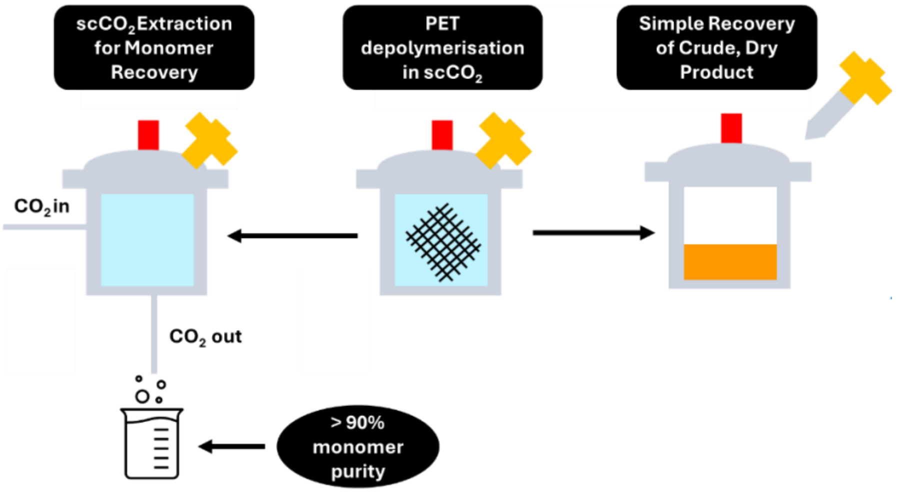
E-mail: pazbh@nottingham.ac.uk

Keywords: $scCO_2$, plastics, recycling

Polyethylene terephthalate (PET) is a widely used plastic material, commonly for water bottle production, with 70 million tonnes produced annually.[1] Closed-loop recycling describes approaches designed to degrade polymers to their monomers by chemical reaction. Utilising plastic waste as a feedstock for monomers enables manufacture of new plastics of equal quality to the original material.[2]

Monomers have been successfully produced through a range of closed-loop strategies, but obstacles remain. Large volumes of solvent are required to drive the depolymerisation to completion, as well as to recover monomers. This is a key issue for closed-loop recycling, which has now been discussed beyond academic literature.[3]

Supercritical carbon dioxide ($scCO_2$) is well documented as a green solvent. The simple removal of $scCO_2$ from a reaction through pressure reduction, going back to CO_2 gas, opens a route for easy solvent recycling. This work will present a novel closed-loop recycling strategy capable of degrading PET to monomers in short reaction times with minimal solvent waste.



1. H. Liu, Z. Wang, Y. He, X. Hu and L. Liu, *Applied Catalysis B: Environment and Energy*, 2025, **361**, 124667.
2. R. A. Sheldon and M. Norton, *Green Chemistry*, 2020, **22**, 6310-6322.
3. c&en, https://cen.acs.org/environment/recycling/Chemical-recycling-wont-fix-plastic/101/web/2023/11, (accessed 18th November, 2024).

The Lough Neagh Emergency: Development of New Hydrogen Peroxide based Treatments for Cyanobacterial Blooms and Toxins

Caitlin Duffy Heath, Jaimie T. A. Dick, Peter K. J. Robertson and Andrew C. Marr.
Queen's University Belfast, Belfast, United Kingdom

E-mail: Cduffyheath01@qub.ac.uk

Keywords: water treatment, catalytic oxidation, cyanotoxins.

A combination of previous invasion, increased eutrophication and increased water temperatures have accelerated the growth of toxic cyanobacteria, also known as blue-green algae. Their decomposition produces cyanotoxins, which threaten the water supply and wildlife at Lough Neagh [1, 2]. Sixty percent of Belfast's and forty percent of Northern Ireland's water comes from Lough Neagh. Destruction of these cyanotoxins is difficult. Without the proper procedures in place to ensure removal of these cyanotoxins before the water reaches our tap, our access to clean water is under serious threat.

Hydrogen Peroxide (H_2O_2) is an effective treatment widely used for water purification in the Netherlands[3]. H_2O_2 decomposes to water and oxygen. Conventional peroxide treatment is expensive and requires large volumes of peroxide, making it impractical for large bodies of water like Lough Neagh. A solution is to utilise catalysts which enhance peroxide effectiveness, producing similar or improved results with lower peroxide concentrations. TAML catalysts are biomimetic catalysts that resemble the active site of peroxidases. These catalysts are used in ultra-dilute concentrations and are composed of solely biochemical elements, which enhances their environmental compatibility. TAMLs significantly increase the effect of H_2O_2, allowing larger volumes of water to be treated with small amounts of 'supercharged' peroxide. Recent studies have shown the effectiveness of Fe-TAML/H_2O_2 systems for water purification, and the removal of cyanotoxins and difficult pollutants. New Fe^{III}-TAML/H_2O_2 has been proven to completely degrade microcystin-LR in 3 minutes.

This project aims to investigate methods to catalytically supercharge peroxide treatment, focusing on optimising the Fe-TAML/H_2O_2 system to destroy cyanobacteria and cyanotoxins. Ecotoxicological analysis will be performed in parallel to understand the green design of this treatment, providing invaluable information on how this method should be used to treat badly impacted areas of the Lough.

(1) BBC. Learning toxic algae lessons for Lough Neagh from across the pond. **2023**.
(2) Huisman, J.; Codd, G. A.; Paerl, H. W.; Ibelings, B. W.; Verspagen, J. M.; Visser, P. M. Cyanobacterial blooms. *Nature Reviews Microbiology* **2018**, *16* (8), 471-483.
(3) Sector, D. W. Chemical input -free advanced oxidation for water treatment. **2021**.

Selective CeO_2-Based Materials with Controlled Morphology Doped with Zn, Zr and Ca for Glycerol Carbonation: Effect of Morphology and Surface Modifiers

D. Goma-Jiménez[1*], P. Inrirai[1], H. Manyar[1]
[1]*School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmills Road, Belfast BT9 5AG, UK.*

[*]E-mail: d.gomajimenez@qub.ac.uk

Keywords: *Glycerol carbonate, Shape-controlled CeO_2 nanomaterials, Net Zero fuels*

The large-scale production of biodiesel generates glycerol as major byproduct, necessitating innovative valorisation strategies for the success of bio-refinery concept. One promising approach is to upgrade glycerol to glycerol carbonate, using CO_2 as carbonating agent. Glycerol carbonate is a high-value platform chemical with several applications such as green solvent, pharmaceuticals, and as high-energy density fuel additive, aligning with circular economy principles by enabling CO_2 utilization, waste reduction and improving overall economy of biorefineries.

CeO_2-based catalysts play a crucial role in this reaction, leveraging their redox properties, oxygen vacancies, and amphoteric nature with tuneable acid-base properties to facilitate CO_2 activation and glycerol conversion. Doping with ZnO, ZrO_2, and CaO further optimize the acidity-basicity balance, improving catalytic performance. However, the electronic interactions between the support and active phase remain insufficiently understood. This study explores the impact of CeO_2 morphology and support-active phase interactions in ZnO, ZrO_2, and CaO modified systems. Catalysts (20 mol% dopants) were synthesized on CeO_2 nanorods and nanocubes via hydrothermal methods and characterized using XRD, TGA, N_2 adsorption, FTIR, SEM, EDX, H_2-TPR, CO_2-TPD, and NH_3-TPD analyses. Catalytic tests were performed in high-pressure autoclave (30 bar CO_2, 170°C, 24 h) using DMF as solvent and 2-cyanopyridine as dehydrating agent. All tested materials exhibited good activity in direct carbonation of glycerol. However, while glycerol conversion remained largely unaffected by CeO_2 support morphology, both nanocubes and nanorods achieving similar glycerol conversion rates, selectivity to glycerol carbonate was influenced by support type, with CeO_2 nanorods yielding higher glycerol carbonate production. The effect of the supported oxide as a promoter was more pronounced on CeO_2 nanorods, with ZnCe-r showing the highest performance. This suggests that electronic interactions enhance CO_2 capture and promote its conversion with glycerol into glycerol carbonate.

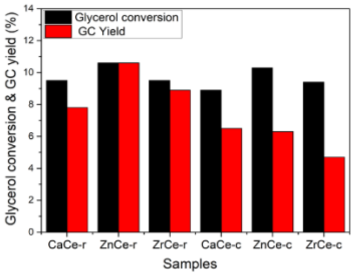


Figure 1: Glycerol conversion and glycerol carbonate yield after 24 hours at 170ºC for Ca-, Zn-, and Zr- supported CeO_2 nanorods (-r) and nanocubes (-c) into glycerol carbonate.

Non-Thermal Plasma For The Degradation of Aqueous Microplastics

Daniel Molloy, Róisín Cellarius, Chunfei Wu, James A Sullivan
UCD, Dublin, Ireland

E-mail: Daniel.molloy3@ucdconnect.ie

Keywords: Non-Thermal Plasma, Microplastic Degradation

Microplastic pollution is an escalating global environmental issue, with particles pervasive across aquatic ecosystems posing significant health and ecological risks. Studies indicate that microplastics can accumulate in organs, potentially leading to toxic effects.[1] Their small size also makes them difficult to remove using conventional filtration or wastewater treatment methods. This research Measures the effectiveness of using non-thermal plasma (NTP) technology in degrading microplastics in water, focusing on the common polymers polystyrene (PS) and polymethylmethacrylate (PMMA), by breaking down these plastics into smaller, fragments, or mineralizing them. NTP is a promising technology for environmental remediation due to its ability to generate reactive oxygen species (e.g., OH• and O•) under ambient temperature and pressure conditions. These species have previously been shown to degrade a wide range of pollutants,[2] without the need for added chemicals or excessive energy input. The experimental setup consists of a point-to-plate dielectric barrier discharge (DBD) in contact with 5 mL suspensions of microplastic particles of polystyrene (PS; 2.5 µm diameter) and polymethylmethacrylate (PMMA; 0.917 µm diameter) for different lengths of time. The suspensions were subjected to optical microscopy, SEM, and DLS, to assess morphological and particle size changes, and FTIR to identify changes in surface functional groups.

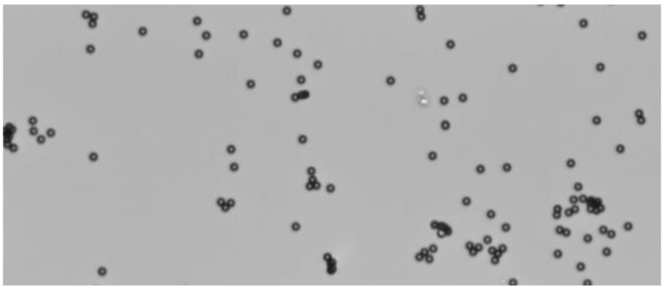


Fig. 1 Optical Microscope image of Polystyrene Microparticles before plasma treatment

[1] Chunhui Wang, Jian Zhao, Baoshan Xing, Environmental source, fate, and toxicity of microplastics, Journal of Hazardous Materials 2021, Volume 407
[2] He Y, Sang W, Lu W, Zhang W, Zhan C, Jia D. Recent advances of emerging organic pollutants degradation in environment by non-thermal plasma technology: A Review. Water. 2022 Apr 21;14(9):1351.

Optimisation of 5-hydroxy methyfurfural (5-HMF) production from biomass through heterogeneous catalysis

E.I. García-López[1], S. Lima[2], A. Marchese[2], A. Cosenza[2], G. Caputo[2],
G. Marcì[2], F. Scargiali[2]
[1]Dipartimento STEBICEF, Università di Palermo, Palermo, Italy.
[2] Dipartimento di Ingegneria, Università di Palermo, Italy

Email: elisaisabel.garcialopez@unipa.it

Keywords: biomass valorization, Nb_2O_5*;* $NbOPO_4$

Biomasses are renewable resources with great potentialities. Bio-based molecules derived from biomasses are of great interest and recent research has focused on the sustainable production of platform molecules, which can be used for the obtaining of fuels or biomaterials. One of the most interesting platform chemicals derived from biomass is 5-(Hydroxymethyl)furfural (5-HMF). This chemical bio-compound, different from petroleum-derived ones, possesses a high added value and it is generally obtained from lignocellulosic biomasses through acid catalysis. It is the precursor of several compounds for the chemical industry as polyesters, polyamides and polyurethane [1]. The 5-HMF molecule can be obtained from biomass in a three step process: i) hydrolysis of complex sugars into monomers ii) isomerization of glucose to fructose iii) dehydration of fructose to 5-HMF. These reactions are catalysed in acidic medium. A greener alternative to a mineral acid is the use of a solid acid catalyst, which may be harvested and reused. In this work, we have prepared, characterized and use for the 5-HMF obtaining form biomass two home prepared acidic catalysts, i.e. niobium oxide Nb_2O_5 and niobium oxyphosphate $NbOPO_4$. Nb_2O_5 has been obtained by a hydrothermal treatment of an aqueous solution of ammonium niobium oxalate. The obtained solid was not calcined to preserve the surface acidity. Mesoporous $NbOPO_4$ was prepared from $NbCl_5$ in a solution of H_3PO_4 in the presence of a surfactant. Both solids, Nb_2O_5 and $NbOPO_4$, resulted non crystalline showing specific surface area of ca. 195 $m^2\ g^{-1}$, with a well-developed porous structure. Both catalysts possess a strong acidity together with the presence of both Lewis and Brønsted acid sites, which can catalyse all the reaction steps. Glucose was initially used as a model substrate (6 g/L) to optimize the reaction conditions, hence the catalysts were applied with good success to real biomass substrates, such as microcrystalline cellulose and brewery wastewaters.

[1] R.J. Van Putten, J.C. Van der Waal, E. De Jong, C.B. Rasrendra, H.J. Heeres, J.G. De Vries, *Chem. Rev.* **2013**, 113, 1499–1597.

Understanding the Applications of Mechanochemistry for Pharmaceutical and Agrochemical Synthesis

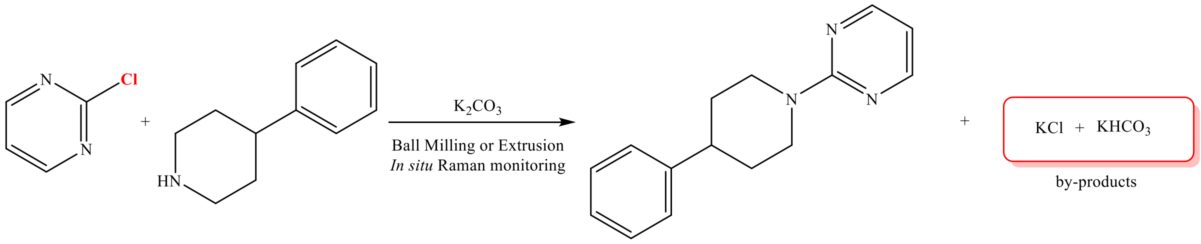
Emer Rooney,[a] Steven Bell,[a] Paul Dingwall,[a] Maria Ciaccia,[b] Matthew Burns,[c] Stuart James,[a]*
[a] QUB School of Chemistry and Chemical Engineering, David Keir Building, Stranmillis Road, Belfast BT9 5AG
[b] Syngenta, Process Studies Group, Jealott's Hill International Research Centre, Bracknell, Berkshire RG42 6EY, UK
[c] Chemical Development, Pharmaceutical Technology & Development, Operations, AstraZeneca, Macclesfield SK10 2NA, UK

E-mail: erooney20@qub.ac.uk

Keywords: Mechanochemistry, Kinetics, S_NAr reactions

Nucleophilic aromatic substitution reactions are commonly used in industry and typically involve the use of polar aprotic solvents (i.e. DMSO, DMF) in both the reaction and isolation of product. This is highly unfavoured from a sustainability point of view. Conducting these reactions mechanochemically via ball milling or twin screw extrusion offers conditions which use little or no solvent, simplified methods for the isolation of products and have potentially increased reaction rates. However, to date there have been limited studies on S_NAr systems conducted mechanochemically. Of particular interest is to characterise and understand the kinetics of such reactions.

For this work, a number of reactions have been identified and investigated mechanochemically to determine their suitability for kinetic analysis based on a set of essential and desirable criteria. The selected systems are to be optimised and then undergo kinetic analysis to generate mechanochemical kinetic models for ball milling. The reaction between 2-chlorpyrimidine and 4-phenylpiperidine (see Scheme) achieved a reasonable yield (76.2 %) in 60 minutes with no excess of any reagent and so therefore, was identified as the suitable system for further study. *In situ* Raman monitoring has been developed to give insight into the kinetics of this reaction. The use of continuous solvent-free synthesis by twin screw extrusion will also be presented.



Scheme Solvent-free mechanochemical reaction between 2-chlorpyrimidine and 4-phenylpiperidine in the presence of potassium carbonate as an inorganic base.

Advancing chemical recycling of polyethylene terephthalate (PET) using ionic liquids

E. B. McCrea, J. D. Holbrey, M. Swadzba-Kwasny
The QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University Belfast, UK

E-mail: emccrea06@qub.ac.uk

Keywords: Ionic liquid, polyethylene terephthalate, methanolysis

Polyethylene terephthalate (PET), a widely used polyester polymer, consists of repeating ester linkages, making it susceptible to chemical depolymerisation via glycolysis, methanolysis, or hydrolysis to recover valuable monomers.[1] Methanolysis, which converts PET into dimethyl terephthalate (DMT) with methanol, faces challenges such as high energy requirements, long reaction times, and the need for efficient and robust catalysts capable of handling impurities.

This study investigates of low-cost sulfuric acid based ionic liquids and microwave irradiation for PET methanolysis. These ionic liquids, developed by our group with known catalytic activity, facilitate PET breakdown into DMT, while microwave irradiation enables rapid, uniform, and energy-efficient heating, addressing key process limitations.[2-4] Key reaction parameters, including temperature, product separation and ionic liquid composition are systematically optimised to enhance depolymerisation efficiency, along with recyclability and stability of the catalyst for long-term viability. The findings demonstrate ionic liquid-assisted microwave methanolysis as a scalable, sustainable approach for PET recycling.

[1] Y. Luo, E. Selvam, D. G. Vlachos and M. Ierapetritou, ACS Sustain Chem Eng, 2023, 11, 4209–4218.
[2] A. McGrogan, E. L. Byrne, R. Guiney, T. F. Headen, T. G. A. Youngs, A. Chrobok, J. D. Holbrey and M. Swadźba-Kwaśny, Physical Chemistry Chemical Physics, 2023, 25, 9785–9795.
[3] A. Brzęczek-Szafran, J. Więcławik, N. Barteczko, A. Szelwicka, E. Byrne, A. Kolanowska, M. Swadźba Kwaśny and A. Chrobok, Green Chemistry, 2021, 23, 4421–4429.
[4] A. Brzęczek-Szafran, K. Erfurt, M. Swadźba-Kwaśny, T. Piotrowski and A. Chrobok, ACS Sustain Chem Eng, 2022, 10, 13568–13575.

CO$_2$ hydrogenation on hollow tube MIL-68(FeIn)-catalysts for enhanced methanol production

F. Zafar, J. J. V. Pico, D. G. Jimenez, C. Wu, J. Thompson, H. Manyar
School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast BT9 5AG, UK

E-mail: h.manyar@qub.ac.uk

Keywords: Hydrogenation, Heterogeneous catalysis, Methanol, CO$_2$ utilization, MOF catalyst

The urgent need to reduce CO$_2$ emissions and mitigate climate change has spurred interest in converting CO$_2$ into valuable chemicals such as methanol, a key energy carrier and chemical feedstock[1]. While traditional methanol production from syngas is well-established, direct CO$_2$ hydrogenation offers significant environmental and economic advantages. This study explores Fe-doped MIL-68(In) MOF catalysts for CO$_2$ hydrogenation, driven by the goal of enhancing CO$_2$ conversion efficiency and methanol yield using indium based catalysts. The Fe-doped indium catalyst demonstrated an 82% increase in CO$_2$ conversion at 230 °C and a 40% rise in methanol formation rate at elevated temperatures compared to undoped MIL-68(In) catalyst, as shown in Figure 1. This improved performance is attributed to Fe incorporation, which introduces multiple Fe oxidation states, increased Fe-In interfacial interactions, and promotes oxygen vacancy formation through lattice distortion. These structural modifications enhance CO$_2$ adsorption and activation, leading to superior methanol selectivity and yield, highlighting the potential of Fe-doped MOF catalysts for sustainable methanol production.

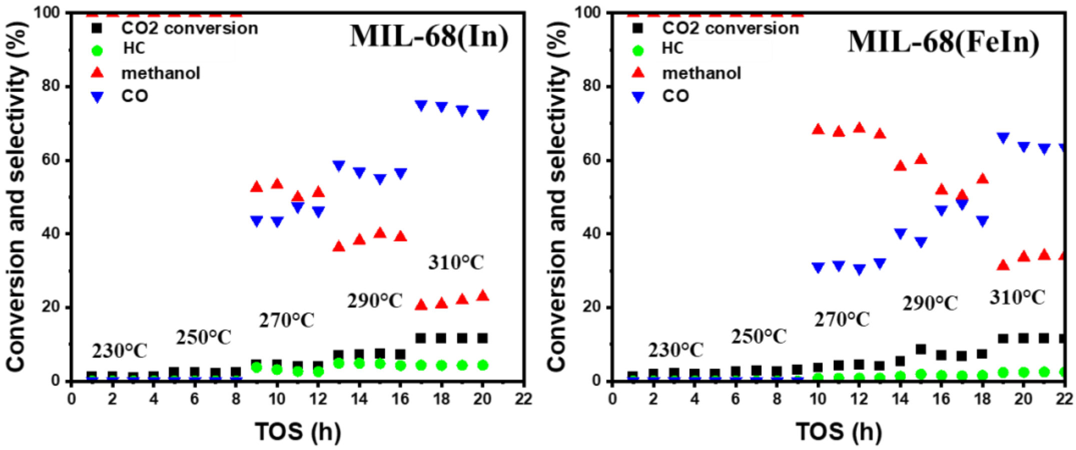


Figure 1. Catalytic performance comparison between MIL-68(In) and MIL-68(FeIn) catalysts at different reaction temperatures.

[1] F. Zafar, et. al., *Chemical engineering Journal* **2022**, 439, 135649.

Direct Synthesis of Polyesterether from Ethylene glycol

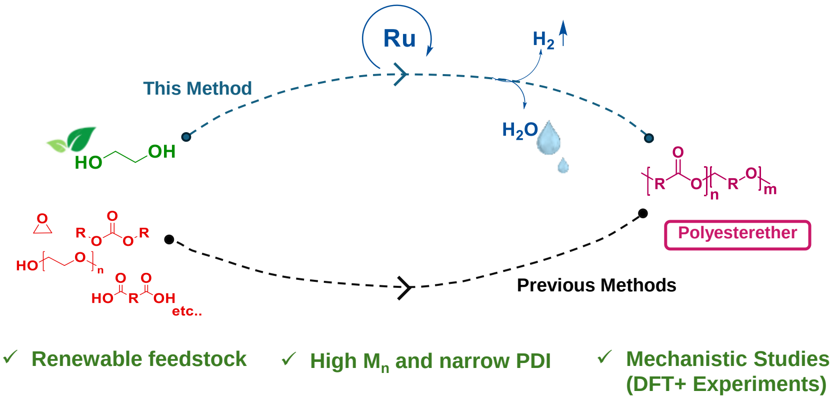
G. Saini,[1] P. Kulyabin,[1] A. McLuskie,[1] N. von Wolff,[2] and A. Kumar[1]

[1]EaStCHEM, School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, KY169ST, UK.
[2]eMOCA, Institut Parisien de Chimie Moléculaire, Sorbonne Université, CNRS, 4 Place Jussieu, 75005 Paris, France.

E-mail: g1@st-andrews.ac.uk

Keywords: dehydrogenation • ethylene glycol • ruthenium

Aliphatic co-polyesterethers are gaining significant attention nowadays for their excellent biocompatibility, biodegradability, and potential applications in tissue engineering and packaging.[1] However, their conventional synthesis involves complex polymerisation processes that make their large-scale application challenging.[2] To address this, we disclose here a new method of making polyesterether directly from ethylene glycol. The reaction is catalysed by a ruthenium complex and liberates only H_2 gas and H_2O as by-products. The mechanistic studies conducted by experiments and DFT computation suggest that the chain growth of the polymerization process involves both dehydrogenation and dehydration pathways stemming from a hemiacetal intermediate leading to the formation of esters and ethers respectively. The method is also applicable to other renewable substrates as well where diols with a lower number of carbons between both the alcohol groups (propylene glycol, glycerol, and 1,3-propanediol) lead to the formation of polyester-ether while α, ω-diols containing a higher number of carbons (1,6-hexanediol, and 1,10-decanediol) lead to the formation of polyester.



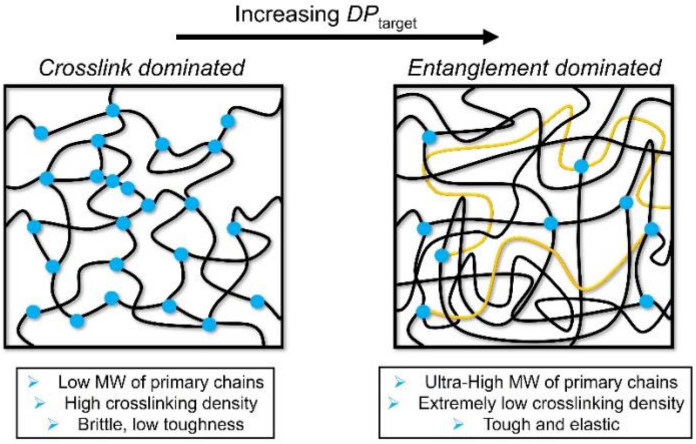
[1] E. M. Alosime, Journal of Polymer Research 2019, 26, 1–20.
[2] A. B. Biernesser, K. R. D. Chiaie, J. B. Curley and J. A. Byers, Angewandte Chemie International Edition 2016, 55, 5251–5254.

Highly Entangled Hydrogels by Photoiniferter-Mediated Polymerization

G. Irvine, K. Myronidis, F. Pinto and M. Kopeć
University of Bath, Bath, United Kingdom
E-mail: gi217@bath.ac.uk

Keywords: hydrogels, polymer networks, entanglements

Recently, synthesis of ultra-high molecular weight (UHMW) linear polymers using photo-initiated controlled radical polymerization techniques has been studied in literature [1]. We set out to apply and expand on this adaptable method by using photoiniferter-mediated polymerization to synthesize UHMW poly(*N,N*-dimethylacrylamide) (PDMA) hydrogels and analyze their physical properties The gels were synthesized with targeted degrees of polymerization (DP_{target}) between 100 – 100,000 (M_n ~ 990 – 9.9 x 10^6 g/mol) with an acrylamide based crosslinker. Equilibrium swelling ratio, shear storage modulus, compression stress and kinetic data were obtained for each DP_{target}, while keeping a constant crosslinker loading (between 2 - 10 mol% of MBAm). Interestingly, both *G'* and ESR tend to plateau at high targeted DP_{target} (above 10,000) despite drastically decreased crosslinking density, indicating the formation of highly entangled hydrogels. This resulted in a crosslink dominated region at low DP_{target} and an entanglement dominated region at high DP_{target} with both regions yielding hydrogels with different properties. Additionally, a disulfide containing crosslinker was added to the hydrogels to assess their degradability, with some hydrogels being fully degradable (DP_{target} 1000 or 100,000). The entanglements act as transient crosslinks and are responsible for the hydrogel's softness and elasticity, while sparse covalent crosslinks help to maintain its structural integrity for potential use in sustainable applications [2].



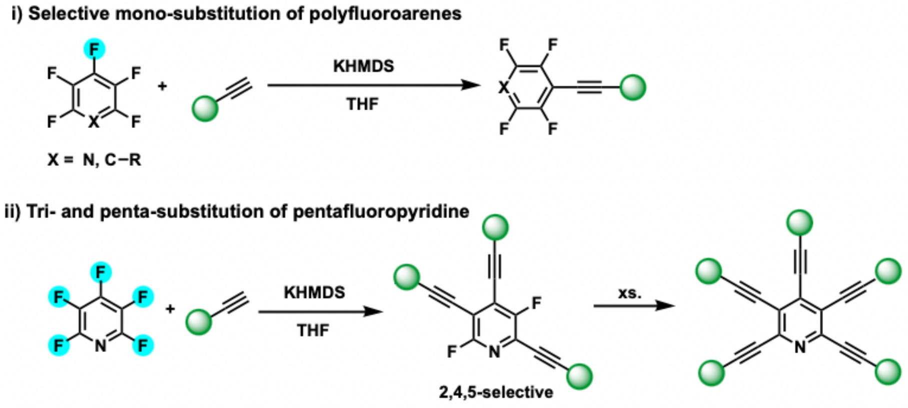
[1] R. Nicholas Carmean, T. E. Becker, M. B. Sims, B. S. Sumerlin, *Chem,* **2017**, 2,(1), 93-101.
[2] J. Kim, K. G. Zhang, M. Shi, Z. Suo, *Science,* **2021**, 374, 212-216.

Poly- substitution of polyfluoroarenes by S$_N$Ar mediated by KHMDS generated acetylides

George Cadman, Miriam O'Duill, Deborah Kays, Andrew C. Marr and Peter Licence
University of Nottingham, Nottingham, UK
E-mail: pcygtc@nottingham.ac.uk

Keywords: Defluorination, S$_N$Ar, Transition metal-free

Polyfluoroaromatic compounds serve as versatile and cost-effective precursors for the synthesis of valuable partially defluorinated building blocks through C–F functionalisation. Among these transformations, nucleophilic aromatic substitution (S$_N$Ar) is particularly advantageous due to its metal-free nature, making it highly desirable for applications in pharmaceuticals and electronic materials.[1-3] In this study, we present a rapid and efficient S$_N$Ar reaction between polyfluoroarenes and terminal acetylides, facilitated by mild bis(trimethylsilyl) amide bases. We explore the unique role of aryl acetylenes as electron-withdrawing groups, enabling controlled polysubstitution through stoichiometric adjustments and extended reaction times. The resulting products were isolated and characterised using various spectroscopic techniques, highlighting the potential of this approach for the selective functionalisation of polyfluoroarenes.



1. C. Liu, H. Zhao, H. Zhao, Z. Wang and B. Zhang, *RSC Adv.*, 2015, **5**, 31993–31997.

2. M. Shigeno, T. Okawa, M. Imamatsu, K. Nozawa-Kumada and Y. Kondo, *Chemistry – A European Journal*, 2019, **25**, 10294–10297.

3. T. Song, H. Liu, H. Zou, C. Wang, S. Shu, H. Dai and L. Duan, *Angewandte Chemie International Edition*, 2024, **63**, e202411228.

The CO2 Tree: The Potential for Carbon Dioxide Utilization Pathways

Heather O. LeClerc,[1,2] Hanno C. Erythropel,[1,2] Andreas Backhaus,[1,2] Darren S. Lee,[2,3] Dylan Judd,[2] Maria Paulsen,[2,4] Momoko Ishii,[1,2] Avery Long,[2,5] Lars Ratjen,[2] Gabriel Gonsalves Bertho,[1,2] Cosima Deetman,[2,5] Yan Du,[1,2] Mary Kate M. Lane,[1,2] Predrag Petrovic,[2] Andrew T. Champlin,[2,6] Alexis Bordet,[7] Nicolas Kaeffer,[7] Gregor Kemper,[7] Julie B. Zimmerman,[1,2] Walter Leitner,*[7,8] Paul T. Anastas*[1,2,6,9]
[1] Department of Chemical and Environmental Engineering, Yale University, New Haven, CT, 06511, USA
[2] Center for Green Chemistry and Green Engineering, School of the Environment, Yale University, New Haven, CT, 06511, USA
[3] School of Science & Technology, Nottingham Trent University, Nottingham NG11 8NS, U.K.
[4] Department of Energy, Aalborg University, 9220 Aalborg Øst, Denmark
[5] Yale College, New Haven, CT, 06511, USA
[6] Department of Chemistry, Yale University, New Haven, CT, 06511, USA
[7] Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim a.d. Ruhr, Germany
[8] Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, 52074 Aachen, Germany
[9] Yale School of Public Health, New Haven, CT, 06511, USA
E-mail: hanno.erythropel@yale.edu

Keywords: CO_2 transformation, green innovation, climate change

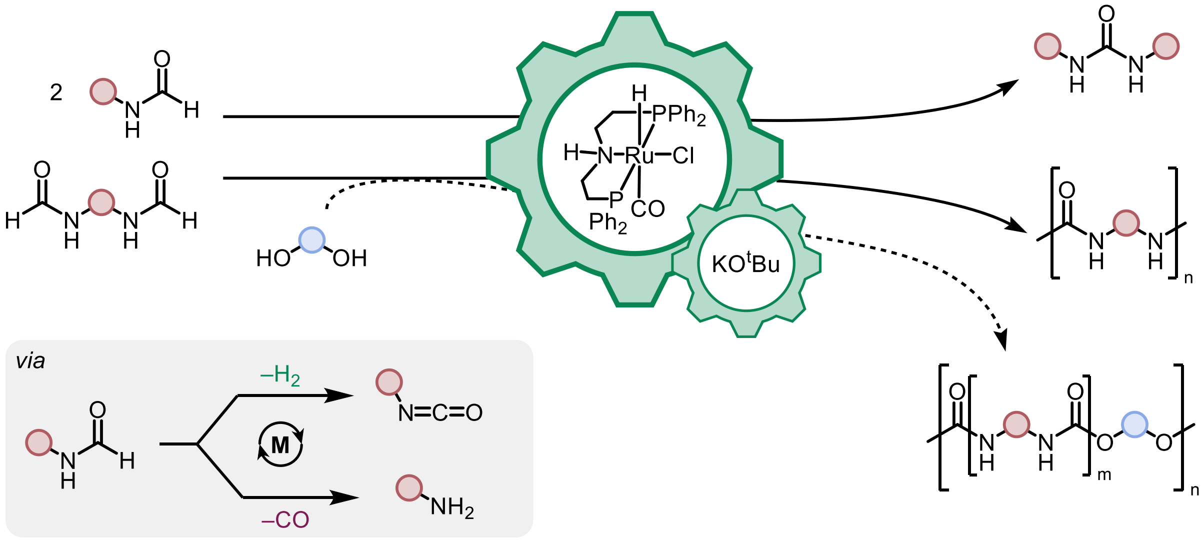
Among the most active areas of chemistry research today is that of carbon dioxide utilization; an area of research that was viewed as futile and commercially impractical not so long ago due to the energetic stability of the CO_2 molecule. The breakthroughs that largely began in earnest in the 1990s have accelerated, and now make up a diverse and plentiful portfolio of technological and scientific advances and commercialized technologies. Here, the imagery of "The CO_2 Tree" is presented as a tool to illustrate the breadth of potential products from CO_2 utilization and to communicate the potential of these chemical breakthroughs to address the greatest challenge that society faces today: climate change. It is intended to be useful for scientists, engineers, legislators, advocates, industrial decision-makers, policy makers, and the general public to know what is already possible today and what may be in the near future.

Exploiting decarbonylation and dehydrogenation of formamides for the synthesis of ureas, polyureas and polyureaurethanes

J. Luk, A. Kumar
University of St Andrews, St Andrews, United Kingdom

E-mail: jl304@st-andrews.ac.uk

Homogeneous, Catalysis, Polymers



Polyureas and poly(urea-urethanes) are important with various applications ranging from construction materials, foams, coating, adhesives and the biomedical industry.[1,2] However, these polymers are conventionally synthesised using highly toxic feedstocks. Requiring the use of diisocyanates, which are estimated to be the leading cause of occupational asthma globally,[3] while diisocyanates themselves are synthesised from phosgene gas, which was used as a chemical warfare agent in the First World War. According to our studies, it was found that formamides can undergo catalytic dehydrogenation and decarbonylation at different rates depending on the reaction conditions. By balancing these conditions, we were able to achieve simultaneous dehydrogenation and decarbonylation of formamides and diformamides to form ureas, polyureas from significantly safer starting reagents. By introducing diols to this system, the reaction was able to be expanded for the formation of poly(urea-urethanes).

[1] N. N. Melnikov, *Chemistry of Pesticides;* Springer New York, 1971.
[2] Polyureas. In Ullman's Encyclopedia of Industrial Chemistry, Chiriac C. I., Tanasaã F., 2016
[3] J. Kim, Y. Jang, S. Jang, K. Jung, S. Kim, Y. Ye, H. Park, *Exp. Mol. Med.*, **2017,** 49, e299

Functionalization of the butenolide scaffold – Towards responsive polymers and coatings

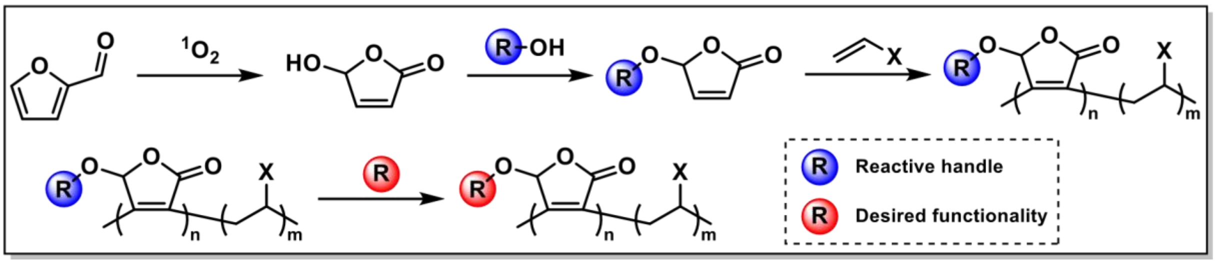
J. T. Meijer, B. L. Feringa
Rijksuniversiteit Groningen, Groningen, The Netherlands

E-mail: j.t.meijer@rug.nl

Keywords: Biomass conversion, Polymerizations, Functional polymers

When designing new stimuli-responsive features in sustainable coatings, the responsive building blocks need to be compatible with green and naturally sourced monomers. One such recently developed sustainable monomer is based on the alkoxybutenolide scaffold, which is derived from biowaste, and can be functionalized through acetal groups. Polymers and coatings from butenolides show excellent and tunable properties, which offer a more sustainable alternative to conventional acrylates.[1]

In this project, reactive molecular units will be designed and synthesized that can be incorporated within such butenolide polymers. Post-modification on these molecular units allows for straightforward incorporation of desired functionalities. Finally, incorporation of responsive units into such polymers will allow for on-demand disassembly and recycling of the coatings, as well as controlling surface structure and properties of the final coatings.



Scheme 1: General reaction overview towards functional butenolide polymers.

[1] Hermens, J. G., Freese, T., van den Berg, K. J., van Gemert, R., & Feringa, B. L., *Science Advances*, **2020**, *6* (51).

Sustainable Paired Electrooxidation Using Recyclable Multifunctional Ionic Liquids

J. Streets, P. Licence, D. Walsh
University of Nottingham, Nottingham, UK

E-mail: jessica.streets2@nottingham.ac.uk

Keywords: electrochemistry, ionic liquids, flow

Selective oxidations of alcohols and allylic systems represent a crucial area of research in synthetic chemistry. Electrooxidation methods minimise waste and maximise atom-efficiency and are becoming increasingly more attractive in solving challenging problems in green chemistry. *N*-oxyl radicals such as TEMPO (2,2’6,6′-tetramethylpiperidin-N-oxyl) have shown efficacy as selective redox catalysts in electrooxidation reactions and can be considered a greener reaction than traditional thermochemical methods relying on expensive and toxic metal reagents. The use of ionic liquids as both solvents and electrolytes for electrochemistry is attractive due to their tuneable properties and excellent solvation of TEMPO over traditional electrolytes.[1]

Introducing multi-functionality to these systems can further reduce waste production and eliminate the use of stoichiometric ancillary reagents. Our work has designed a recyclable *N*-oxyl-based ionic liquid system fulfilling the roles of catalyst, counter-electrode reagent, base, electrolyte, and solvent in alcohol electrooxidations. The novel strategy involves a paired electrosynthesis approach, where reactions at both electrodes contribute to completing the catalytic cycle.[2]

The flow methodology has already been applied to a range of primary, secondary, aromatic and aliphatic alcohols, with excellent conversion efficiencies and selectivities. The novel ionic liquids system can also be adapted for a series of alternative oxidative transformations to obtain α-β unsaturated ketones, nitriles and carboxylic acids using flow or batch methodologies.

[1] A. E. Delorme, V. Sans, P. Licence, D. A. Walsh, *ACS Sustainable Chem. Eng*. **2019**, 7, 11691−11699.
[2] F. Marken, A. J. Cresswell, *Chem. Rec*. **2021**, 21 (9), 2585-2600.

Enhanced CO_2 Hydrogenation to Hydrocarbons via SIL-Modified Fe-Ru/Al_2O_3 Catalysts: Tailoring Activity and Selectivity Through Support Engineering

J.J. Villora-Pico[1], F. Zafar[1], C. Wu[1], J. Thompson[1], N. Artioli[2], H. Manyar[1,*]
[1]*School of Chemistry and Chemical Engineering. Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, Northern Ireland, UK*
[2]*CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy.*

E-mail: h.manyar@qub.ac.uk

Keywords: CO_2 hydrogenation, Supported Ionic Liquid, Sustainable Chemistry

Rising CO_2 emissions require immediate innovative solutions to tackle the current climate emergency. Selective hydrogenation to methane valorises CO_2 into a fuel compatible with existing energy infrastructure. Using catalysts based on Earth-abundant and low-cost Fe decorated with minimal Ru as promoter reduces costs and aids industrial implementation. Optimising nanoparticle size and metal-metal interactions is critical[1]. Incorporating Supported Ionic Liquids (SILs) enhances nanoparticle formation and interactions. This study shows that modifying Al_2O_3 with an ionic liquid improves catalytic activity and methane selectivity in Fe-Ru catalysts with a low metal loading (1 wt.%).

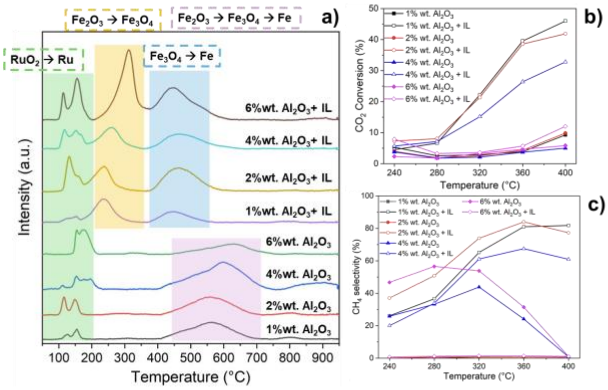


***Figure 1**. a) TPR profiles (hydrogen consumption) of prepared catalysts. b), c) Catalytic activity comparison of the catalyst samples.*

The SIL was incorporated onto an Al_2O_3 support via ball milling, while Fe-Ru/Al_2O_3 catalysts were prepared by wet impregnation followed by *in situ* $NaBH_4$ reduction. Their structural properties were analysed using N_2 physisorption, TPR, XRD, FTIR, TGA, and XRF. Catalytic performance was evaluated in a fixed-bed reactor at 20 bar with a gas mixture of 24% CO_2, 72% H_2, and 4% N_2, a GHSV of 1800 mL/g·h, across a temperature range of 240–400 °C.

The incorporation of SIL significantly enhances catalytic activity and CH_4 selectivity (Fig. 1b, 1c), especially at low metal loadings, indicating excellent metal dispersion with small NPs, as evidenced by absence of corresponding peaks in XRD patterns. The improved selectivity suggests that SIL incorporation improves Fe-Ru interaction, further supported by TPR (Fig. 1a), where the shift of Fe reduction peaks to lower temperatures indicates closer contact with Ru. This work highlights the role of SILs in enhancing catalyst performance for CO_2 hydrogenation, enabling the development of highly active catalysts with lower metal loadings.

[1] Maddaloni, M. et al. Catalysts **2023**, 13, 1499.

Catalytic Depolymerisation of Polyurethanes

Julian Sinclair Janko, Benjamin Sole, Raymundo Marcial Hernandez, Oxana Magdysyuk,
Aaron Naden, Gary Walker, Daylan Sheppard and Amit Kumar*

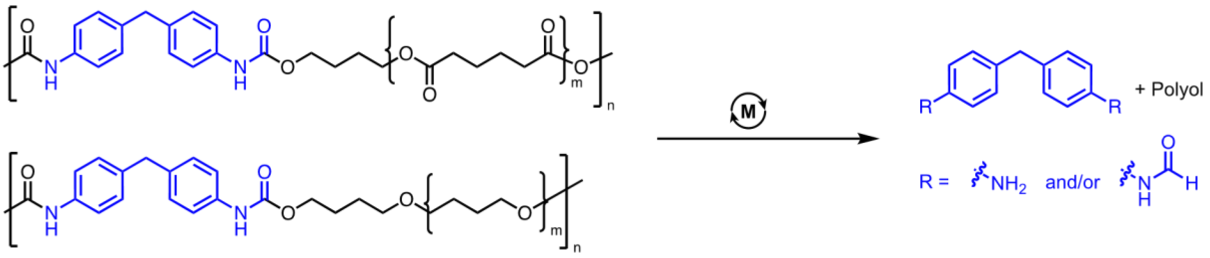
University of St Andrews, St Andrews, Scotland

E-mail: jsk6@st-andrews.ac.uk

Keywords: Polyurethane, Catalysis, Hydrogenation, Sustainability

Addressing the challenge of developing sustainable solutions for plastic recycling is a critical focus in today's world. Polyurethanes (PUs), which account for 8%[1] of all plastics produced, are divided into thermoplastic and thermoset polyurethanes. In this project, thermoplastic polyurethanes are of interest. Common types of recycling, such as mechanical recycling does not work towards reducing waste, which is where chemical recycling emerges as a promising alternative, with catalytic hydrogenation standing out as a particularly attractive strategy. This method offers an atom-efficient, green, and sustainable approach to reducing organic functional groups, such as carbonyl compounds, without generating stoichiometric waste. Furthermore, hydrogen gas, essential to the process, can be derived from renewable sources.[2]

Although the hydrogenation of polyurethanes using various organometallic homogeneous catalysts has been explored, the application of heterogeneous catalysts remains largely unexplored. In collaboration with The Lubrizol Corporation, our research focuses on hydrogenating two types of polyurethanes, containing polyester-based or polyether-based polyols. We have achieved in building a method that allows us to hydrogenate the aforementioned polyurethanes, including polyurethane waste, and recover the monomers up to a 90% yield.



[1] L. Gausas, S. K. Kristensen, H. Sun, A. Ahrens, B. S. Donslund, A. T. Lindhardt, and T. Skrydstrup, *JACS Au*, 2021, (1), 517-524
[2] B. Reda, A. A. Elzamar, S. AlFazzani, and S. M. Ezzat, *Environ. Dev. Sustain.*, 2024.

Lignin Oxidative Depolymerization on Graphitic Carbon Nitride - Explore the Cleavage of β-5 Linkage

Junhong Liu, Kathryn Ralphs, Nathan Skillen, Peter K.J. Robertson

Queen's University Belfast, School of Chemistry and Chemical Engineering, Stranmillis Road, Belfast, BT95AG.

E-mail jliu56@qub.ac.uk

Keywords: photochemistry, circular economy, biomass

As Net Carbon Zero and the development of the circular economy become critical global environmental issues, developing alternative green energy and chemical resources for fossil fuels are an area of significant research activity. Lignocellulosic biomass as the most abundant biomass throughout the world has aroused much attention as a green energy and value-added product source. As one of lignocellulosic biomass components, lignin which is comprised of different aromatic monomers, is a potential feedstock for value added chemical production. However, the method and mechanism of the cleavage of linkages between monomers to obtain high-value monomers still requires much investigation. Therefore, this study focuses on photocatalytic conversion of a β-5 lignin model compound. In this study it was found that a higher yield of aromatic products were obtained from a β-5 lignin model compound which underwent photocatalytic conversion over a carbon nitride catalyst compared to P25. The final conversion products of β-5 model compound were identified by GC-MS. According to GC-MS analysis, the cleavage occurs at the carbon-carbon bond between the benzene ring and the α-carbon, producing two aromatic monomers. The above results reveal for the first time the products and possible mechanism of photocatalytic transformation of β-5 model compounds under carbon nitride.

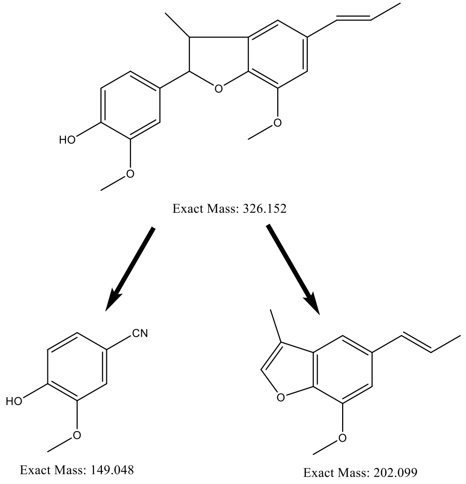


Fig. 1: β-5 model compound conversion

References:

[1] Junhong Liu, Kathryn Ralphs, Christopher W. J. Murnaghan, Nathan Skillen, Gary N. Sheldrake, Philip McCarron, Peter K. J. Robertson. *Chem.Sus.Chem.,* 2024, Article e202400955.

The alliance of mechanochemistry and environment. Solvent-free protocol for β-sulfenylated compounds.

K. Hanek, A. Duch, D. Frąckowiak, P. Żak
Adam Mickiewicz University, Poznań, Poland
E-mail: kamhan1@amu.edu.pl

Keywords: mechanochemistry, hydrothiolation, green chemistry

The changing state of the environment has become one of the main factors in designing chemical protocols for obtaining a wide range of products. Nowadays we can observe a shift from "novelty" to "sustainability" but it would be ideal if these two terms could be applied together. Most modern procedures for obtaining new materials, such as organosulfur compounds used in medicine,[1-2] are charged with significant drawbacks, e.g., high temperature or toxic catalyst, thus the search for new alternatives that would follow green chemistry principles is very desirable. A possible way out would be the mechanochemistry that appears to be superior in the organosulfur science[3], because the ball milling can lead to the ultimate green methods of chemical syntheses allowing a complete removal of harmful solvents while providing great selectivity.[4]

Herein, we present the very first instance of using ball milling in the solvent-free synthesis of sulfur-functionalized materials from thiols and unsaturated ketones and esters. This green protocol makes use of accessible reagents to prepare β-sulfenylated carbonyl compounds with yields exceeding 91% under ambient air and solvent-free conditions. Thirty new organosulfur compounds were obtained and all of them were characterized using available spectroscopic and spectrometric methods. The performance of solvent-based and ball milling syntheses was compared in terms of Process Mass Intensity (PMI).

[1] P. Srivastava, et al., *Bioorg. Med. Chem.*, **2004**, 12 (24), 6347-6450.

[2] E. A. Illard, et al., *J. Med. Chem.*, **2014**, 57 (7), 2832-2842.

[3] M. Bołt, K. Hanek, D. Frąckowiak, P. Żak, *Inorg. Chem. Front.*, **2023**, 14 (10), 4190-4196.

[4] K. Hanek, P. Żak, D. Frąckowiak, *ChemSusChem*, **2024**, e202401591.

Mechanochemically prepared photocatalysts

K. Ralphs, S. L. James, N. Skillen, P. K. J. Robertson
School of Chemistry and Chemical Engineering, Queen’s University Belfast

E-mail: k.ralphs@qub.ac.uk

Keywords: photochemistry, mechanochemistry, solvent-free

Mechanochemistry is the induction of chemical reactions through the input of mechanical energy, often with little or no added solvent.[1] It can be as simple as grinding solids together by hand and can extend to tonne scale ball mills. Typically, it is a low energy solvent free method. Mechanochemistry has a long history in the context of material processing as well as inorganic synthesis. It has more recently been investigated for organic transformations, metal organic frameworks and catalyst synthesis. Mechanochemically prepared catalysts have shown considerable promise over their conventional counterparts. [2-5]

In this work we have prepared active and selective photocatalysts via simple mechanochemical methods. Typical synthesis of metallo-porphyrins is lengthy and requires potentially toxic solvents such as DMF. We have prepared metalated meso-tetraphenylporphyrins (M-TPP) by milling meso-tetraphenlyporphrin and metal acetate at 20 Hz for 20 min in a shaker mill with no added solvent with the only side products being acetic acid and water. A ZnO photocatalyst was then doped with 1% M-TPP by gently milling in a shaker mill. The catalyst was then tested in the photo reforming of glucose under ambient conditions and using H_2O as the solvent. It was found that when using ZnO doped with Cu-TPP the selectivity of the reaction could be significantly enhanced compared to using ZnO alone.

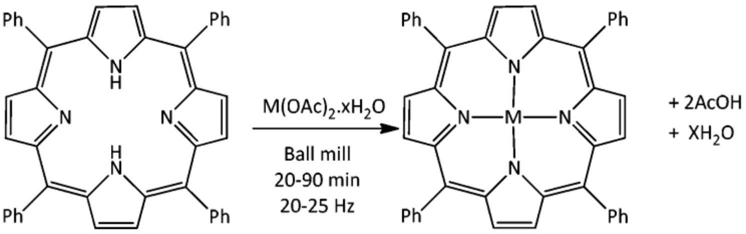


Figure 1 Solvent-free mechanochemical metallation of *meso*-tetraphenylporphyrin (H_2TPP).

[1] K. Ralphs, et al., Chem. Soc. Rev., 2013, 42, p 7701-7718
[2] K. Ralphs, et al., Catalysis, Science & technology. 2014, 4, 2, p. 531-539.
[3] K. Ralphs, et al., Catal. Today, 246, p.198-206.
[4] K. Ralphs, et al., Green Chem., 2017, 19, p 102-105.
[5] K. Ralphs, et al., ACS Sus. Chem. Eng., 2022, 10, 21, p 6394-6941.

Identifying the Catalytic Species in Indium Ionic Liquids for Sustainable Alkylation

K. E. Savage,[a] C. J. Clarke,[a] P. Stevenson,[b] E. Sampler,[b] P. Licence[a]
[a] University of Nottingham, Nottingham, UK, [b] Lubrizol, Hazelwood, UK
E-mail: katie.savage@nottingham.ac.uk

Keywords: indium ionic liquids, catalysis, chemical properties

Alkylated aromatics are important molecules used extensively in a wide range of applications including fuel, pharmaceuticals and agriculture. Produced globally on a 100 million tonne scale,[1] they are typically prepared through Friedel-Crafts alkylations using an excess of acid catalysts such as H_2SO_4 and BF_3. These catalysts pose environmental and safety concerns due to high toxicity, moisture sensitivity and inability to be re-used. Industry desire more sustainable alternatives which are easier to handle on scale. Halometallate ionic liquids (ILs) are a promising alternative. They are free flowing salts, comprised of metal and organic halides, which can act as catalytic mixtures. They have many unique properties, including tuneable Lewis acidity, easy synthesis, are involatile and have a high thermal stability.[2] Previous work has successfully demonstrated the use of indium ILs as catalysts for alkylation reactions, however current speciation knowledge is insufficient to explain the observed catalytic Lewis acidity. Building upon work completed by the Licence group,[3] this study aims to further investigate the speciation and chemical properties of a series of indium ILs (Fig. 1).

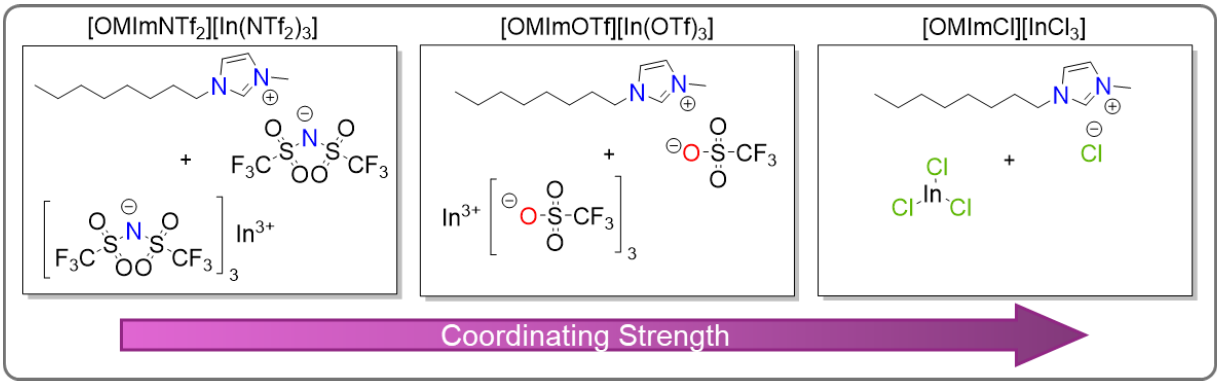


Figure 1:Indium ILs investigated in study.

Herein, we probe the oxidation state and bonding of indium (XPS and XAS), quantify the Lewis acidity (^{31}P NMR), and investigate ligand-catalyst interactions in these ILs with ligands of different coordinating strengths. These structural and mechanistic insights will allow us to design more efficient and sustainable ILs, tailored to industrial processes.

[1] S. Zheng et al., *Nat. Sustain*., **2023**, 1–10 ; [2] C. J. Clarke et al., *Green Chem.*, **2022**, 24, 5800–5812; [3] D. C. Apperley et al. *Dalton Trans*., **2010**, 39, 8679–8687

Graphitic Carbon Nitride/CeO_2 Nanocomposite for Photocatalytic Degradation of Methyl Red

Khansaa Al-Essa, Ethar M. Al-Essa, Alaa Qarqaz, Suhad Al-Issa , Solhe F. Alshahateet and O'la Al-Fawares
Department of Chemistry, Jerash University, Jerash 26150, Jordan

E-mail: khansaa.essa@gmail.com

Keywords: ceria; graphitic carbon nitride/ceria nanocomposite; photocatalytic degradation

Nanosized ceria (CeO_2) and a graphitic carbon nitride-loaded ceria (CeO2/GCN) nanocomposite were synthesized using a straightforward and efficient method and characterized by XRD, FTIR, SEM, TEM, TGA, and BET analyses. These techniques confirmed that CeO_2 was effectively supported on the surface of GCN, with particle sizes of the CeO_2/GCN composite in the range of 10–15 nm and a pore size of 3.33 nm. The photocatalytic activity of the CeO_2/GCN nanocomposite and CeO_2 NPs in the degradation of methyl red dye under sunlight radiation was studied using UV–visible spectroscopy. A noticeable red shift in the CeO_2/GCN nanocomposite compared to pure CeO_2 NPs suggests a reduction in its band gap energy, calculated at 3.90 eV for CeO_2 NPs and 2.97 eV for the CeO_2/GCN nanocomposite. This band gap reduction enhances the photocatalytic degradation process, achieving a removal efficiency of 99.92% within a short irradiation time of 40 min for the CeO_2/GCN nanocomposite, compared to 69.47% for CeO_2 NPs. These findings indicate that graphitic carbon nitride significantly enhances the photocatalytic properties of CeO_2 NPs.

Sustainable Porous Liquids (SUPLI)

Maebh Fitzsimons, Leila Moura, Stuart James
QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University Belfast, N. Ireland

E-mail: mfitzsimons14@qub.ac.uk

Keywords: Porous liquids, Biobased Polymers, CO_2 capture

Addressing the urgent need for carbon dioxide (CO_2) capture is critical for achieving the goals of the Paris Climate Agreement and commitments discussed at COP29. Current industrial CO_2 capture methods, such as amine scrubbing, are widely used but face significant drawbacks, including high energy demands for regeneration, toxicity, and environmental harm.[1] These limitations underscore the need for alternative technologies that are efficient, sustainable, and environmentally friendly.

This project focuses on the development of biobased porous liquids (PLs) as a promising alternative to traditional CO_2 capture methods. Porous liquids represent a new and emerging class of materials that combine the high gas uptake capabilities of microporous solids with the fluidity of liquids.[2] Unlike conventional liquid sorbents, porous liquids retain the porosity of solids within a liquid matrix, enabling efficient gas capture and separation. Their tuneable nature and ability to operate under a wide range of conditions make them particularly attractive for industrial applications.

Designed to be inexpensive, non-toxic, and highly efficient, these PLs will combine microporous solids derived from biobased polymers with non-volatile liquid carriers. The microporous solids will be sourced from natural and sustainable polymers such as cellulose[3], chitosan[4], and cyclodextrins.[5] These materials offer advantages such as biodegradability, cost-effectiveness, and ease of functionalisation to target specific gases, making them ideal for scalable commercial applications. By leveraging the unique properties of these biobased components and the versatility of porous liquids, this research aims to create a next-generation CO_2 capture material that aligns with global sustainability goals. With their potential for widespread industrial application, biobased porous liquids represent a transformative step toward reducing industrial carbon emissions and transitioning to a low-carbon future.

[1] M. Hanifa, R. Agarwal, U. Sharma, P.C. Thapliyal, L.P. Singh, *Journal of CO_2 Utilization* 2023, 67, 102292.
[2] P.F. Fulvio, S. Dai, *Chem* 2020, 6, 3263–3287.
[3] Dinesh, H. Wang, J. Kim, *Global Challenges* 2022, 6, 2200090.
[4] A. Muxika, A. Etxabide, J. Uranga, P. Guerrero, K. de la Caba, *International Journal of Biological Macromolecules* 2017, 105, 1358–1368.
[5] I. Roy, J.F. Stoddart, *Accounts of Chemical Research* 2021, 54, 1440–1453.

Direct air capture and CO_2 transformation into added-value chemicals

J.E Sánchez-Velandia[1,2*], Vitoria Gonçalves Pina, [2,3], Víctor Sans[2], E. García-Verdugo[1], M. Zanatta[2,3]

[1] *Departamento de Química Inorgánica y Orgánica, Grupo de Química Sostenible y Supramolecular,Universidad Jaume I, Castellón, Spain*

[2] *Institute of Advanced Materials (INAM), Universitat Jaume I, Avda Sos Baynat s/n, 12071, Castellón, Spain*

[3] *Departament de Química Física i Analítica, Universitat Jaume I, Avda Sos Baynat s/n, 12071 Castellón de la Plana, Spain*

E-mail: zanatta@uji.es

Keywords: capture and conversion, efficient hydrogenation, direct air capture, catalysis

The increasing concentration of atmospheric CO_2 due to human activities has become a major challenge, impacting both the environment and public health. Engineering solutions for CO_2 mitigation have gained significant attention, with direct air capture (DAC) and catalytic transformation emerging as promising approaches. These strategies not only contribute to reducing CO_2 emissions but also enable the production of added-value chemicals under sustainable conditions.

This study investigates the efficiency of different basic solutions and solvent systems for CO_2 absorption through air bubbling. The role of organic and inorganic cations in bicarbonate formation was evaluated, with TBA^+ demonstrating superior CO_2 sorption capacity. The captured CO_2 was then hydrogenated under mild conditions using Ru-based catalytic systems, where $Ru_3(CO)_{12}$ exhibited the highest catalytic performance and recyclability across multiple reaction cycles. The results highlight the potential of integrating DAC with catalytic transformation to enhance carbon utilization efficiency. This approach provides a scalable and energy-efficient pathway for CO_2 conversion, reinforcing its applicability in industrial decarbonization strategies and sustainable chemical production.

[1] Zanatta, M., García-Verdugo, E.; Sans, V. *ACS Sustainable Chem. Eng.*, **2023**, *11*, 9613– 9619.

[2] Bruch, M.; Sanchez-Velandia, J. E.; Rodríguez-Pereira, J.; Rich, M.; Pearcy, N.; Narancic, T.; Garcia-Verdugo, E.; Sans, V.; O'Connor, K.; Zanatta, M. *Green Chem.*, **2024**, *26*, 11885–11898.

Recombinant xylanolytic enzymes production by *Komagataella phaffii* and their application in biorefineries

M. Kočenda, M. Legíň, P. Dobrovodský, K. Kántorová, Z. Marčeková, M. Rebroš
Institute of Biotechnology, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Slovakia

E-mail: mario.kocenda@stuba.sk

Keywords: xylan; xylanolytic enzymes; Komagataella phaffii

As the global demand for sustainable industrial processes continues to rise, developing of innovative ways to utilize renewable resources and repurpose industrial by-products is crucial. Among these resources, plant biomass—comprising cellulose, hemicellulose, and lignin—is the most abundant and can be transformed into valuable products such as biofuels, biochemicals, and materials.

Xylan, the most prevalent hemicellulose, consists of a linear chain of β-1,4-linked xylosyl units, that are often substituted with different side chains (e.g. glucuronosyl, methylglucuronosyl and arabinofuranosyl groups). Due to structural variability of xylan, the cocktails of enzymes, such as endo-1,4-xylanases, β-D-xylosidases, α-L-arabinofuranosidases, acetyl xylan esterases and glucuronoyl esterases, are often necessary to achieve its complete hydrolysis.

In this way, a production of recombinant xylanase by *Pichia pastoris* (*Komagataella phaffii*) utilizing crude glycerol from biorefinery was explored. This enzyme breaks down the xylan backbone into xylooligosaccharides, which can be further hydrolyzed into xylose. High cell-density cultivation using pure glycerol resulted in an extracellular xylanase activity of 0.89 U/mL and a productivity of 6.28 U/L/h. Interestingly, the presence of impurities in crude glycerol positively influenced xylanase expression. The highest enzyme activity and productivity were observed when using partially purified (1.50 U/mL and 7.34 U/L/h) and nonpurified crude glycerol (1.59 U/mL and 9.13 U/L/h).

These findings demonstrate the potential of utilizing biodiesel by-products to enhance biofuel production and promote more sustainable practices in biorefineries.

This work was supported by the Research and Development Support Agency based on Contract No. APVV-22-0207.

Recycling Lithium-ion Batteries using Dielectrophoretic Filtration

M. C. O'Donnell, G. R. Pesch

University College Dublin, Dublin, Ireland

E-mail: mary.c.odonnell@ucdconnect.ie

Keywords: battery recycling, dielectrophoresis, particle separation

Lithium-ion batteries (LIBs) offer a reliable energy storage solution and are particularly relevant in the electric vehicle (EV) sector. In the next 10 years, EV sales are forecasted to rise significantly, increasing demand for LIB raw materials (Co, Mn, Li, graphite) and generating 20.5 million tonnes of LIB waste by 2040.[1] A mere 5 % of LIBs are recycled globally owing to chemically and energy intensive recycling technologies.[2] Graphite – a major component of LIBs and an EU critical raw material – is lost in current processes, among other materials that cannot be effectively recycled. Therefore, we must develop energy-efficient and cost-effective LIB recycling techniques to reach EU battery recycling targets and reduce our reliance on volatile foreign markets to supply LIB raw materials.

Dielectrophoretic (DEP) filtration offers an environmentally friendly method to directly recycle each LIB component without chemical modification. DEP filtration electrokinetically separates particles based on differences in composition, size and polarisability.[3] Black mass (BM), an intermediate product during LIB recycling, contains graphite and lithium metal oxide (LMO). DEP filtration allows separation of LMO and graphite; this will not only recover the valuable graphite but will also increase recovery efficiencies of LMO materials in subsequent recycling steps. Thus, DEP filtration can be used as a pre-treatment method to increase efficiency in established LIB recycling plants.

In this project, non-selective DEP filtration is performed on common LIB particles to determine DEP trapping rates. Next, artificial BM mixtures of pristine graphite and LMOs are separated using DEP filtration based on their distinct conductivities. DEP parameters resulting in optimal separation efficiency and purity of particle streams will be determined to demonstrate the viability of employing DEP filtration as a reliable separation technique to recycle LIB waste.

[1] McKinsey & Company, https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular, accessed Jan 2025
[2] Li-Ion Battery Recycling: A Review of the Current Methods and Global Developments, CAS White Paper, 2022
[3] G. Pesch, F. Du, Electrophoresis, **2021**, 42, 134–152

Renewable Molecules of Relevance to Agriculture from Biomass Sources

M. A. Goss*[a], H. E. Chapman[a], C. I. Lindsay[b], W. G. Whittingham[b], A. S. Matharu[a], H. F. Sneddon[a]

[a]Green Chemistry Centre of Excellence, University of York, York, United Kingdom

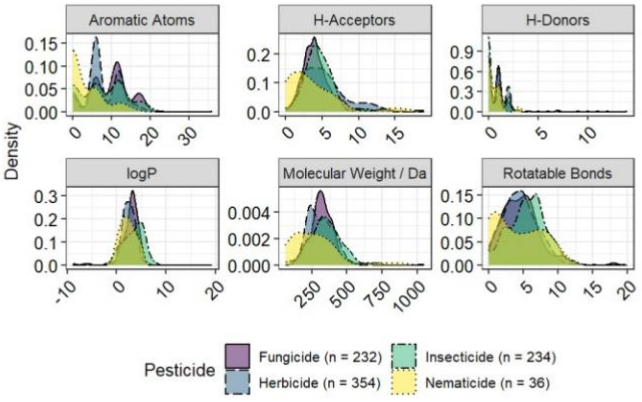
[b]Syngenta Ltd, Jealott's Hill International Research Centre, Berkshire, United Kingdom

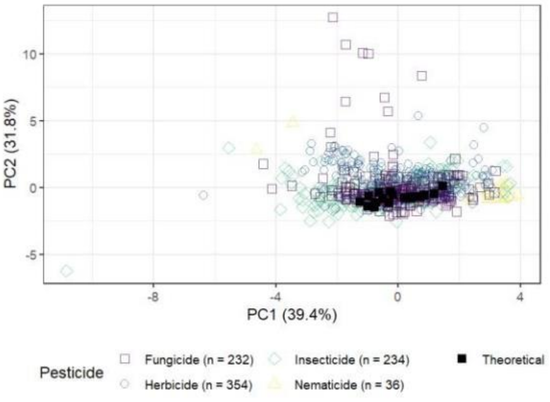
E-mail: megan.goss@york.ac.uk

Keywords: agrochemical, bioderived, PCA

Agrochemicals are imperative to meet the demand for crops across the world. Agrochemical formulations contain several components, including active ingredients, co-formulants and solvents, many of which are derived from fossil fuels, which are finite. To ease the reliance on petrochemical resources, increased usage of bio-derivable molecules is necessary when designing new compounds.

In attempt to design products relevant to agriculture, predicted physical properties of over 850 commercial pesticide active ingredients were compared and visualised through principle component analysis (PCA). PCA is a method of visualising multiple variables in fewer dimensions, by minimising unnecessary information. A comparison of the spatial positioning of the designed with the commercial products on the PCA guided the relevance of the products *in silico.* before attempt of synthesis was completed.





Ionic liquids for CO_2 capture from high temperature technical gas streams

Michael Sweeney, Leila Moura, John D. Holbrey
QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University Belfast, N. Ireland

E-mail: msweeney22@qub.ac.uk

Keywords: CO_2 capture, Ionic Liquids, gas separation

Carbon dioxide (CO_2) is a major contributor to climate change brought on by global warming. Governments across the globe are bringing forward directives to reduce anthropogenic CO_2 emissions.[1–4] A technical report on the application of amine scrubbers which are the current industrial standard used for CO_2 scrubbing of high temperature flue gas found major flaws in their implementation and operation.[5] ILs can mimic the CO_2 capture of amines scrubbers by utilizing basic anions and offer minimal degradability issues. [6] Thusly making them well suited to work at high temperatures (90 - 160 °C) and low CO_2 partial pressures (40 – 80 mbar) i.e. industrially relevant conditions. They offer a competitive advantage for specific niche markets i.e. CO_2 capture from wet flue gas streams such as those originating from refinery or cement plants, notoriously hard-to-decarbonise sectors.

ILs can be categorised into two groups; protic and aprotic. Protic ILs offered straightforward synthesis (as shown in Figure 1) and a commercially competitive alternative to amine scrubbers. However we found that there is an inherent volatility associated with protic ILs and as such experience mass loss below their nominal decomposition temperatures, i.e. at conditions similar to amine scrubbers (90 °C).[7] However aprotic ILs offer a higher thermal stability and a more sustainable recyclable capacity.

Figure 2. Protic IL synthesis example. (IL=[DBUH][Im])

In this context, we study a range of protic and aprotic ILs containing anions with varying basicities for CO_2 absorption in industrially relevant conditions. We also investigated aprotic ILs that overcome inadequacies with regards to thermal stability and showed nearly double the mass loss onset temperature (180 °C). This study encompasses (A) a CO_2 uptake screening of protic (1,8-diazabicyclo(5.4.0)undec-7-enium **[DBUH]$^+$** and 1,5-diazabicyclo[4.3.0]non-5-enium **[DBNH]$^+$**) and aprotic (phosphonium **[P$_{xxxx}$]$^+$** and ammonium **[N$_{xxxx}$]$^+$**) based ILs paired with imidazolide [Im]$^-$ and succinimide [Suc]$^-$ analogous anions and (B) a critical assessment on each IL's thermal stability within the industrially relevant temperature range.

1 G. Erbach, *Regulations (EU)*, 2021.
2 S. M. S. U. Eskander and S. Fankhauser, *Nat Clim Chang*, 2020, **10**, 750–756.
3 S. M. Madden, A. Ryan and P. Walsh, *Agriculture*, 2021, **12**, 34.
4 A. Averchenkova, S. Fankhauser and J. J. Finnegan, *Climate Policy*, 2021, **21**, 251–263.
5 Schlissel, D.; Wamsted, D. *Institute for Energy Economics and Financial Analysis* 2018.
6 X. Y. D. Soo, J. J. C. Lee, W.-Y. Wu, L. Tao, C. Wang, Q. Zhu and J. Bu, *Journal of CO2 Utilization*, 2024, **81**, 102727.
7 M. Wei, A.-C. Huang, C.-M. Shu and L. Zhang, *Sci Rep*, 2019, **9**, 1592.

Designing Polysaccharide-Derived Mesoporous Carbon Materials (Starbon) for Selective Metal Recovery

N. Garland,[a] R. Gordon,[b] I. Hopkins,[b] A. Parkin,[a] C. R. McElroy,[c] D. MacQuarrie.[a]
[a] Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK
[b] Johnson Matthey Technology Centre, Sonning Common, RG4 9NH, UK
[c] School of Chemistry, University of Lincoln, Lincoln, LN6 7TS, UK

E-mail: nphg500@york.ac.uk

Keywords: Polysaccharide, Mesoporous, Adsorption

The Starbon process, first published in 2006, provides a route to producing non-templated mesoporous carbon materials sustainably from a range of polysaccharide feedstocks. Utilising the inherent porosity of polysaccharide hydrogels, the Starbon process does not rely on pore activation during pyrolysis, providing access to a range of surface chemistries dependent on the feedstock polysaccharide and pyrolysis temperature of choice. This has been shown to result in the ability to 'fine tune' material properties towards a range of applications. To this end, we present two examples of the design of Starbons as cost effective and sustainable materials for metal adsorption and recovery:

1) Base metals – In response to the ever increasing need to develop more efficient and sustainable means for removing heavy metal contaminants from aqueous systems, alginatederived Starbon materials have been designed and evaluated for the adsorption of the common contaminant ions: Cu^{2+}, Ni^{2+} and Co^{2+}.[1] Preservation of weakly acidic oxygencontaining groups was found to result in large adsorption capacities (0.7-1.7 $mmol.g^{-1}$) and selectivity for Cu over other metal ions.

2) Platinum group metals (PGMs) – Modern societal dependence on the platinum group metals has resulted in substantial incentive to develop cost effective and sustainable means for their recovery from increasingly low-grade feeds. Exploring the development of metallophilic Starbon surface chemistry during pyrolysis has enabled the synthesis of materials that exhibit extensive capacity for the reversible adsorption of both Pt(II) (1.3 $mmol.g^{-1}$) and Pd(II) (1.5 $mmol.g^{-1}$). In addition, these materials exhibited excellent selectivity for Pt and Pd even in the presence of large excesses of base metals and other PGMs, under conditions relevant to lowgrade refinery feeds.

[1] N. Garland, R. Gordon, C. R. McElroy, A. Parkin, D. MacQuarrie, *ChemSusChem* **2024**, 17 (17).

Synthesis, Characterisation and Application of Polystyrene-supported BrØnsted-Acidic Ionic Liquid as an Efficient and Reusable Catalyst for Groebke-Blackburn-Bienaymé Multicomponent Reaction

N. S. Anjos,[a,b] *L. S. Longo Jr.* [b] *and P. Licence* [a]
a) The University of Nottingham, Nottingham, United Kingdom
b) Federal University of São Paulo, Diadema, Brazil

E-mail: nicolas.santosdosanjos@nottingham.ac.uk

Keywords: polymer-supported ionic liquids, multicomponent reactions, catalysis

Multicomponent reactions are highly atom-efficient transformations between three or more reactants within a single reaction flask, usually requiring mild and eco-friendly conditions.[1] The Groebke-Blackburn-Bienaymé multicomponent reaction (GBBR) was first described in 1998 and involves an acid-catalysed transformation between 2-aminoazoles, aldehydes and isocyanides for the efficient synthesis of imidazo heterocyles (*i.e.* imidazo[1,2-*a*]pyridines).[2–4] Since then, this reaction has been extensively exploited towards the optimization of reactional conditions, including the investigation of reusable catalytic systems. Previously, it was reported by our group the use of BrØnsted-acidic ionic liquids (BAILs) as reusable catalysts for GBBR, in which they could be reused up to four consecutive reaction cycles, despite of a laborious recovery procedure employed.[5] In this scenario, the direct linkage of the ionic liquid phase to a polystyrene resin (heterogenisation) could make the recycling process straightforward and easier. Herein, we report the synthesis and characterisation of novel polystyrene-supported BrØnsted-acidic ionic liquids (PS-BAILs) and their role as an efficient and reusable catalysts for GBBR. First, a PS-BAIL derived from 1-(butyl-4-sulfonic acid)-3-methylimidazolium trifluoromethane sulfonate was synthesised and characterised by FTIR, SEM, TGA and XPS. Its catalytic activity was then evaluated in a model GBBR between 2-aminopyridine, *tert*-butyl isocyanide and benzaldehyde. The best reaction condition was found when the reaction was carried out with 50 mg mmol^{-1} of PS-BAIL using ethanol as solvent under microwave heating at 150ºC for 1 hour, leading to the desired imidazo[1,2-*a*]pyridine in 91% yield. The heterogeneous catalyst could be recovered and reused for up to five consecutive cycles without significant loss of catalytic activity (91%-72%). The study of the scope and the limitations of this methodology is under investigation by our group.

1 R. C. Cioc, E. Ruijter and R. V. A. Orru, *Green Chem.*, **2014**, 16, 2958–2975.
2 K. Groebke, L. Weber and F. Mehlin, *Synlett*, **1998**, 661–663.
3 C. Blackburn, B. Guan, P. Fleming, K. Shiosaki and S. Tsai, *Tetrahedron Lett.*, **1998**, 39, 3635–3638.
4 H. Bienayme and K. Bouzid, *Angew. Chem., Int. Ed.*, **1998**, 2234–2237.
5 N. S. Anjos, A. I. Chapina, A. R. Santos, P. Licence and L. S. Longo, *Eur. J. Med. Chem.*, **2022**, e202200615.

The Effects of Salinity on Exo-polysaccharides Productivity Towards Algal Bioplastics

N. Bahari, S.Vaidyanathan

The University of Sheffield, Sheffield, United Kingdom

E-mail: zuria.idayu@sheffield.ac.uk

Keywords: microalgae, Exo-polysaccharides (EPS), bioplastics

Plastic waste pollution and the increasing level of CO_2 emission into the atmosphere critically need resolution. Microalgae is one of the sustainable approaches to mitigate the problems as they can produce precursors such as polysaccharides, proteins and lipids that can be utilized as base polymers to produce bioplastics. These bio-compounds can be influenced by changing parameters including salinity, nutrient, temperature, pH, etc.

This research investigates the effect of salinity at different concentrations on EPS productivity in a halotolerant strain of Chlorella vulgaris. Microalgae was cultivated in growth media with different salt concentrations in which the growth rate, carbohydrate as well as protein and lipid compositions were evaluated afterwards. The strain used reveals the preference to grow significantly in less salt concentration and EPS was found to be higher alongside.

Evidence has shown that salinity stress affects the production of exopolysaccharides and the results are important to fill the gaps in assessing the benefits of microalgae in terms of the metabolites potentiality to generate film in developing bio-based plastics. Perhaps more EPS produced could make more bioplastics. Thus, incorporation of EPS into bioplastic production is hoped to be part of the initiative to lessen the environmental issues addressed above.

Mechanochemically Engineered CaO-CeO_2 Catalysts for Solvent-Free Synthesis of Glycerol Carbonate

Patcharaporn Inrirai, Runzhe Yu, Daniel Goma Jimenez, Nancy Artioli, and Haresh Manyar*

School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Belfast BT9 5AG, United Kingdom

E-mail: pinrirai01@qub.ac.uk

Keywords: Glycerol carbonate, Mechanochemistry, Fuel additives.

Glycerol is an abundantly available waste from biodiesel industry, but it has high potential for value addition due to its extensive utilisation in various industrial sectors. One of the most attractive avenues for glycerol upgradation is its transformation to glycerol carbonate using transesterification. For this transformation, we have utilised a dual-function CaO-CeO_2 material prepared by green mechanochemical synthesis. Herein, by tuning the morphology and electronic properties of CaO-CeO_2, the interaction between the two species can enhance the generation of O^{2-} vacancies and promote the carbonation reaction known as sorption enhanced catalysis. Also, CaO-CeO_2 materials are cost-effective and easily scalable catalysts.

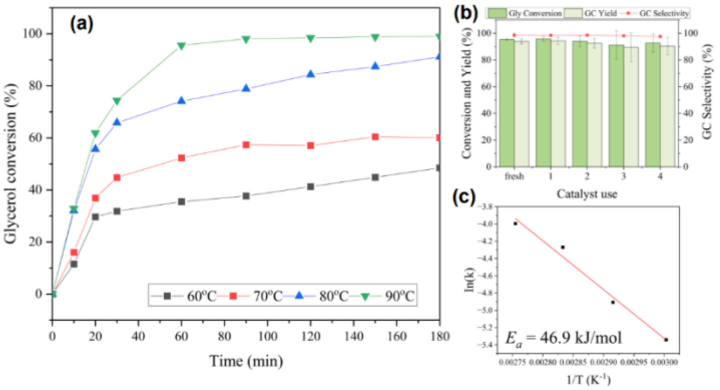


Figure 1. ***(a)*** *Reaction time profile for Glycerol carbonate production at different temperatures,* ***(b)*** *Reusability of catalyst, and* ***(c)*** *Arrhenius plot for irreversible second-order kinetic model*

A green route for synthesising glycerol carbonate from glycerol and dimethyl carbonate was successfully demonstrated using supported-CaO catalyst. CeO_2, as a support material, enhances the stability and activity of heterogeneous catalysts. The most effective catalyst was 40%wt CaO/CeO_2, which exhibited the highest catalytic activity with more than 95% yield of glycerol carbonate (Figure 1a) at 90°C. Furthermore, the catalyst showed good stability and recyclability with up to four reuses (Figure 1b). In this study, we developed a detailed kinetic model based on the irreversible second-order kinetics (Figure 1c). The transesterification reaction activation energy was calculated using the Arrhenius plot and found to be 46.9 kJ/mol, indicating that the reaction occurred in kinetic regime.

[1] J. Keogh, G. Deshmukh, H. Manyar, *Fuel*, **2022**, 310, 122484.

Seaweed Bioactives Supplemented Animal Feeds. Green Chemistry Methods of Seaweed Extraction

P. A. Bailie, P. C. Marr, P. J. Walsh, A. C. Marr
Queen's University Belfast, Belfast, United Kingdom

E-mail: pbailie08@qub.ac.uk

Keywords: ionic liquid, phlorotannin, alginate

There is strong industrial interest in the development of more sustainable biorefinery processes. The emergence of non-toxic and bioderived **ionic liquids (ILs)** has opened up new possibilities for the design of greener processes for the isolation of valuable organic functional molecules from biomass.

Emergence of multidrug resistant bacteria and persistence of non-degradable pollutants in the environment are driving interest in the procurement of natural compounds from abundant sources to replace synthetic alternatives in livestock feed. **Brown algae** are farmed abundantly and are valuable sources of a range of commercially important compounds including **phlorotannins** and **alginic acid**. Phlorotannins are polyphenols recognised for their biological and therapeutic capacity including antimicrobial, antioxidant, anti-inflammatory, antitumour, and antidiabetic properties with interest in replacing zinc oxide as growth promoters in swine feed. Alginic acid is a widely used degradable hydrocolloid added to animal feed as a binding agent.

In this study, the simultaneous extraction of phlorotannins and alginic acid from brown algae species *Fucus vesiculosus*, *Fucus serratus*, and *Fucus spiralis* was performed using IL-based solid-liquid extraction techniques. A selection of biocompatible ILs demonstrated enhanced extraction efficiency of both compounds compared to traditional solvent-based extraction routes. The extraction process was optimised on several extraction parameters including extraction time, IL concentration and solid/liquid ratio.

Part of a larger project **SeaFEED**, a 1.2 million euro cross-border partnership of Queen's University Belfast, University of Limerick, and ATU Sligo joint funded by DAFM (RoI) and DAERA (NI) in collaboration with Finnebrogue, Devenish Nutrition Ltd, JMW Farms Ltd, Sealac, and The Seaweed Company, investigating the use of seaweed as a source of ingredients for animal feed.

Mechanistic Study of Chirality Transfer on a Catalyst Surface

El Mamoune Zahidi, Yi Dong, Peter H. McBreen
Department of Chemistry, Laval University, Québec (Qc.), Canada G1V 0A6

E-mail: peter.mcbreen@chm.ulaval.ca

Keywords: heterogeneous enantioselective hydrogenation

Heterogeneous catalysis is privileged strategy in green chemistry. Control of enantioselection is an especially demanding challenge in heterogeneous catalysis and its study explores phenomena ranging from ligand-induced rate-enhancement to the interplay between chemisorption and intermolecular forces in determining the structure and dynamics of chirality transfer complexes. In this investigation, a combination of STM, DFT and reflectance-IR data is used to define the structure of individual chirality transfer complexes, the intermolecular interactions involved, the activation of prochiral functional groups, and complexation state changes within isolated complexes. Although the studies are carried out on model systems under vacuum conditions, the observed phenomena are largely consistent with the *operando* heterogeneous asymmetric catalysis literature. Emphasis will be placed on the three most important insights gained from studies of single complexes formed by chiral molecules (chiral modifiers) and activated ketones on Pt(111): (i) complexation is driven by multiple attractive non-covalent interactions; (ii) weak non-covalent interactions play a determining role in stereodirection; (iii) precursor state dynamics are key to forming privileged complexation structures. The studies also show that DFT calculations perform well in predicting the structure and dynamics of individual chemisorbed chirality transfer complexes. In addition to a better understanding of reaction mechanism, the study reveals key differences between homogeneous and heterogeneous asymmetric catalysis.

Enzyme-Inspired Gel Materials: Tuneable, Bio-Based Gels for Catalysis

P. McNeice,[a] A. C. Marr,[b] P. C. Marr,[b] W. Leitner,[ac] A. J. Vorholt[a]

[a]*Department of Molecular Catalysis, Group Multiphase Catalysis, Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34–36, 45470 Mülheim an der Ruhr, Germany.*

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

[c] *Institute for Technical and Macromolecular Chemistry, RWTH Aachen University,*
Worringerweg 2, 52074 Aachen, Germany

E-mail: peter.mcneice@cec.mpg.de

Keywords: Gels, Catalysis

In nature, many reactions are performed by multiple enzymes, and therefore multiple active sites working in tandem.[1] Gel materials consist of a solid matrix with a liquid phase dispersed throughout it. The solid matrix can be polymer, molecular, or colloidal, while the liquid phase can be organic (organogel), aqueous (hydrogel) or ionic liquid (ionic liquid gel). Both components can be selected to form a designer material. Furthermore, metal catalysts can be entrapped within gels, which can enhance their activity and facilitate their reuse.[2,3,4]

We present the synthesis of novel, bio-based silica/alginate hybrid gels, with entrapped metal catalysts (See Figure). We vary the solid and liquid phases, as well as the entrapped metal catalyst, building functionality into each component of the material. This allows the active site of the gels, along with their morphology, to be tailored for a specific reaction, or multiple reactions, thereby mimicking enzymatic processes.

[1] X. Yhang, G. Li, G. Chen, D. Wu, W. Yongning, T. D. James, *Adv. Funct. Mater*. **2021**, 31, (50), 2106139.

[2] S. J. Craythorne, A. R. Crozier, F. Lorenzini, A. C. Marr, P. C. Marr, *J. Organomet. Chem*. **2005**, 690, (15), 3518- 3521.

[3] S. J. Craythorne, K. Anderson, F. Lorenzini, C. McCausland, E. F. Smith, P. Licence, A. C. Marr, P. C. Marr, *Chem. Eur. J.* **2009**, 15, (29) 7094-7100.

[4] P. McNeice, A. Reid, H. T. Imam, C. McDonagh, J. Walby, T. J. Collins, A. C. Marr, P. C. Marr, *Environ. Sci. Technol.* **2020**, 54, (21), 14026-14035.

Extraction and Characterisation of Seaweed Polyphenols

Riddhi Salotra[1, 2], Gary Sheldrake[1], Pamela J Walsh[2]
[1] School of Chemistry and Chemical engineering, [2] School of Mechanical & Aerospace Engineering
Queens University Belfast, United Kingdom

E-mail: r.salotra@qub.ac.uk

Keywords: Polyphenols, Supercritical CO_2 extraction, Nuclear magnetic resonance (NMR) spectroscopy

Seaweeds are plant-like organisms recognised as an important components of the marine ecosystem. They are identified as an untapped resource with a rich variety of compounds. In recent years there has been significant interest in seaweed polyphenols, for their pharmaceutical and nutraceutical applications. Polyphenols are secondary metabolites in seaweeds and protect them against environmental stressors like UV radiation. Structurally, polyphenols are the hydrophilic polymers with wide distribution of phenolic groups from simple moieties to more complex forms. This structural diversity of polyphenols provides a challenge for the scientists to perform efficient extraction and quantitative analysis. The present work focuses on the development of supercritical CO_2 extraction and developing the quantitative ^1H NMR spectroscopy for brown seaweed polyphenols. In this work, three brown seaweeds were studied- *Ascophyllum nodosum*, *Fucus vesiculosus*, and *Fucus serratus*. Initial extractions were using conventional extraction method (maceration) to be used as a benchmark for the supercritical CO_2 extraction and for the development of novel ^1H NMR method [5]. The ^1H NMR experiment was obtained first for equivalence compound phloroglucinol in DMSO-d_6 using Trimesic acid as internal standard that involved the irradiation of residual water signal which causes the suppression or elimination of the phenolic -OH groups due to proton exchange. This method was first applied to conventional extracts of all seaweeds and the results of the total phenolic content (TPC) were compared with Folin-ciocalteau (FC) reagent method to ensure the correlation between the two quantitative methods. Thereafter, this new ^1H NMR method was used to measure the TPC in supercritical extracts of seaweeds. The supercritical CO_2 extraction was optimised for all seaweeds using design of experiments (DOE) software based on high TPC and high extraction yield. The TPC obtained for all three seaweeds extract from the respective optimised supercritical experiments were compared to the TPC obtained from conventional extracts. Overall, the TPC yield from supercritical extracts was found to be significantly higher than the maceration yield, which proved the efficiency of the supercritical extraction.

Selective extraction of platinum group metals utilising novel non-ionic hydrophobic (deep) eutectic solvents

Sahar Gholami[a]; María Pérez-Page; Carmine D'Agostino[a]; Jesús Esteban[a]
[a] Department of Chemical Engineering, School of Engineering, The University of Manchester. Oxford Road. Manchester, United Kingdom

E-mail: sahar.gholami@manchester.ac.uk

Keywords: platinum group metals; deep eutectic solvents; solvent extraction

The growing economic significance and finite availability of platinum group metals (PGMs) underscores the need of efficient recovery methods, aligning with sustainability and circular economy principles. Hydrophobic deep eutectic solvents (H(D)ESs) have emerged as environmentally benign alternatives for PGM extraction from acidic leaching solution of metal-bearing waste[1,2]. Here type V H(D)ESs, namely trioctylphosphine oxide (TOPO):carvacrol and lidocaine:carvacrol, were evaluated as novel extractants for extraction from PGM containing solutions. This research includes characterises solid-liquid equilibrium phase diagrams and physicochemical properties (density, viscosity, and thermal and chemical stability) across varying compositions and temperatures. The solvents were tested for Pt(IV) and Pd(II) recovery from acidic solutions, analysing operating parameters like (D)ES composition, shaking time, organic-to-aqueous phase volumetric ratio, acidity, and salinity. The results highlight the remarkable potential of H(D)ESs as cleaner and tunable solvents for PGM extraction, achieving over 90% extraction efficiency for either depending on conditions. Adjusting eutectic components and acidity allows precise tuning of metal selectivity, with TOPO:carvacrol and lidocaine:carvacrol showing excellent selectivity for Pt(IV) and Pd(II), respectively. UV-visible, NMR, and FT-IR spectra indicate that PGM extraction utilising these novel H(D)ESs occurs through neutral ion association mechanism.

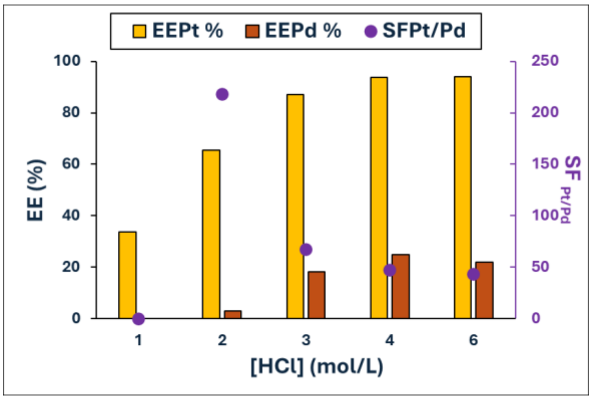


Figure 1. Extraction efficiency (EE %) and separation factor of Pt (IV) over Pd(II) ($SF_{Pt/Pd}$) as a function of HCl concentration (mol/L) using TOPO:carvacrol H(D)ES (x_{TOPO}=0.40, [Pt]=[Pd]=5 mmol/L, V_{org}:V_{aq} =1:2, time=4 h, T=25 °C)

[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 (Under review).

Electrochemical dicarboxylation of 1,3-butadiene with CO_2 to 3-hexenedioic acid with non-sacrificial anode

S.U. Khan[1], R. Zaffaroni[2], W. de Jong[1], E. Goetheer[1] , R. Kortlever[1]

[1]Large Scale Energy Storage, Department of Process and Energy (P&E), Delft University of Technology, Delft, The Netherlands
[2]Sustainable Process & Energy Systems (SPES), TNO, Netherlands

E-mail: s.u.khan-1@tudelft.nl

Keywords: Electrocarboxylation, 1,3-butadiene, non-sacrificial anodes.

The expansion of industrial processes and energy-related activities has increased anthropogenic greenhouse gas emissions, driving global temperature rise.[1] Carbon dioxide (CO_2), a major contributor to the greenhouse effect, presents opportunities for sustainable conversion into valuable products using sustainable technology.[2] Especially, the fixation of CO_2 via electrochemical carboxylation is a green and promising approach in the synthesis of a variety of organic compounds especially carboxylic acid derivatives.

This electrocarboxylation processes are of high scientific and commercial interest as only one or two electron is required per CO_2 molecule. However, at the moment electrochemical carboxylation processes are limited by some serious drawbacks that hinder the progress of these technologies towards industrial scale deployment.[3] One of them is by the use of sacrificial anodes, which necessitates batch mode operation with periodic complex and labour intensive anode replacement procedures.[4]

In this context, we demonstrate the electrochemical dicarboxylation of 1,3-butadiene with CO_2 for the production of 3-hexenedioic acid (3-HDA), a precursor of adipic acid. The electrochemical carboxylation is carried out using Nickel (Ni) cathode and by replacing typical Aluminium (Al, sacrificial anode) with platinum (Pt, non-sacrificial anode) in the presence of organic electrolyte. We study how operating parameters such as applied potential, electrode materials, and supporting electrolyte and substrate concentration affect the overall process and the reaction product distribution. The finding from this study will be extended to other electrocarboxylation processes to produce valuable carboxylic acids.

[1] S. Yang et al., Environ. Sci. Pollut. Res., **2023**, 30, 81725-81744.
[2] S. V. Jr et al., Clean. Eng. Technol., **2022**, 8, 100456.
[3] R. Matthessen et al., Beilstein J. Org. Chem. **2014**, 10, 2484–2500.
[4] Silvestri, G. et al., Acta Chem. Scand. **1991**, 45, 987–992.

Producing Monomers for Sustainable Coatings Using Photochemistry – Utilising Reactor Design and Process Analytical Chemistry for Scale-up

Tara S. Lambert,[a] Oliver H. Goodrich,[a] Thomas Freese,[b] Ben L. Feringa,[b] Martyn Poliakoff,[a] Michael W. George.[a]
(a) University of Nottingham, Nottingham, UK and (b) University of Groningen, Groningen, The Netherlands.

E-mail: tara.lambert@nottingham.ac.uk

Keywords: Photochemistry, PAT, Scale-up

Our reliance on polymers is dependent on the availability of affordable fossil fuel feedstocks, the development of polymers and materials that are derived from renewable sources drives us toward Net Zero production and a circular economy. There is increasing interest in using biomass and lignocellulose as feedstocks, and of particular relevance to this poster, several bio-based acrylate resins for coating applications have been prepared. We recently described the optimization and scale-up of the photooxidation of furfural, over two consecutive reaction steps for the synthesis of bio-derived alkoxybutenolide monomers, these have been reported as potential replacements for acrylate-based coatings.[1,2] The use of a Taylor vortex reactor allows you to enhance this reaction's sustainability. It achieves this by the generation of Taylorvortices which provide intense alternating areas of mixing, greatly improving mass-transfer and subsequently overall reaction performance. This poster describes investigations into this reaction particularly exploiting Process Analytical Techniques (PAT) for providing real-time information on what is happening within a reaction vessel. In particular, we investigate the application of a new approach namely **A-TEEM** spectroscopy (absorption, transmission, fluorescence, excitation-emission-matrix), which offers a fast, specific, highly sensitive, and sustainable approach to continuously monitoring reactions in real-time.[3] We illustrate the versatility of **A-TEEM** spectroscopy in monitoring the production of a range of monomers and APIs while detecting side products and impurities.

We thank the EPSRC and HORIBA UK Ltd for funding and support at Nottingham.

[1] J. G. H. Hermens, T. Freese, K. J. Van Den Berg, R. Van Gemert and B. L. Feringa, *Sci. Adv.,* **2020**, 6, eabe0026.

[2] M. D. Edwards, M. T. Pratley, C. M. Gordon, R. I. Teixeira, H. Ali, I. Mahmood, R. Lester, A. Love, J. G. H. Hermens, T. Freese, B. L. Feringa, M. Poliakoff and M. W. George, *Org. Process Res. Dev.,* **2024**, 28, 1917–1928.

[3] D. S. Lee, A. Love, Z. Mansouri, T. H. Waldron Clarke, D. C. Harrowven, R. Jefferson-Loveday, S. J. Pickering, M. Poliakoff and M. W. George, *Org. Process Res. Dev.,* **2022,** 26, 2674–2684.

Flow Biocatalysis: Application of Monolithic Porous Open Tubular Capillary Reactors

Vishnu Ganthimeri[1], Declan Daly[1], Adam Porter[1], Alexander Yavorskyy[1], David Collins[2], Ciaran Fagan[2], Rangasamy Savitha[3], Gemma Kinsella[3], Barry Ryan[3], Gary Henehan[3] and Kieran Nolan[*1]

1: School of Chemical Sciences, Dublin City University, Dublin, Ireland.
2: School of Biotechnology, Dublin City University, Dublin, Ireland.
3 School of Food Science and Environmental Health, Technological University Dublin, Dublin Ireland

E-mail: vishnu.ganthimeri2@mail.dcu.ie

Keywords: Flow biocatalysis, capillary reactors, peroxidase.

Flow biocatalysis has emerged as a transformative approach in sustainable chemical manufacturing by integrating enzymatic catalysis with continuous flow systems. Unlike traditional biocatalytic batch processes, flow biocatalysis offers enhanced mass transfer, precise reaction control and scalability in the production of pharmaceuticals, fine chemicals and bio-based materials. Typical approaches to continuous flow biocatalysis involves the immobilisation of the enzyme of interest onto a support material within the channel thereby allowing for the recycling/recovery of the enzyme for further usage. Most supports that are applied for the immobilisation of enzymes in continuous flow are typically packed bed systems involving either monoliths or inert particles that are packed within the channel. Consequently, undesirable fluctuating back pressures can be observed with these packed channels.

The work presented in this poster offers a solution to the back pressure problem. We have recently employed a monolithic porous layer open tubular (monoPLOT) capillary (100µm) system to eliminate backpressure. With the monoPLOT capillary the polymer synthesised within the channel is controlled so only a layer of the monolith exists on the walls of the capillary leaving the centre of the capillary open, therefore backpressure is eliminated. In this work we report the successful immobilisation of soy bean peroxidase onto the monoPLOT, using vinyl azlactone as linker, and demonstrated complete sulfoxidation of thioanisole under flow conditions and the immobilised enzyme could be used for 10 reaction cycles before losing activity. We now envisage extending this technology to both lipases and glucosidases.

[1]. A Lambarska, K Szymanska, *Green Chem., 2024, 26, 10718-10738.*

Understanding aldol condensation kinetics in complex feed streams

J. W. Medlin, B. E. Oliphant, L. I. Paz Herrera
University of Colorado, Boulder, USA

E-mail: medlin@colorado.edu

Keywords: Sustainable aviation fuel; metal oxide catalysts; selectivity control

Coupling reactions such as aldol condensation have received increased attention in recent years due to the interest in producing sustainable aviation fuel from small, biomass-derived oxygenates. Streams of light oxygenates arise in many contexts within biorefining. For example, mixtures of acetaldehyde, propanal, and butanone are produced as volatile products from fast pyrolysis processes, and it is desirable to convert these products into a liquid stream. While aldol condensation is a strong candidate chemistry and has been widely studied, there is little understanding of how interactions between mixture components affect condensation rates and product selectivity. We have therefore studied aldol condensation reactions on TiO_2 and a series of other catalysts using single component, binary and ternary mixtures of the three reactants. On the canonical TiO_2 catalyst, pathways for major reaction products generated at industrially relevant temperatures were identified by comparing the product mixtures for each reaction. In both binary and ternary mixtures, conversion of acetaldehyde was enhanced while the conversion of alkanones was suppressed.[1]

To understand the origins of these effects and develop the ability to manipulate selectivity, we used a combination of kinetic studies, temperature programmed desorption methods, and chemical probes of acid and base sites. We found that acetaldehyde strongly outcompetes the ketones for adsorption as an electrophile on all materials studied to date. However, the ketones can more effectively compete for aldol sites on the surface, and this competition can be tuned by surface doping of TiO_2. In the case of aluminosilicate materials, the Brønsted acid strength enables tuning of aldol condensation selectivity. Finally, we observe that water present in the reaction environment has a complex effect on reaction kinetics, promoting activity under some conditions but suppressing it under others. Findings in this study will be related to ongoing efforts to develop catalysts for biomass upgrading reactions.

[1] B. E. Oliphant, M. Rasmussen, L. Paz Herrera, M. B. Griffin, J. W. Medlin, *Catal. Sci. Technol.* **2024**, 14, 1911-1922.