Società
Chimica
Italiana

Gruppo Interdivisionale di
Green Chemistry — Chimica Sostenibile

TORINO, 24-25 Ottobre 2024

Evento sotto il patrocinio di

DSTF
DIPARTIMENTO DI SCIENZA E
TECNOLOGIA DEL FARMACO
UNIVERSITÀ DEGLI STUDI DI TORINO

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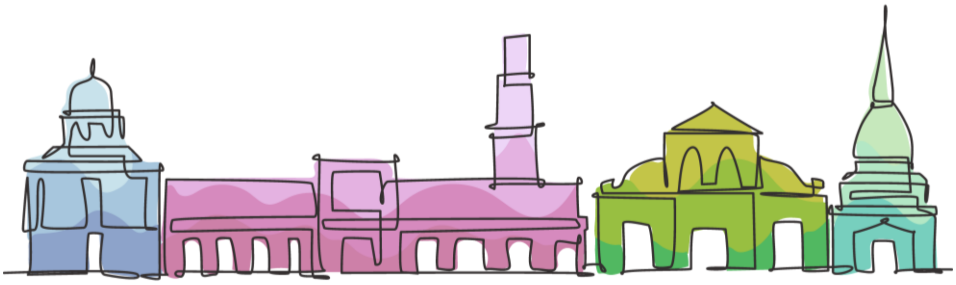
Green Chemistry — Chimica Sostenibile

Gruppo Interdivisionale
Green Chemistry – Chimica Sostenibile
(*GC-CS*)

Nato per rispondere alla crescente attenzione verso le tematiche di **sostenibilità** e di **rispetto per l'ambiente**, il *Gruppo Interdivisionale di Green Chemistry – Chimica Sostenibile (GC-CS)* ha lo scopo di raccogliere e convogliare i diversi interessi in questo ambito, ispirandosi ai **principi della Chimica Verde**. Il *GC-CS* fa dell'interdisciplinarietà e della compenetrazione delle tematiche il proprio fondamento, nella convinzione che la vera innovazione possa avere origine da un'efficace **sinergia** tra diverse sfere di competenza. Il Gruppo si rivolge sia al mondo di ricerca, accademica ed industriale, nonché ad attività di **didattica** e di **divulgazione**.

Appuntamento fisso per il *GC-CS* è il **Workshop annuale**, organizzato con lo scopo di permettere il confronto tra le diverse realtà esistenti in Italia, coinvolgendo gruppi di ricerca e aziende attivi nel settore. Il Gruppo inoltre **supporta ed aiuta a promuovere** qualunque evento basato su questi principi, offrendo i propri canali di comunicazione e social media.

Nel 2024, il *GC-CS* bandisce un **Premio alla Ricerca (Junior)**, nell'ambito della *Green Chemistry***,** per un/una **giovane** ricercatore/ricercatrice che si sia particolarmente distinto/a per le sue **linee di ricerca** e la **produzione scientifica.**



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Società Chimica Italiana
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XI WORKSHOP NAZIONALE
Green Chemistry – Chimica Sostenibile

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GIOVEDÌ 24 OTTOBRE 2024

8:30 – 9:00	**REGISTRAZIONE**
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Chairperson: **L. Travaglini, M. Manzoli**

9:20 – 9:50	**KN-1 Prof.ssa Michela SIGNORETTO**, *Università Ca' Foscari Venezia* Pyrolysis: a key value for the circular economy
9:50 – 10:10	**CHEMSUSCHEM Lecture Prof. Gianvito VILÉ,** *Politecnico di Milano*

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Chairperson: **G. Cravotto, A. Salvini**

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10:30 - 10:40	**OR-3 Matteo CORRADINI**, *Università di Bologna* Ru/Pd catalytic system for the reductive amination of furfural
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11:40 - 11:50	**OR-7 Silvia RIZZO**, *Università di Bologna* A Sustainable Chemo Enzymatic Approach to the Synthesis of Liraglutide
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12:50 - 12:53	**FL-1 Clelia AIMONE**, *Università di Torino* Chestnut Wood Valorization: A Green Strategy for Extraction, Fractionation, and Biopolymer Design (+ poster **P-1**)
12:53 - 12:56	**FL-2 Chiara BRUSCHETTA**, *Università di Torino* Ultrasound-Assisted Procedure for the Preparation of Ru- and Pd-Iron Oxide Catalysts (+ poster **P-2**)
12:56 - 12:59	**FL-3 Camilla CALLEGARI**, *Università di Pavia* Carbon nitride materials as sustainable photocatalysts in C-H bonds functionalization processes (+ poster **P-3**)
12:59 - 13:02	**FL-4 Laura PALOMBI**, *Università degli studi dell'Aquila* Electrocatalytic activation of acetone cyanohydrin with hydrogen evolution: synthesis of β-cyano ketones and α-aminonitriles (+ poster **P-4**)
13:02 - 13:05	**FL-5 Alireza SAFDARI**, *Università degli Studi di Milano* Flotation Technique for Recycling Black Mass from Spent Lithium-ion Batteries (+ poster **P-5**)
13:05 - 13:08	**FL-6 Federica TUFANO**, *Università degli Studi di Salerno* Sustainable Polymers obtained by Schiff Base-Based Zn and Mg Complexes (+ poster **P-6**)

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Chairperson: **C. Samorì, G. Grillo**

14:30 - 15:00	**KN-2 Prof. Fabrizio PASSARINI**, *Università di Bologna* Life cycle perspective supporting green chemistry
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	Applications
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15:40 - 15:50	**OR-13 Francesca ANNUNZIATA**, *Università degli Studi di Milano* Chemo-enzymatic sustainable flow synthesis of biologically active nature-inspired carbonates and carbamates
15:50 - 16:00	**OR-14 Mattea Carmen CASTROVILLI**, *CNR-Istituto di Struttura della Materia* Electrospray deposition: a green technique to fabricate low-cost and eco-friendly biosensors
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16:20 - 16:30	**OR-17 Federica PALMERI**, *La Sapienza Università di Roma* One-Pot Synthesis of Water-Soluble Metallophthalocyanines for Eco-Friendly Sensing Applications
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16:40 - 16:50	**OR-19 Carlo PUNTA**, *Politecnico di Milano* Cellulose-based eco-safe nanostructured materials for water treatment

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18:00 - 19:00 **ASSEMBLEA SOCI GC-CS**

Programma

VENERDÌ 25 OTTOBRE 2024

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Chairperson: **G. Licini, D. Zuccaccia**

09:00 - 09:30	**KN-3 Prof. Vito CAPRIATI**, Università di Bari Harnessing the Weirdness of Water and Deep Eutectic Solvents for a Sustainable Future and Reaction Discovery

Comunicazioni orali (OR)

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09:40 - 09:50	**OR-21 Federico LOCARDI**, *Università di Genova* Colloidal nanocrystals synthesized in green solvent
09:50 - 10:00	**OR-22 Andrea MEZZETTA**, *Consorzio INSTM* Reactive Deep Eutectic Solvents (ReDESs) in the preparation of new generation of pyrrolidinone-based solvents
10:00 - 10:10	**OR-23 Stefano NEJROTTI**, *Università di Torino* Improving sustainability in the construction of conjugated molecular scaffolds: ionic liquids and (waste)water as solvents
10:10 - 10:20	**OR-24 Monica RIGOLETTO**, *Università di Torino* Cellulose fibres from soybean hulls: efficiency and sustainability of different isolation methods
10:20 - 10:30	**OR-25 Gabriele VIADA**, *Università di Torino* BHET-based prepolymers: advancing the sustainability of polyurethane resins
10:30 - 10:40	**OR-26 Federico VERDINI**, *Università di Torino* Dual-Action Approach for Wastewater Purification: Synergistic Impact of Hydrodynamic Cavitation and Electrical Discharge (Cold) Plasma
10:40 - 10:50	**OR-27 Marco NICOSIA**, *Università di Bologna* Effect of activation conditions on properties of biomass derived biochar for H_2 storage
10:50 - 11:00	**OR-28 Alessia GIORDANA**, *Università di Torino* Hydroxyapatite from Eggshells: A Green Approach to Nanofertilizers

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12:00 - 12:10	**OR-32 Daily RODRIGUEZ-PADRON**, *Università Ca' Foscari di Venezia* Biomass-Derived Catalytic Architectures by Mechanochemical Extrusion
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12:20 - 12:30	**OR-34 Maria Chiara CABUA**, *Università degli Studi di Cagliari* Microcrystalline cellulose from Aloe plant waste: preparation, chemical functionalization and application in 3D printing
12:30 - 12:40	**OR-35 Alice CAPPITTI**, *Università degli Studi di Firenze* Biomass valorisation towards new materials

12:40 - 13:00	**CHIUSURA LAVORI**

POSTER

P-1 Clelia AIMONE, *Università di Torino*
Chestnut Wood Valorization: A Green Strategy for Extraction, Fractionation, and Biopolymer Design

P-2 Chiara BRUSCHETTA, *Università di Torino*
Ultrasound-Assisted Procedure for the Preparation of Ru- and Pd-Iron Oxide Catalysts

P-3 Camilla CALLEGARI, Università di Pavia
Carbon nitride materials as sustainable photocatalysts in C-H bonds functionalization processes

P-4 Laura PALOMBI, *Università degli studi dell'Aquila*
Electrocatalytic activation of acetone cyanohydrin with hydrogen evolution: synthesis of β-cyano ketones and α-aminonitriles

P-5 Alireza SAFDARI, *Università degli Studi di Milano*
Flotation Technique for Recycling Black Mass from Spent Lithium-ion Batteries

P-6 Federica TUFANO, *Università degli Studi di Salerno*
Sustainable Polymers obtained by Schiff Base-Based Zn and Mg Complexes

P-7 Claudia ANTONETTI, *Università di Pisa*
Renewable diphenolic acid synthesis in batch and continuous reactor: an eco-friendly substitute for bisphenol A

P-8 Giorgio Capaldi, *Università di Torino*
PHENOCYCLES: Exploiting the Multifuctional Proprierties of Polyphenols from Waste to High Value Products

P-9 Antonella Cartoni, *Università di Roma La Sapienza*
GREEN TECHNOLOGY FOR LACTATE OXIDASE-BASED BIOSENSOR FABRICATION

P-10 Eleonora Conterosito, *Università del Piemonte Orientale*
μ-FTIR reflectance spectroscopy coupled with multivariate analysis: rapid and robust method for identifying the extent of photodegradation on microplastics

P-11 Ilaria Di Stefano, Università di Bologna
Solid Phase Peptide Synthesis using side-chain unprotected arginine and histidine, with Oxyma Pure/TBEC in green solvents

P-12 Sara ESPOSITO, *Università di Salerno*
Synthesis of Block and Multi-Block Copolymers Based on Polyesters from ROCOP of Phthalic Anhydride and Epoxides from Renewable Sources

P-13 Alessandro MASSI, *Università di Ferrara*
Organocatalytic Keratin Sponges for the Chemical Fixation of CO2 into Cyclic Carbonates

P-14 Michele OFFIDANI, *Università di Bologna*
In-situ and ex-situ thermocatalytic pyrolysis of plastics: a comparison of two different approaches

P-15 Vanessa SPADAVECCHIA, *Università di Bologna* Natural urease inhibitors from lignocelluloses
P-16 Oscar TRENTIN, *Università di Venezia* Upcycling of chitin to cross-coupling catalysts: tailored supports and opportunities in mechanochemistry
P-17 Federica ZIMBARDI, *Università di Bologna* Green retrofitting of a vintage reaction: production of acetone from renewable sources via pyrolysis of acetates

Premio alla Ricerca *Junior*

Linee di Ricerca

[1] Emilia Paone

[1] *Università degli Studi Mediterranea di Reggio Calabria*
(emilia.paone@unirc.it)

Le attività di ricerca di Emilia Paone si inseriscono nel campo della catalisi eterogenea, con particolare attenzione alla **valorizzazione sostenibile di scarti e residui per la produzione di prodotti ad alto valore aggiunto**.
Le sue ricerche si articolano in diverse aree chiave, ognuna delle quali contribuisce a una gestione più efficiente e sostenibile delle risorse e dei rifiuti, quali:

- **Valorizzazione e Trasformazione catalitica delle biomasse lignocellulosiche** Utilizzando un approccio innovativo, la ricerca si concentra sulla rottura selettiva dei legami C-O nella lignina tramite reazioni di transfer hydrogenolysis, impiegando alcoli come donatori di idrogeno. Questo metodo consente di trasformare la lignina, una risorsa rinnovabile e abbondante, in prodotti chimici di alto valore. Inoltre, la ricerca si estende alla valorizzazione delle altre frazioni della biomassa lignocellulosica, come cellulosa ed emicellulosa, nonché alle molecole modello derivate da biomassa, attraverso processi di transfer hydrogenolysis e transfer hydrogenation per la produzione di sostanze chimiche di elevato valore aggiunto. Viene inoltre approfondita la valorizzazione di scarti lignocellulosici industriali e rifiuti agroindustriali, come il pastazzo di agrumi, tramite lo sviluppo di metodologie sostenibili. Queste metodologie mirano a ridurre l'impatto ambientale dell'industria agroalimentare e a migliorare i processi di estrazione e bioraffinazione, trasformando i rifiuti in risorse utili e contribuendo a una gestione più sostenibile delle risorse.

- **Valorizzazione degli e-waste per la produzione di catalizzatori innovativi**

Questa ricerca esplora sull'uso di materiali di scarto, come le batterie al litio esauste, per la produzione di catalizzatori eterogenei a base di cobalto e nichel.
Questo approccio non solo riduce la quantità di rifiuti, ma promuove anche il riciclo di materiali per la produzione di catalizzatori impiegati nella valorizzazione della biomassa, in un'ottica di economia circolare, che dimostra come i materiali di scarto possano essere trasformati in risorse utili.
In questo contesto si inserisce anche lo **studio di processi sostenibili di fotocatalisi**, in cui scarti come gli e-waste vengono utilizzati per valorizzare altri rifiuti, come quelli agroindustriali. Un esempio è lo sviluppo di reazioni fotocatalitiche per la produzione di idrogeno e composti chimici biobased. Nell'ambito del progetto PRIN 2022 PNRR (PHOTOLION), vengono impiegati catalizzatori derivati da batterie esauste e risorse sostenibili, come il pastazzo di agrumi, per sviluppare processi chimici eco-compatibili.
Questo approccio dimostra come sia possibile valorizzare risorse già disponibili, favorendo una transizione verso una chimica più sostenibile e circolare.

- **Valorizzazione di fish-waste**

Questa linea di ricerca si focalizza in particolar modo sugli scarti della lavorazione del pesce, che attraverso processi ecosostenibili vengono utilizzati per estrarre molecole ad alto valore aggiunto, come oli naturali ricchi di acidi grassi e omega-3. In particolare, si stanno studiando metodologie per l'estrazione e la purificazione di questi composti, utilizzando tecniche innovative come l'estrazione con solventi verdi (limonene). Questi approcci non solo massimizzano il recupero delle sostanze nutritive, ma minimizzano anche l'uso di sostanze chimiche nocive, rendendo il processo più sostenibile. Il residuo solido rimanente prevede l'impiego nella produzione di energia mediante processi di digestione anaerobica o la trasformazione in fertilizzanti naturali. Gli impatti ambientali dell'intero processo vengono valutati utilizzando modelli di valutazione del ciclo di vita (LCA) su scala di laboratorio ed industriale. Queste iniziative mirano a ridurre l'impatto ambientale del settore ittico, promuovendo pratiche di gestione più sostenibili e contribuendo a una maggiore valorizzazione delle risorse marine.

- **Valorizzazione di plastic waste**

La ricerca si concentra sulla valorizzazione chimica dei residui plastici, in particolare attraverso processi di idrogenolisi e idrogenazione delle **poliolefine**. L'ottimizzazione delle condizioni di reazione è cruciale per massimizzare il rendimento e la purezza dei prodotti ottenuti, trasformando gli scarti plastici in combustibili alternativi e sostanze chimiche di valore. La ricerca esplora anche l'uso di **catalizzatori innovativi** per migliorare l'efficienza dei processi e affrontare la sfida della depolimerizzazione di materiali plastici complessi, mediante processi di upcycling catalitico riduttivo. Questo approccio prevede l'uso di solventi biobased (d-limonene e α-pinene), per migliorare la solubilità delle poliolefine e rendere i processi più sostenibili.

Inoltre, l'implementazione di **processi in flusso continuo** rappresenta un ulteriore avanzamento, offrendo un migliore controllo delle condizioni di reazione, rendimenti ottimizzati e una riduzione della formazione di sottoprodotti e dell'impatto ambientale. Questi approcci mirano a promuovere strategie di gestione dei rifiuti plastici più efficaci, contribuendo così a una transizione verso un'economia circolare e a basse emissioni di carbonio, in cui i rifiuti possano diventare risorse preziose per il futuro.

ChemSusChem Lecture Award

Copper Single Atoms Chelated on Ligand-Modified Carbon for Ullmann-type C−O Coupling

Vincenzo Ruta[1] and Gianvito Vilé[1]

[1]*Department of Chemistry, Materials, and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Piazza Leonardo da Vinci 32, IT-20133 Milano, Italy.*
(gianvito.vile@polimi.it)

Cross-coupling reactions are of great importance in chemistry due to their ability to facilitate the construction of complex organic molecules. Among these reactions, the Ullmann-type C−O coupling between phenols and aryl halides is particularly noteworthy and useful for preparing diarylethers. However, this reaction typically relies on homogeneous catalysts that rapidly deactivate under harsh reaction conditions. In this study,[1] we introduce a novel heterogeneous catalyst for the Ullmann-type C−O coupling reaction, comprised of isolated Cu atoms chelated to a tetraethylenepentamine- pyrrole ligand that is immobilized on graphite nanoplatelets. The catalytic study reveals the recyclability of the material, and demonstrates the crucial role of the pyrrole linker in stabilizing the Cu sites. The work expands the potential of single-atom catalyst nanoarchitectures and underscores the significance of ligands in stabilizing metals in cationic forms, providing a novel, tailored catalyst for cross-coupling chemistries.

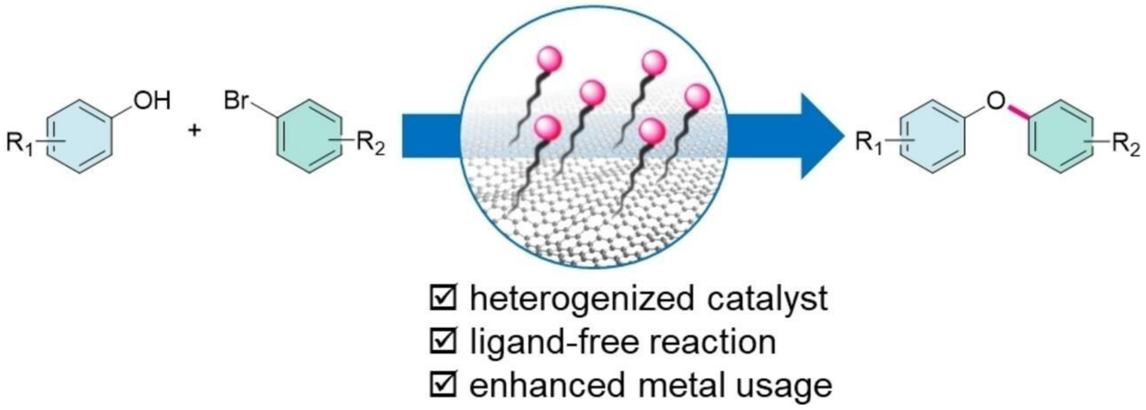

Figure 1. Sketch of the reaction process and catalyst development.

Acknowledgements. GV acknowledges funding from the European Commission Horizon Europe programme (grant agreement 101057430, SusPharma).

References:

[1] Ruta, V. et al.. *ChemSusChem* **2024**, *17,* e202301529.

KN-1

Pyrolysis: a key value for the circular economy

[1] Michela Signoretto

[1] *Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Venice, Italy*
(michela.signoretto@unive.it)

The presentation aims to demonstrate that wastes properly treated by pyrolysis can be efficiently upgraded and not only recycled. Pyrolysis, a thermal process conducted in the absence of oxygen, is a versatile technique that allows the treatment of different types of industrial or civil waste. The obtained biochars, as carbon rich materials with tunable properties and a chemical composition of various doping and functionalized elements, are a promising option for many different applications.

In this work, some examples of different applications of biochars will be presented. Biochars were obtained by pyrolysis of different biomasses such as hazelnut shells, artichokes, leather tannery waste, mixed plastic waste.

Firstly, activated biochars from hazelnut shells and leather tannery waste, were selected as novel supports for metal catalysts for biomass valorization reactions[1]. The catalytic performances will be discussed in terms of activity, selectivity, and stability, comparing them to the performances of commercial references.

Moreover, the biochars, due to their absorption capacity, were also used as one of the ingredients of cosmetic formulations[2], such as face creams or hair masks. In fact, artichoke extracts were highly efficient in the formulation of cosmetics for hair polishing and protective pre-drying treatment, pre-shampoo for skin and roots, and after-wash masks. The biochars obtained from fibrous waste after the extraction of the actives were very fruitful in the final formulations. The high surface area and porous texture helped with their high absorbency efficiency.

Finally, a process in collaboration with Versalis for recovering the carbon contained in a char (solid carbonaceous residue) from a pyrolysis of mixed plastic waste or secondary raw material obtained from the recycling and/or treatment of plastic wastes will be described[3].

Overall, selecting the proper biomass waste and optimizing the best pyrolysis and activation conditions could help in achieving the best properties for each application.

References:

[1] Longo, L.;Taghavi, S.; Ghedini, E.; Menegazzo, F.; Di Michele, A.; Cruciani, G.; Signoretto, M. *ChemSusChem* **2022**, *15*, 13.

[2] Signoretto, M.; Menegazzo, F.; Ghedini, E. **2019** PCT/IB2019/053710.

[3] Vecchini, N.; Galeotti, A.; Gradella, C.; Signoretto, M.; Longo, L. **2024** WO2024141843A1.

KN – 2

Life cycle perspective supporting green chemistry

[1] Fabrizio Passarini, [1] Daniele Cespi, [1] Luca Ciacci

[1] *Department of Industrial Chemistry "Toso Montanari" – University of Bologna (Italy), v. Gobetti 85, 40129, Bologna* (*fabrizio.passarini@unibo.it*)

A fundamental contribution to support the implementation of green chemistry arises from the assessment of chemical products and processes through a life cycle perspective. This helps going beyond the classical green metrics, that could provide some useful indications, but often neglect important steps of the chemicals value chain or some environmental impact categories, thus they can be used mainly as screening methods. Assuming a life cycle approach allows the inclusion of all input and output flows (mass, energy, emissions, waste), for all classes of chemicals, considering the whole production chain, in order to avoid the trade-off of impacts from one environmental category to another.

Life Cycle Assessment, which is defined by ISO Standards (particularly 14040 and 14044), has a long history of applications in the chemical sector, assuming some peculiar features. In general, a "cradle-to-gate" approach is more frequently adopted, since one chemical can have multiple uses. The choice of a proper functional unit could be an issue, due to the complexity of chemical reactions, that could lead to different outputs simultaneously. Data collection is often a difficult task, due to confidentiality issues usually raised by private companies. The application of one or a few principles of Green Chemistry to a process does not ensure that it will be more sustainable, because only an overall assessment of environmental effects can provide a thorough view of the system. If applied at an early stage, LCA could be an important aid in the eco-design of chemicals.

LCA has been successfully applied also in the pharmaceutical sector, in the production of nanomaterials, in the formulations, but also in the field of analytical chemistry.

Furthermore, it can be fruitfully integrated with other tools, to obtain an important insight for the development of new scenarios. In particular, it can be coupled with MFA (Material Flow Analysis) to better understand present and future situations regarding the availability and the recovery of critical resources. It can be used in support of the DoE (Design of Experiment), to maximise the environmental benefits in the production of chemicals or in the waste and wastewater treatment. It could be complemented by social and economic analysis, to have a complete assessment of the overall sustainability.

In conclusion, LCA is certainly the most comprehensive methodology to check the environmental effects of chemical products and processes and its application could bring important benefits to the development of green chemistry.

KN – 3

Harnessing the Weirdness of Water and Deep Eutectic Solvents for a Sustainable Future and Reaction Discovery

[1] Vito Capriati

[1] Dipartimento di Farmacia-Scienze del Farmaco, Università di Bari Aldo Moro,
Consorzio C.I.N.M.P.I.S., Via E. Orabona 4, – 70125 Bari, Italy.
(vito.capriati@uniba.it)

The environmental impact of chemical synthesis has recently posed severe and compelling demands for sustainable chemistry, driving research into cost-effective, eco-friendly alternatives to harsh and volatile organic compounds (VOCs). Deep eutectic solvents (DESs) have proven today to be versatile, sustainable solvents that transverse several fields of research.[1] Besides DESs, also water, which is the Nature's favourite solvent, offers a readily available and non-toxic alternative to VOCs. Over the past quarter century, many scientists have become aware that switching to water can greatly improve a reaction.[2]

In this communication, an overview of the potential applications of DESs and water in organic synthesis and catalysis will be given.[3] In particular, the regioselective functionalization of a wide range of organic substrates using highly polarized organometallic reagents (e.g., organolithium, organozinc, and organosodium reagents) under aerobic conditions in DESs, and more challenging also in water, will be discussed.[4] Their lack of protonation in such strongly hydrogen-bonded systems underscores some unusual aspects of their chemistry, challenging the commonly accepted view of air- and moisture-sensitive reagents, thereby opening the door to the discovery of novel reactions that contribute to a sustainable futur

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KN – ELSEVIER

Chemistry Landscape: Research Insights, Impact, Trends, & Opportunities under a Green Chemistry lenses

[1] Marta Da Pian, [1] Basak Candemir, [1] Ahmed Helmy, [1] Khalid Shalan, [1] Willeke Bakker, [1] Giulia Moncelsi

[1] Elsevier B.V, (Raderweg 29, 1043 NX Amsterdam, The Netherlands).
(m.dapian@elsevier.com)

With new research directions and dynamic scientific networks, the field of Chemistry is evolving rapidly. It is now crucial to reevaluate research priorities to stay competitive in light of the emergence of AI and increased attention to cutting-edge fields like Green Chemistry. Which fields of chemistry should you focus on, and how can you build collaborations to optimize your research output?

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- Future of Chemistry Research[1]

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Figure 1. Future of Chemistry

Acknowledgements.
Andy Steel for its contribution to the project's landing page

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OR – 1

Aerobic C-C bond cleavage of 1,2-diols: photoactivated vanadium-driven catalysis

[1] W. Bertoluzzo, [1] F. Sanz Azcona, [1] E. Cesprini, [1] T. Carofiglio, and [1] G. Licini
[1] *Department of Chemical Sciences, University of Padova*
(william.bertoluzzo@phd.unipd.it)

The cleavage of C–C bonds in 1,2-diols (known as glycol cleavage) stands as a significant organic reaction, originating circa 1930 through the pioneering work of Malaprade and Criegee[1]. Over the years, several aerobic diol cleavage reactions have been documented, catalysed by Mo, Ru, Pd, Ag[2] or V[3,4]. More recently light-mediated oxidative cleavages of glycols have been reported, catalysed by iron^{III}-porphyrin, quinones[5], or 9,10-dicyanoanthracene[6]. However, most of these methodologies rely on harsh reaction conditions (high temperature or prolonged reaction times), afford over-oxidations to carboxylic acids or they are limited to aromatic substrates.

In this communication, we will report on the photo-driven aerobic oxidative cleavage of glycols under blue light irradiation catalysed by (V(V)-aminotriphenolates at room temperature, affording quantitative conversions and high yields of the corresponding carbonyl compounds for a wide variety of substrates, both aromatic and aliphatic, with a much simpler and greener approach. We will report on the optimisation of the system using green solvents, the substrate scope of the reaction and preliminary results of the photo-catalytic reaction in a flow system. (Figure 1)

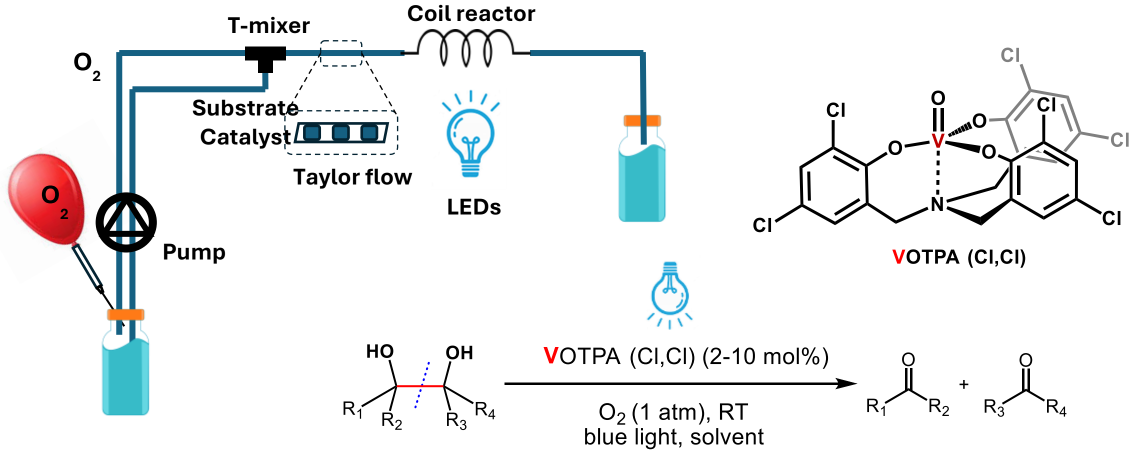

Figure 2. Photo-induced aerobic oxidative cleavage of glycols catalyzed by VOTPA (Cl,Cl).

Acknowledgements: The project was carried out in the frame of MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (Piano Nazionale di Ripresa e Resilienza (PNRR)–Missione 4 Componente 2, Investimento 1.3) (W. B. and E. C. fellowships) and progetto PON "Ricerca e Innovazione" 2014-2020 Azione IV.5 – Dottorati su tematiche green (F. S. A. fellowship).

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OR – 2

Merging Heterogeneous Photo- and Organo- Catalysis in continuous flow for Cross Dehydrogenative Coupling (CDC) between Glycine Derivatives and Ketones to Afford Non Proteinogenic Amino Acids (NPAAs)

[1] Graziano Di Carmine, [2] Daniele Ragno, [1] Olga Bortolini, [2] Carmela De Risi, [2] Lorenzo Poletti and [2] Alessandro Massi

[1]*Department of Environmental and Prevention Sciences, University of Ferrara, Via L. Borsari, 46, 44121 Ferrara (Italy).*
[2] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari, 46, 44121 Ferrara (Italy)*
(graziano.dicarmine@unife.it)

We present a new sustainable and efficient approach, which consists of a telescoped CDC/Mannich reaction in continuous flow to access enantiopure carbonyl derivatives of AAs (Figure 1).[1] The protocol consists of a C-H activation of glycine, by photocatalysis enabled by mesoporous graphitic Carbon Nitride (mpg-CN), affording the corresponding electrophilic imine which is directly inlet into the second reactor, charged with a proline-like organocatalyst supported onto SBA-15 to promote the Mannich reaction with an aldehyde or a ketone in enantioselective fashion (Yield up to 91%, ee up to 99%). Gram-scale (1.8 gr) and long-term stability studies were performed providing excellent results in terms of durability of the system, which can be restored to its full efficiency by washing it after 24 hours of operative use for at least 200 hours. Furthermore, NMR measurements ({1H}^{13}C CPMAS NMR, T_1, T_2 relaxometry measurements and diffusometry) were employed to shine a light on deactivation of the catalysts during the operative conditions.

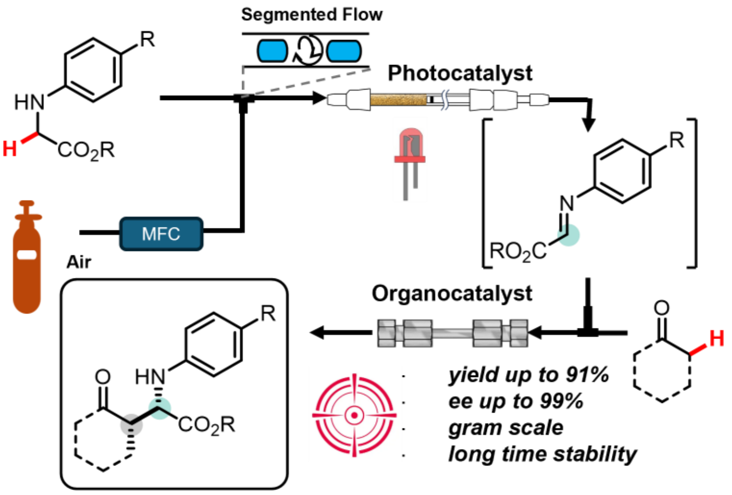

Figure 3. telescoped CDC/Mannich reaction in continuous flow apparatus

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OR – 3

Ru/Pd catalytic system for the reductive amination of furfural

[1] Matteo Corradini, [1] Francesca Liuzzi, [1]Alessandro Allegri, [1]Nikolaos Dimitratos, [1]Stefania Albonetti

[1] *Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Bologna, Italy*
(matteo.corradini7@studio.unibo.it)

In the last decades, supported metal nanoparticles (NPs) have been widely employed for the preparation of high-performance heterogeneous catalysts. Sol-immobilization is an efficient way for the synthesis of such catalysts, allowing the deposition of metal NPs, previously formed in an aqueous solution, on the support's surface[1]. The aim of the present work was to explore the preparation of some ruthenium-based catalytic systems supported on TiO_2, also evaluating how the activity changes adding palladium in the active phase with various metal:metal ratio. The catalytic performances of the prepared solids have been evaluated in the reductive amination of furfural to furfurylamine.

After an initial study of the influence of various reaction parameters, such as reaction time and temperature, H_2 pressure and ammonia concentration, conducted on ruthenium catalyst, it was possible to identify optimized conditions that allowed achieving a selectivity for furfurylamine around 95%. The effect of various parameters and the results of reactions conducted without a catalyst were then used to delve into the intermediates involved in the process, an investigation that led to the hypothesis of a reaction scheme slightly different from the one usually proposed in the literature regarding the initial species formed (**Figure 1**). Specifically, it was observed that in the first minutes of the reaction, a trimer of furfurylimine forms, which is then converted to N-furfurylidenefurfurylamine (FDA) and, subsequently, to the primary amine of interest. Finally, to improve the reducing properties of the catalyst, bimetallic Ru/Pd catalysts were prepared, and with small amounts of palladium an improvement in catalytic activity was recorded. However, further increase in the palladium fraction leads to the reduction of the aromatic furan ring.

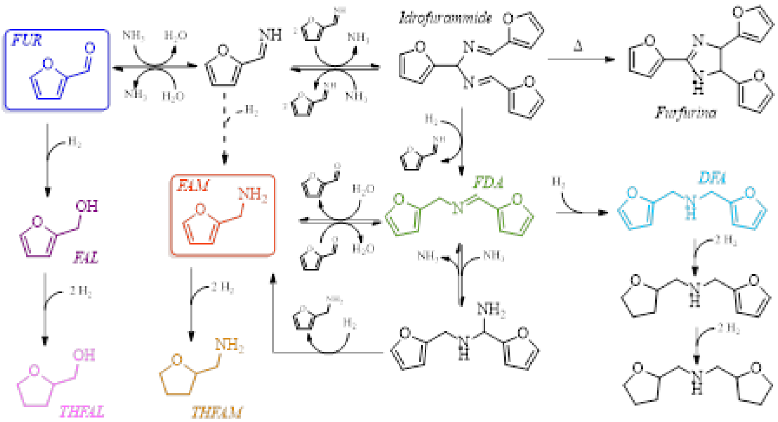

Figure 1 Proposed reaction scheme for the reductive amination of furfural (FUR) to furfurylamine (FAM).

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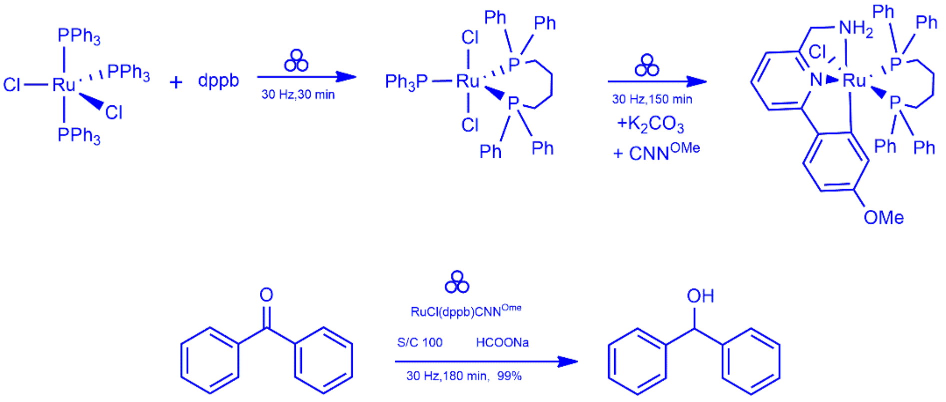
OR – 4

Synthesis and application in catalysis of Ru complexes via mechanochemistry route

[1] Daniele Zuccaccia, [1] Eleonora Aneggi, [1] Talha Munir, [1] Walter Baratta

[1] *DI4A, University of Udine, Udine, Italy*
(daniele.zuccaccia@uniud.it)

Mechanochemistry is commonly associated to green chemistry for its ability to reduce waste production in chemical synthesis and reactions. In addition to their efficiency and practicality, mechanochemical reactions are also recognized for their sustainability.[1] Ruthenium complexes have been widely investigated and applied in homogeneous catalytic reactions and several Ru-catalysts has been developed, and among all, ground-breaking results have been obtained by Grubbs[2] for the olefin metathesis and Noyori for the asymmetric hydrogenation of the C═O bonds.[3] Here, we investigated the possibility of new synthesis route by mechanochemical methods that can be applied for the preparation of Ru-based complexes precursors or catalysts. We started with commonly Ru-precursors (i.e $RuCl_2(PPh_3)_3$), $[(cymene)RuCl_2]_2$, $[(COD)RuCl_2]_2$ $[(CO)RuCl_2]_2$) and ligand such as alkali metal carboxylate, diphosphines or N^N ligands to obtain the correspondent Ru-complexes (Figure). We studied the role of each reaction variable, such as molar ratio of the reagents, number of balls, frequency and time of milling. These results suggest that mechanochemical procedures can be a simple and versatile method for the preparation of Ru-based complexes by solventless strategies. Finally (Figure), catalysts of the type RuCl(dppb)(CCN^{OMe}) can be use in the hydrogenation of benzophenone by sodium formiate (the hydrogen donor)



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OR – 5

Pyrolysis of *Posidonia Oceanica* balls: A comparative evaluation of conventional and microwave-assisted approaches

[1] Domenico Licursi, [1] Claudia Antonetti, [1] Anna Maria Raspolli Galletti, [2] Riccardo Gallorini, [1,2] Luca Rosi

[1] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, Pisa, Italy.*
[2] *Department of Chemistry "Ugo Schiff",University of Florence, Via della Lastruccia 13, Sesto Fiorentino, Italy.*
(domenico.licursi@unipi.it)

Posidonia Oceanica is an abundant plant of the Mediterranean Basin, but its residues should be properly managed to minimize environmental, economic and social concerns. *Posidonia Oceanica* debris are wastes that could be advantageously exploited as source of biofuels and bioproducts. In this work, fibrous spheres of *Posidonia Oceanica* have been considered for studying the pyrolysis approach, comparing the traditional heating and the microwave-assisted one, aimed at the production of solid biochar, liquid bio-oil and gaseous syngas. The pyrolysis technologies were compared keeping similar pyrolysis conditions, e.g. heating rate, set-point temperature and residence time, all affecting the product distribution and the corresponding compositions. The comparison between the conventional and microwave-assisted approaches ascertained a reduction of secondary cracking reactions in this latter case, highlighting the improved control of the degradation mechanisms [1]. The addition of a deflagmator unit increased the residence times of the hot vapors within the microwave reactor, favoring the secondary cracking reactions. These different set-ups lead to differences in the chemical compositions, mainly involving the bio-oil stream, in terms of the concentration of the oxygenates and the amount of water. Remarkably, the use of the same *Posidonia Oceanica* biochar both as an efficient microwave absorber and a reducing agent, was effective for improving the syngas yield, which selectively included H_2 and CO (about 46 and 53 vol% of the microwave test versus 10 and 25 vol% of the conventional one, respectively). Such a significant difference was due to the occurrence of gasification reactions with microwave technology, enabled by local hotspots, making attractive the co-pyrolysis approach for the production of a syngas of higher quality. Finally, preliminary LCA evaluations revealed that the environmental impact of conventional pyrolysis remains lower than that of the microwave one, due to the still higher impact of the electricity cost from fossil resources and energy consumption of the latter technology, which represent the main bottlenecks to be overcome in order to reduce the total environmental impact of this technology, thus favoring its scale-up in the next future.

Acknowledgements
The authors are grateful to the European Union and Italian Ministero dell'Università e della Ricerca for the financial support provided through the PNRR project NEST. Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), (CUP I53C22001450006) Spoke n. 3 BIOENERGY & NEW BIOFUELS FOR SUSTAINABLE FUTURE.

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OR – 6

Solventless synthesis of novel non-ionic bio-based surfactants exploiting glycerol carbonate

[1]Fabio Bucciol, [1]Laura Tedesco, [1]Silvia Tabasso, [2]Pierluigi Quagliotto,
[1]Emanuela Calcio Gaudino, [1]Giancarlo Cravotto

[1] Università di Torino, Dipartimento di Scienza e Tecnologia del Farmaco, via P. Giuria 9, 10125, (TO)
[2] Università di Torino, Dipartimento di Chimica, via P. Giuria 7, 10125, (TO).
(fabio.bucciol@unito.it)

Surfactants are a billion worth industry just in Europe and non-ionic surfactants have the largest market share. Shifting this huge industry from oil-based chemicals to bio-based alternatives is a desirable effort for research. This work aims to take on the challenge for the synthesis of bio-based surfactants with a green approach and in mild conditions (**Fig. 1**). Lignin-derived platform chemicals can be isolated and oxidized to carboxylic acids[1,2] with a remaining phenolic moiety ready for further modifications. Vanillic acid (VA) was thus considered as a lignin model compound. VA esters were prepared from C4-C10 alcohols to obtain the non-polar tail. Complete conversion was observed after just 45 minutes at 120 °C or even 20 minutes using microwaves. For the polar head, direct coupling with glycerol carbonate in neat condition was exploited (100 °C, 24 h) as an alternative to toxic epichlorohydrin[3], using K_2CO_3 as a solid catalyst. Conversions were up to 90.7%, reaching yields of 63.1%. This outperformed epichlorohydrin, which only yielded 20.5% of the desired product. The obtained products were characterized by determining their critical micelle concentration (CMC) via the pyrene fluorescence method to prove their surface activity, showing a correlation between the length of the non-polar tail and the CMC. The C8-derivative showed the lowest CMC, with an estimated value of 5.05 E^{-5} M.

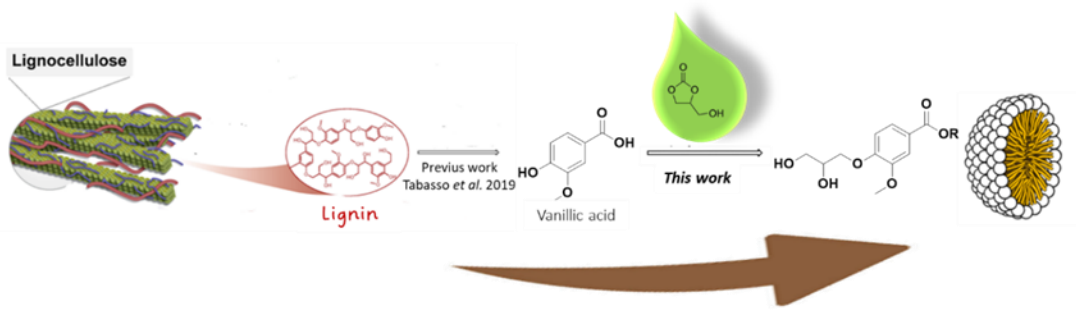

Figure 1. green synthesis of non-ionic surfactants from vanillic acid.

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OR – 7

A Sustainable Chemo Enzymatic Approach to the Synthesis of Liraglutide

[1] Silvia Rizzo, [2] Ana Toplak, [2] Marco Macis, [2] Antonio Ricci, [1] Alessandra Tolomelli, [1] Walter Cabri, [1] Lucia Ferrazzano

[1] Department of Chemistry "Giacomo Ciamician", University of Bologna, via Gobetti 85, 40129 Bologna, Italy.
[2] Fresenius Kabi iPSUM, via San Leonardo 23, 45010 Villadose, Italy.
(silvia.rizzo12@unibo.it)

Peptides represent strong drug candidates thanks to their high biological activity, low toxicity, and enhanced stability when unnatural amino acids and lipophilic side chains are introduced.[1] The standard industrial protocol, solid-phase peptide synthesis (SPPS) is a modular approach that can achieve wide structural variety and offers the chance for process automation. Due to its iterative nature, SPPS is limited to medium length peptides (~20 a.a.), and the extensive use of hazardous solvents, typically DMF, makes it far from sustainable.In the past, the strict quality requirements and the market's competitive pace have justified the preference for robust technologies rather than sustainable ones; today, the adoption of green synthetic processes is essential to transform the industrial landscape of the pharmaceutical sector into a long-term sustainable reality. We proposed an innovative technology focused on more sustainable solvents[3] and a fragment-based approach that can address the current issues faced by peptide synthesis. Green chemo enzymatic peptide synthesis (CEPS) is a convergent approach that forms long peptides by matching the sustainable chemical synthesis of peptide fragments with their selective condensation catalyzed by an enzyme.[4]

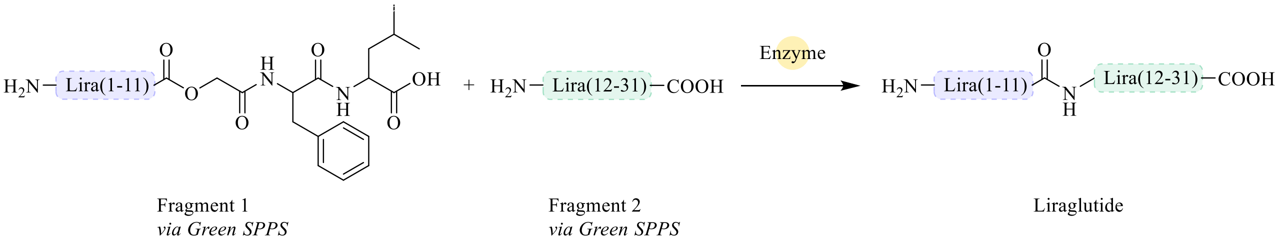

Figure 1. Scheme for the sustainable chemo enzymatic synthesis of Liraglutide

As proof of concept for this technology we selected Liraglutide, a 31-mer peptide analogue of GLP-1 employed for the treatment of type-1 diabetes. Liraglutide is an ideal substrate as its standard SPPS would require around 60 steps, meaning large amounts of hazardous solvents and low yield. In this work, the two peptide fragments 1-11 and 12-31 were obtained via solid-phase synthesis with sustainable solvents, a specific recognition sequence was introduced to ensure enzyme selectivity, and a subtilisin mutant was employed for the enzymatic coupling generating Liraglutide.

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OR – 8

Valorisation of platform chemicals from biopolymers through Hydrogen Atom Transfer (HAT) photocatalysis

[1] Alexandra Jorea, [2] Adriano Parodi, [2] Chiara Samorì, [1] Davide Ravelli

[1] *PhotoGreen Lab, Dipartimento di Chimica, Università di Pavia, viale Taramelli 12, 27100 Pavia, Italia*
[2] *Dipartimento di Chimica "Giacomo Ciamician", via S. Alberto 163, 48123 Ravenna, Italia*
(alexandra.jorea01@universitadipavia.it)

Platform chemicals are defined as bio-based chemicals whose constituting elements totally originate from biomass and could be used as building blocks for the production of refined chemicals, that can be converted into a large number of high-value bio-based chemicals or materials.[1] Herein, we present a methodology for the photocatalyzed functionalization of bio-based platform chemicals derived from the biopolymer polyhydroxybutyrate (PHB), used as traps to intercept photogenerated radical intermediates:[2] trans-2-butenoic acid (i.e. crotonic acid) and its esters.

In our work, we exploited the excellent properties of the tetrabutylammonium decatungstate photocatalyst (TBADT, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$),able to homolytically cleave C–H bonds in a variety of aliphatic derivatives R–H (see **1** in Figure 1), upon absorption of a photon Consequently, the photogenerated radicals (**R$^\bullet$**) from oxygenated heterocycles, cycloalkanes, aromatic or aliphatic aldehydes are trapped by the (bio-based) electron poor olefin (**2**) with formation of a new C–C bond. The adduct radical then undergoes a back-HAT step, in order to obtain the final product (**3**), while TBADT returns to the original state.[3]

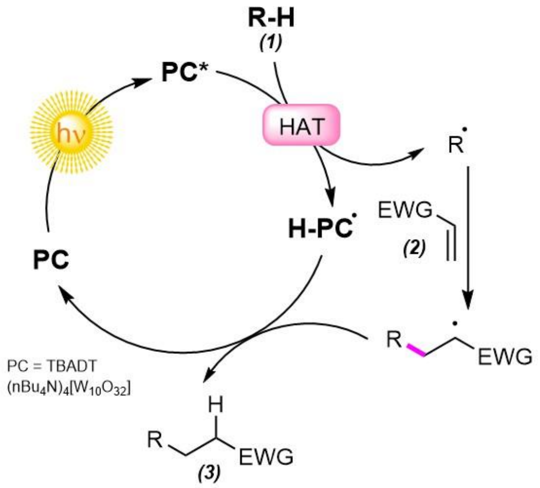

Figure 1. General scheme of photofuntionalitation of platform chemicals via Hydrogen Atom Transfer

Reactions were first carried out under batch conditions and then by implementing a flow approach,[4] which allowed to increase the reaction yields and significantly reduce reaction times (from 24 hours in batch to 4 hours in flow).

Acknowledgements. The PhD project of A. J. was supported by the "PON Ricerca e Innovazione" program (action IV.5; D.M. 1061-2021).

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OR – 9

Chemo-enzymatic synthesis of vorinostat

[1] S. Princiotto, [1] F. Annunziata, [2] L. Tamborini, [1] M. Christodoulou, [1] M.L. Contente, [1] A. Pinto, [1] S. Dallavalle

[1] Department of Food, Environmental and Nutritional Sciences, University of Milan, via Celoria, 2, 20133, Milan
[2] Department of Pharmaceutical Sciences, University of Milan, via Mangiagalli, 25, 20133, Milan
(salvatore.princiotto@unimi.it)

Thanks to its ability to chelate metal ions, hydroxamic acid is one of the most interesting functional groups in medicinal chemistry, especially in the context of metalloenzyme inhibition. Vorinostat, also known as suberoylaniline hydroxamic acid (SAHA), is a pan HDAC inhibitor approved by the FDA in 2006 for the treatment of relapsed/refractory cutaneous T cell NHL, inhibiting cell proliferation and selectively inducing apoptosis in hematologic and solid tumor malignancies. [1] Its large-scale preparation has been widely studied and essentially consists of the cyclic suberic anhydride opening by aniline, followed by acid activation with highly reactive chloroformates and condensation with hydroxylamine. Herein, we report the design of a new chemoenzymatic pathway for the synthesis of vorinostat. The preparation of the suberoylaniline acid was performed in water, in presence of *Mycobacterium smegmatis* acyl transferase (MsAcT), [2] and further functionalized with an *O*-protected hydroxylamine, via lipase-catalyzed condensation. Final deprotection in presence of acidic cationic resins afforded pure vorinostat in 60% yield. In order to improve the productivity of the process, all the steps were performed testing several solvent mixtures, based on the most recent guidelines about solvent sustainability. In the best case, pure vorinostat was obtained in a 3-step-5-hour synthesis in 79% overall yield. Finally, the entire procedure was further optimized and transferred to a continuous flow system, where the final product can be obtained in a time-saving automated way, large scale, high yield and high purity, paving the way for a more sustainable preparation of pharmacologically active hydroxamic acid derivatives.

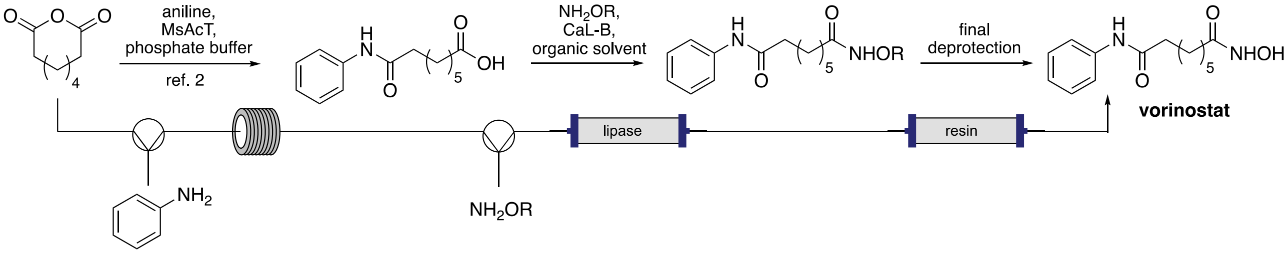

Figure 1: Schematic chemo-enzymatic preparation of vorinostat**.**

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OR – 10

Adding Value to Renewable Resources: 3 Stories

[1,2] Massimo Carraro, [3] Giuseppe Satta, [4]Andrea Beccu, [1] Silvia Gaspa, [1] Lidia De Luca, [1,2] Luisa Pisano

[1] Department of Chemical, Physical, Mathematical and Natural Sciences, University of Sassari, Via Vienna 2, Sassari, 07100, Italy
[2] Consorzio Interuniversitario Reattività Chimica e Catalisi, Via C. Ulpiani 27, Bari, 70126, Italy
[3] Slovenian NMR Centre, National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
4 Institute of Biomolecular Chemistry, CNR, Trav. La Crucca 3, 07100, Sassari, Italy
(mcarraro@uniss.it)

”A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable” states 7th principle of Green Chemistry[1]. Realization of this principle for large-scale commodities of very low value, such as fuels (e.g. biodiesel), poses a problem of land use and low revenues. Designing new products, such as fine chemicals or drugs from renewable resources, therefore, can be a boost to add value to the biorefinery economy. We want to report the development of three fine chemicals coming from glycerol[2], glucose and amino acids to obtain , respectively, an ingredient suitable for cosmetic use, a bicyclic heterocycle of interest for medicinal chemistry and as oxidation catalyst, and finally a ligand[3] for G-quadruplexes.

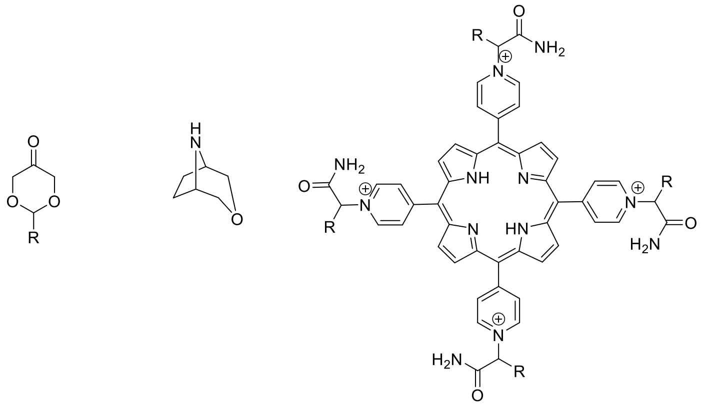

Figure 4. fine chemicals from glycerol, glucose and aminoacids

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OR – 11

Greener Synthetic Strategy for New Triarylamine Derivatives for Optoelectronic Applications

[1] V. Raglione, [2,1] F. Palmeri, [1] G. Zanotti

[1] *Institute of Structure of Matter, National Research Council (CNR), Strada provinciale 35d/9, 00010 Montelibretti, Italy.*
[2] *Department of Chemistry, La Sapienza University, Ple Aldo Moro, 5, 00185 Rome, Italy.*
(venanzio.raglione@mlib.ism.cnr.it)

In this work we successfully synthesized a series of novel three-legged triphenylamine derivatives, employing a sustainable and efficient approach using glycerol as a solvent, in short times and in high yields, up to 94%, using Sonogashira couplings.[1] Lower E-factors and lower costs than standard conditions have been achieved. These compounds, characterized by their distinctive optical and electrical properties, demonstrate significant potential for integration into energy conversion devices such as perovskite solar cells[2] and luminescent solar concentrators.[3]

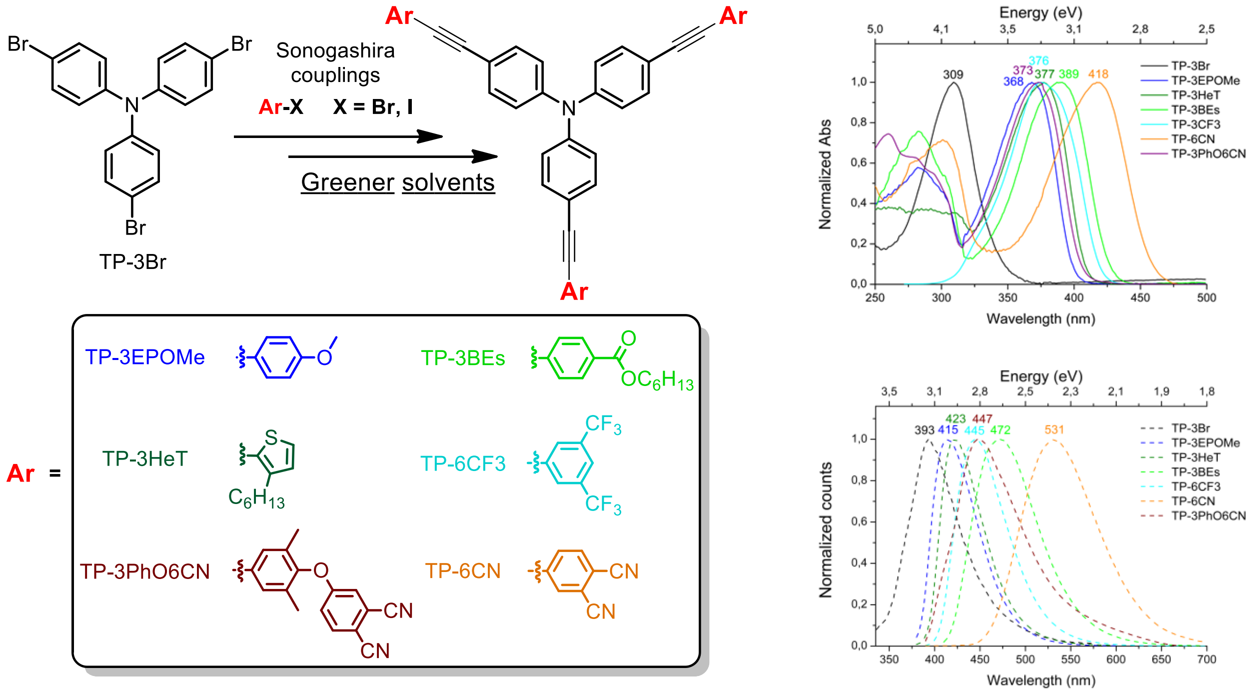

Figure 5. Greener synthetic strategy for the synthesis of TPA derivatives and their absorption and emission spectra.

Acknowledgements.
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OR – 12

Condensation of ethyl levulinate with phenol on Amberlyst-15

[1,2] Vincenzo Russo, [1,2] Federica Orabona, [2] Tapio Salmi, [1] Martino Di Serio

[1] *University of Naples Federico II, Department of Chemical Sciences, via Cintia. IT-80126 Naples.*
[2] *Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering, Henrikinkatu 2. FI-20500 Turku/Åbo*
(*v.russo@unina.it*)

Diphenolic acid (DPA) and its ester derivatives (DPEs) are considered as the most promising bio-based alternatives to the toxic bisphenol A in the synthesis of epoxy resins and polycarbonates [1], and as a precursor of non-isocyanate polyurethanes [2]. DPA is produced by solvent-free condensation of two molecules of phenol and levulinic acid in the presence of Brønsted acid catalysts, generating two stereo-isomers: p,p'-DPA, has a higher market value as it mimics the chemical structure of BPA. In this work, ethyl levulinate has been employed as the substrate in the condensation reaction. ^{1}H- and ^{13}C-NMR analysis revealed that only the p,p´-DPE isomer is produced in the main reaction under the investigated conditions. The kinetic investigation revealed that the reaction temperature and the Amberlyst-15 load have a positive effect on the ethyl levulinate conversion and the DPE selectivity (Figure 1), while water was revealed to be detrimental on both parameters. A two-step reaction mechanism was proposed considering that the reaction takes place between adsorbed ethyl levulinate and bulk phenol through the formation of an intermediate and in two elementary steps. In particular, the quasi-equilibrium approximation was employed to retrieve the concentration of the intermediate. The resulting kinetic model managed to successfully describe the experimental data.

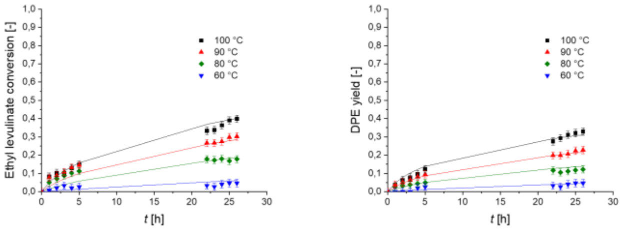

Figure 6. Temperature effect on ethyl levulinate conversion and DPE yield.

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OR – 13

Chemo-enzymatic sustainable flow synthesis of biologically active nature-inspired carbonates and carbamates

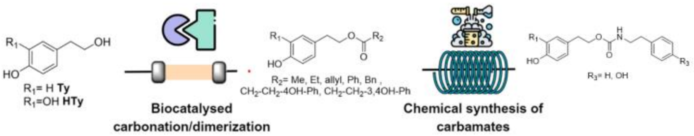
[1, 2]Annunziata Francesca, [2]Vicinanza Sara, [2]Mombelli Lara, [3]Martino, Piera A., [1]Contente, Martina L., [3]Meroni Gabriele, [1]Dallavalle Sabrina, [1]Pinto Andrea, [2]Tamborini Lucia

[1] Department of Food, Environmental and Nutritional Sciences, UniMI, Via Celoria 2, 20133 Milan, Italy
[2] Department of Pharmaceutical Sciences, UniMI, Via L. Mangiagalli 25, 20133 Milan, Italy
[3] Department of Biomedical, Surgical and Dental Sciences, UniMI, Via Pascal 36, 20133 Milan, Italy
(francesca.annunziata@unimi.it)

Food-derived phenolic compounds are well known for their antioxidant and antimicrobial effects. [1]Because of their hydrophilic nature and their intrinsic instability and bioavailability issues, their use as active ingredients is limited. Lipophilization of phenolic derivatives is a valid strategy to obtain amphiphilic compounds that can be used as multifunctional additives in the pharmaceutical, nutraceutical, and cosmetic fields.[2] In particular, the synthesis of carbonates and carbamates is an attractive strategy to increase the lipophilicity of phenolic derivatives. However, their classic synthesis requires the employment of toxic acylating agents, unsafe solvents and drastic experimental conditions.

In this context, we developed a reproducible, green, and scalable chemo-enzymatic flow process (Scheme 1) for the obtainment of a series of lipophilic carbonate and carbamate derivatives of natural tyrosol (Ty) and hydroxytyrosol (HTy). [3,4] Immobilized CaLB was used in a packed bed reactor for the selective carbonation of the primary alcohol of Ty and HTy in green solvents as dimethylcarbonate or *tert*-amyl alcohol. Then, two selected carbonates were reacted in flow with the appropriate amine to obtain the desired carbamates. A telescoped two-step process was set up allowing to reduce the manual handling, time, and costs of the process.

All compounds were tested as antimicrobials and radical scavengers and they showed similar or even better activity compared to the parent compounds, with a significant increase in their lipophilicity.



Scheme 7. Schematic representation of the chemo-enzymatic continuous synthesis of carbonates and carbamates.

Acknowledgements:
The project was realized within the MUSA – Multilayered Urban Sustainability Action – project, funded by the European Union – NextGenerationEU, under the National Recovery and Resilience Plan (NRRP) Mission 4 Component 2 Investment Line 1.5: Strengthening of research structures and creation of R&D "innovation ecosystems", set up of "territorial leaders in R&D".

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OR-14

Electrospray deposition: a green technique to fabricate low-cost and eco-friendly biosensors

[1] M. C. Castrovilli

[1] *Istituto di Struttura della Materia-CNR, (ISM-CNR), Area della Ricerca di Roma 1, 00015, Monterotondo, Italy*
(matteacarmen.castrovilli@cnr.it)

Nowadays, the demand for eco-friendly and reusable sensors and biosensors is constantly increasing due to pollution from disposable devices, as the recent pandemic has highlighted. In the biosensor field, many existing techniques for immobilizing enzymes on electrodes rely on entrapment matrices and harmful chemicals, which pose environmental risks and restrict the biosensors' reusability and storage potential. Consequently, a new approach is needed, that must be sustainable, non-toxic, and enable extended reuse and room-temperature storage of the biosensor. We show how the ambient electrospray deposition (ESD)[1,2] technique can be successfully exploited for manufacturing new promising green friendly electrochemical amperometric enzyme-based biosensors with unprecedented reuse and storage performance[3]. The ESD biosensors show extraordinary enhanced performances compared to other immobilization methods. They retain a 100% activity up to two/three months of storage at ambient temperature and pressure and exposed to humidity and light, and working stability never reached before on the electrode just prepared and on one year old electrode subjected to redeposition. The ESD is a one-step, environmentally friendly method allowing deposition of the bio-recognition layer without using any hazardous chemicals or additional entrapment matrices. Moreover, the recent study on the composition of the commercial sample of laccase used in the manufacturing of biosensors revealed the presence of starch which is a green, non-toxic and biodegradable biopolymer[4]. These remarkable findings indicate that utilizing inexpensive green starch mixed with enzyme in combination with ESD technique makes it possible to produceas cost-efficient and eco-friendly laccase-based biosensors with unprecedented reuse capability following a manufacturing process more sustainable and economically viable for industrial applications[5],[6]

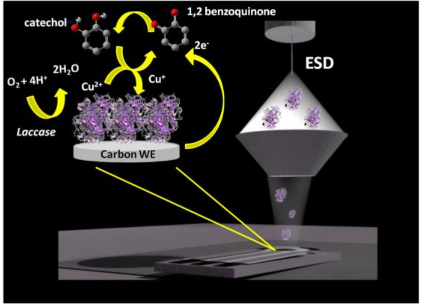

Figure 8. ESD is an environment-friendly immobilization engineered technique to fabricate metal-free laccase-based biosensors with long-term operation and stability, suitable for recycling. On top left it is the laccase mechanism for catechol detection.

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[6] Ateneo **2021** RP12117A5D2DEE6B

OR-15

Electrospray deposition as a green methodology to produce electrochemical sensors for pollutant monitoring: sustainability meets superior analytical performance

[1] Noemi Colozza, [1,2] Federica Palmeri, [1] Venanzio Raglione, [1] Gloria Zanotti, [1,2] Antonella Cartoni, [1] Mattea Carmen Castrovilli

[1] Istituto di Struttura della Materia-CNR, (ISM-CNR), Area della Ricerca di Roma 1, 00015, Monterotondo, Italy
[2] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro,5, 00185, Rome, Italy
(noemi.colozza@mlib.ism.cnr.it)

Sensors are versatile tools that have changed our way of understanding and analyzing the most important aspects of the world around us. The production of sensors for various fields of application grows constantly, raising the challenge of sustainability in both the production processes and their application. Bearing this in mind, Castrovilli et al. recently conceived a green approach to fabricate enzyme-based electrochemical sensors using the ElectroSpray Deposition (ESD) technique.[12] The ESD method needs only a few µL-volume of aqueous solutions (e.g., 30 µL in water with methanol 20% v/v) and it is suitable for low-cost and standardized mass production. ESD was proved to successfully deposit the laccase enzyme on a carbon-based electrode, while preserving the enzyme activity. The resulting enzyme biosensors were characterized by high analytical performance for the detection of catechol at the micromolar level, with unprecedented stability for up to 2 months and possible regeneration after their use, which breaks down waste production and promotes recycling approaches.[3] An unexpected component that contributed to such great performances was identified, namely starch, which was found in the enzyme powder. The role of starch, together with the ESD process, favoured the enzyme immobilization and stability over time.[4]

Our research is now extending the promising features of the ESD method for the deposition of metallophthalocyanines on screen-printed sensors. The metallophthalocyanines are synthesized with a green approach and functionalized with polyethene glycol to be water-soluble. These molecules can interact with the carbon-based surface of the working electrode through π-π stacking and interactions with the -OH groups present on the electrode.[5] The role of the ESD method is compared with drop-casting deposition to highlight the advantages provided in terms of electrochemical performances toward catechol oxidation, using copper- and cobalt-based metallophthalocyanines. The preliminary results show outstanding working and storage stability, disclosing intriguing application possibilities. We believe that these sensors will be pioneers in environmental monitoring, promoting a new vision of analytical method development, based on sustainability from production to application.

Acknowledgements. The authors thank ESILARANTE 202283YHXY Project PRIN 2022 for funding this research.

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OR-16

Complete exploitation of defatted *Cynara cardunculus L.* through an innovative biorefinery approach

[1] Sara Fulignati, [1] Francesca Barsotti, [1] Nicola Di Fidio, [1] Domenico Licursi,
[1] Claudia Antonetti, [1] Anna Maria Raspolli Galletti

[1] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, Pisa, Italy.*
(sara.fulignati@unipi.it)

Cynara cardunculus L. (cardoon) represents an interesting feedstock for the production of chemicals and fuels, being a perennial herbaceous crop able to grow on marginal lands. Up to now, the seeds of the cardoon flower have found applications for bio-diesel production, whilst the cardoon residues are generally pretreated by the steam explosion, which is mainly focused on cellulose exploitation leading to hemicellulose degradation and recovery of low-quality lignin.[1] In this scenario, the present work proposes the effective one-pot fractionation of cardoon through the organosolv pretreatment to recover and valorize all the lignocellulosic fractions. For this purpose, the biphasic system 1-butanol/water acidified with H_2SO_4 was employed to solubilize the sugars deriving from hemicellulose hydrolysis in the aqueous phase and lignin in the organic one, recovering the enriched cellulosic residue as solid. The influence of temperature and acid loading was investigated and the highest lignin and hemicellulose solubilizations of 72 and 97 wt% were ascertained, respectively. Butanol was also employed for the alcoholysis of the recovered enriched cellulosic residue into butyl levulinate, a very promising bio-fuel, through a one-pot reaction catalyzed by H_2SO_4 reaching the highest yield of 46 mol%, higher than that reached starting from not pretreated defatted cardoon (36 mol%), thus proving the effectiveness of this pretreatment. On the other hand, the aqueous phase containing mainly xylose was directly exploited to produce furfural, one of the most important platform chemicals, achieving a yield of 52 mol%. Lastly, very pure lignin was recovered from the organic phase, as proven by FT-IR and elemental analysis characterizations. In conclusion, the complete exploitation of all the cardoon fractions to give a valuable bio-fuel, a platform chemical and lignin was successfully performed.

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OR-17

One-Pot Synthesis of Water-Soluble Metallophthalocyanines for Eco-Friendly Sensing Applications

[1,2] Federica Palmeri, [2] Venanzio Raglione, [2] Gloria Zanotti, [2] Mattea Carmen Castrovilli, [2] Noemi Colozza, [1,2] Antonella Cartoni

[1] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro,5, 00185, Rome, Italy
[2] Istituto di Struttura della Materia (ISM), National Research Council (CNR), Strada provinciale 35d/9, 00010, Montelibretti, Italy
(f.palmeri@uniroma1.it)

The last two decades have witnessed a growing interest in the reduction of the ecological impact of chemical processes, as well as in the development of more environmental friendly methodologies in organic synthesis[1]. In this contribution, a new one-pot procedure for the synthesis of water-soluble metallophthalocyanines is reported. The potential use of such prepared organic materials in the fabrication of sensors has been evaluated in terms of their capability to be immobilized onto the electrode surface and their performance to give an electrochemical response towards target molecules. The former was investigated through the electrospray deposition green technique (ESD) that was previously assessed to immobilize enzymes for the development of biosensors[2,3]. Concerning the latter, preliminary experiments about the detection of cathecol, one of the major industrial by-product that is posing a serious threat to the environment and human health, are presented.

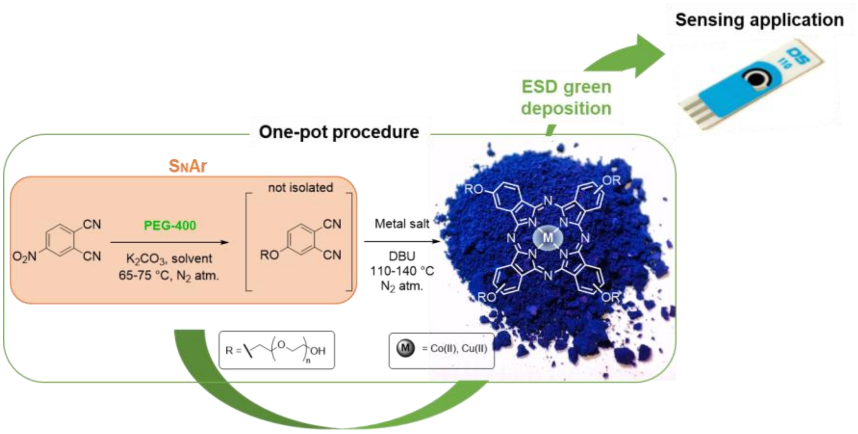

Figure 9. **Design of phthalocyanine-based sensor from the synthetic strategy to the application**

Acknowledgements. The authors wish to acknowledge financial contribution from Sapienza University of Rome research project (Ateneo2023 AR123188B3D54805) and from PNRR Rome Technopole Ecosystem project (B83C22002890005).

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OR-18

Ecosustainable syntheses of pharmaceutical relevant compounds via multicomponent reactions

[1] Sveva Pelliccia

[1] - Department of Pharmacy (DoE 2023-2027), University of Naples Federico II, Via D. Montesano 49, 80131, Naples, Italy
(sveva.pelliccia@unina.it)

Multicomponent reactions (MCRs) represent nowadays an efficient one-pot synthetic strategy to access complex biologically active scaffolds. Thanks to their convergent nature, atom economy, and efficiency, MCRs are considered eco-sustainable reactions due to the reduction of solvents and energy needed for their implementation. Recently, we reported different applications of MCRs for medicinal chemistry purposes, demonstrating the powerful and versatile nature of these processes. We identified a novel interrupted Ugi reaction for the synthesis of N-alkyl- 2,3-diaminoindoles and 2-iminoisatins.[1] Similarly, we applied MCRs for the synthesis of novel anticancer and antiviral agents. In particular, a focused library of imidazopurines with the identification of the first dual BCL2/c-MYC gene promoter G-quadruplex ligand has been synthesized applying a Groebke−Blackburn−Bienaymé three component reaction and a post condensation SN_2.[2] Another multicomponent approach, the Passerini reaction followed by the amine deprotection-acyl migration (PADAM) and oxidation, was employed for the development of novel small peptidomimetic compounds featuring a ketoamide warhead, as covalent reversible inhibitors of the main protease of SARS-CoV-2.[3]

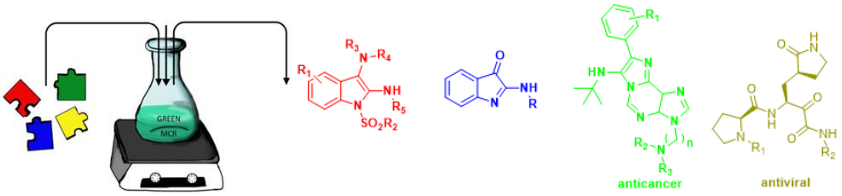

Figure 10. Multiple applications of Multicomponent reactions

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OR-19

Cellulose-based eco-safe nanostructured materials for water treatment

[1] Carlo Punta, [1] Laura Riva

[1] *O^{SCM} Lab, Department of Chemistry, Materials and Chemical Engineering, "Giulio Natta", Politecnico di Milano, via Luigi Mancinelli 7, 20131, Milano, Italia..*

(carlo.punta@polimi.it)

The design and use of manufactured nanomaterials (MNM) as suitable sorbents for an efficient treatment and decontamination of water matrices is attracting more and more interest. At the same time, MNM also raise concerns due to their potential (eco)toxicity and the uncertainty related to their final fate. For this reason, a safe by design strategy is recommended in developing new MNM, which should combine a high decontamination efficiency with verified sustainability and eco-safety[1]. A first step in this route consists into the proper choice of starting material for MNM production[2].

Herein we report an overview of our recent findings on how nanocellulose, simply derived from biomass or agricultural and industrial waste, could represent a sustainable and eco-safe solution for developing new MNM with high sorption performances towards even emerging contaminants for water treatment,[3,4] following the approach of the eco-design.[5,6,7]

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OR-20

Sustainability evaluation to support green chemistry and eco-design

[1] Elza Bontempi

[1] INSTM and Chemistry for Technologies Laboratory, University of Brescia, via Branze 38 - 25123 Brescia.
(elza.bontempi@unibs.it)

Benefits associated with the development of new green markets due to the diffusion of new suitable technologies may be substantial. For example, Meyer[1] evaluated that resource efficiency improvements may allow to obtain 17–24% of raw material savings with a cost savings of more than €600 million in Europe. However, in general, despite continuing dramatic increases in published research about new proposed sustainable materials, there has been poor evaluation of such results.

This work aims to present a tool (ESCAPE) designed to evaluate the sustainability of new emerging technologies and materials, in terms of involved energies and emissions, in comparison, to a reference one[2]. This approach is expressly designed to support laboratory studies that often need preliminary evaluations, allowing the comparison with already available natural and/or commercial materials/technologies. The presentation will demonstrate the potentialities of using the ESCAPE index in materials design synthesis strategies (Fig. 1), with the possibility to account for the difference in countries' energy mix (that derives from the local mix of fossil and non-fossil fuels).

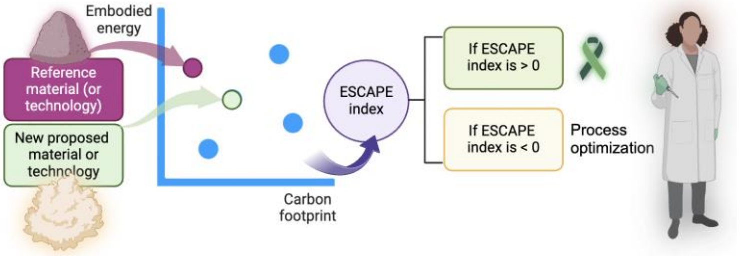

Figure 1: The ESCAPE index evaluation. The figure was realised with Biorender

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OR-21

Colloidal nanocrystals synthesized in green solvent

[1]Federico Locardi, [1,2]Davide Pratolongo, [1,3]Marta Campolucci, [1]Marco Vocciante, [1]Emmanuela Di Giorgio, [3]Liberato Manna, [1]Chiara Lambruschini

[1] *Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy.*
[2] *Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[3] *Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
(federico.locardi@unige.it)

The massive spread of the nanotechnology calls for searching alternative processes that can reduce the impact, both from an environmental and economical point of view, of the syntheses employed to obtain nanocrystals (NCs).

Here, we report the preparation of halide – based perovskites (*e.g.* $CsPbBr_3$) in limonene and pinene, molecules extracted from natural sources and considered green.[1]

The obtained NCs resemble the same structural, optical and morphological properties of the homologues synthesized in traditional solvents, *i.e.* 1-octadecene. Exploiting the relative high volatility of the limonene and pinene, we demonstrated the possibility to recover from the waste of the reactions the pure solvent that can be reused for subsequent syntheses. In addition, the substitution of 1-octadecene with limonene as the reaction solvent was analyzed by examining the consequences of the environmental impact of the entire synthesis process through a Life Cycle Assessment (LCA).

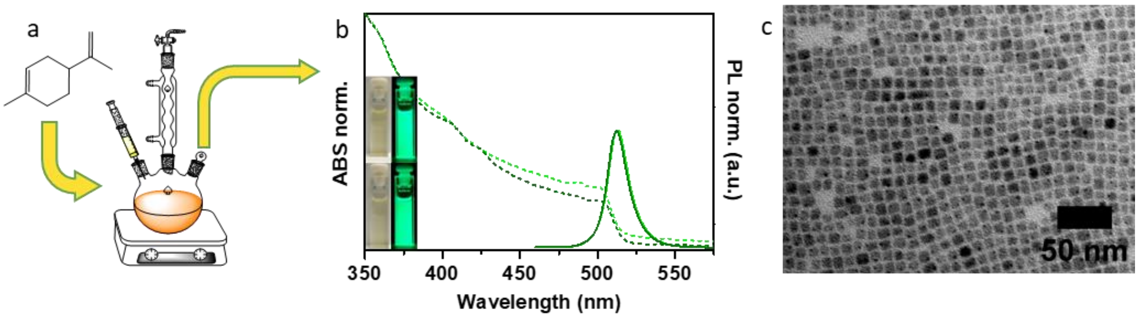

Figure 11. a) scheme of the synthesis, b) absorption and emission spectra and c) TEM image of the synthesized $CsPbBr_3$ nanocrystals.

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Fondazione Compagnia di San Paolo, Bando *TRAPEZIO* project NANOPLUS - ID#118000 and National Recovery and Resilience Plan (NRRP), funded by the European Union – NextGenerationEU, CUP - D33C22001330002 project title "Network 4 Energy Sustainable Transition – NEST".

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OR-22

Reactive Deep Eutectic Solvents (ReDESs) in the preparation of new generation of pyrrolidinone-based solvents

[1]Andrea Mezzetta, [1]Lorenzo Guazzelli

[1] *Università di Pisa, Dipartimento di Farmacia, via Bonanno 33, 56126 Pisa, Italy*
(andrea.mezzetta@unipi.it)

Transition toward sustainable chemistry is boosting the search for solvents endowed with safe, renewable and environmentally friendly profiles which can be suitable alternative to traditional volatile organic solvents. In this context, Deep eutectic solvents (DESs) emerged as one of the most encouraging media for several research areas. DESs are binary mixtures of two distinct species which display freezing temperatures at the eutectic point well below the ideal expected ones[1]. A very attractive feature of the DESs is the possibility to fine-tune their physico-chemical properties by choosing the appropriate partners, molar ratio and amount of water. DESs are regarded as the most promising solvent option for the development of sustainable chemistry on account of the ease of preparation and low cost, their benign (eco)toxicological profiles.

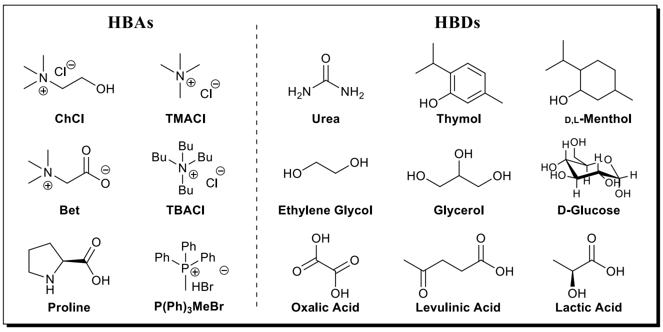

Figure 12. Common hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) DES partners.

In the last years, the use of DESs as green innocent solvents in organic synthesis has been reported for a wide range of reactions.[2] Particular emphasis has been direct towards the possible dual solvent-catalyst role played by DESs. However, their use as reactive media has been almost completely overlooked. In the present work, the potential of reactive DESs (ReDESs) as innovative media for the synthesis of bio-derived compounds has been investigated. Sustainability aspects have been evaluated by using green metric parameters.

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OR-23

Improving sustainability in the construction of conjugated molecular scaffolds: ionic liquids and (waste)water as solvents

[1] Stefano Nejrotti, [2] Sara Gracia Barberán, [1] Barbara Centrella, [1,3] Davide Gallo
[2] Elisabet Pires, [1] Claudia Barolo, [1] Matteo Bonomo

[1] Department of Chemistry, NIS and INSTM Reference Centre, Università degli Studi di Torino, via Quarello 15A, 10135 Torino, Italy.
[2] Instituto de Síntesis Química y Catalisis Homogénea, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain
[3] Ahlstrom Italia S.p.A., via Stura 98, 10075 Mathi (TO), Italy
(stefano.nejrotti@unito.it)

The synthesis of highly conjugated molecular scaffolds, relevant for applications in optoelectronics and organic electronics, is often performed through Pd-catalysed direct C–H arylation.[1] As highlighted in a recent review,[2] a major critical point in the sustainability of direct C–H arylations is represented by their high *E*-factor values, mainly related to the amount of solvent employed in the process, whose nature should likewise not be overlooked. In this framework, we present here our work on the C–H arylation of thiophene derivatives in two non-conventional solvents, namely water and glycerol-based ionic liquids. In the first case, the use of water allows to streamline the post-reaction treatment, significantly improving the mass-related *green* metrics; moreover, we show that the yield is not dependent on the purity grade of the water, allowing the use of industrial wastewater, thus reducing the environmental impact of the methodology.[3] On the other hand, we show that the thoughtful design of a new ionic liquid, containing a carboxylate anion, eliminates the need to add a super-stoichiometric amount of base, and in addition it enables the successful reuse of the reaction medium for five cycles, again improving the mass efficiency of the process.

Figure 13. Industrial wastewater as an effective solvent for Pd-catalysed C–H arylation

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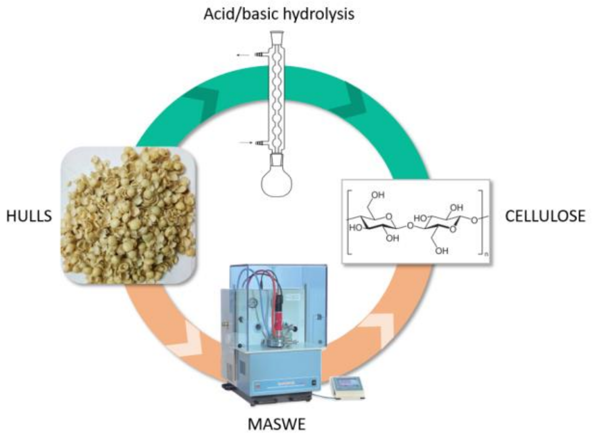
OR-24

Cellulose fibres from soybean hulls: efficiency and sustainability of different isolation methods

[1] Monica Rigoletto, [2] Giorgio Grillo, [1] Elisa Natali, [1] Enzo Laurenti, [2] Silvia Tabasso, [3] Maria Laura Tummino

[1]*Dipartimento di Chimica, Università degli Studi di Torino, Via P. Giuria 7, Torino, Italy*
[2]*Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, Via P. Giuria 9, Torino, Italy*
[3] *Istituto di Sistemi e Tecnologie Industriali Intelligenti per il Manifatturiero Avanzato (STIIMA), Consiglio Nazionale delle Ricerche (Cnr), Corso G. Pella 16, Biella, Italy*
(monica.rigoletto@unito.it)

Biopolymers are becoming more and more employed in several field and the studies for innovative application are widespread. However, the use of virgin crops for their extraction is being overcome and the choice increasingly falls on agro-industrial residues which are thus valorised rather than simply managed as waste. Such residues often consist of lignocellulosic biomass which mainly contains cellulose, hemicellulose and lignin whose fractionation can be achieved through different strategies [1]. Traditional extraction method usually employed multi step processes in strong acidic or alkaline conditions to promote the hydrolysis and allow components' isolation [2]. At the same time, alternative methodologies have been developed. Among them microwave assisted subcritical water extraction (MASWE) represent an interesting option since the extraction occurs in water, in more efficient heating conditions and in less time [3]. In this research work we isolated fibrous cellulose from soybean hulls, one of the most abundant by-products of soybean crushing, through both multi step hydrolysis and MASWE followed by an alkaline treatment. Processes and resulting cellulose have been compared to select the best extraction option in term of selectivity, yield, final product quality, process efficiency and sustainability.



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OR-25

BHET-based prepolymers: advancing the sustainability of polyurethane resins

[1]Gabriele Viada, [1]Simone Galliano, [2]Alberto Menozzi, [2]Federica Tammaro, [1,3]Claudia Barolo, [1]Matteo Bonomo

[1] *Department of Chemistry, NIS Interdepartmental Centre and INSTM Reference Centre, University of Turin, Via Gioacchino Quarello 15/a, 10135 - Torino, Italy*
[2] *Demak Polymers S.r.l., Corso Lombardia 44, 10099 - Torino, Italy*
[3] *ICxT Interdepartmental Centre, University of Turin, Lungo Dora Siena 100, 10153 - Torino, Italy*
(gabriele.viada@unito.it)

The enormous worldwide employment of single-use plastic materials is leading to ever-increasing waste generation. Therefore, the use of the latter as a feedstock for the production of waste-derived materials has emerged as a hot topic within both the scientific community and the industrial area. However, to accelerate the creation of an effective and reliable market for secondary raw materials, an essential requirement for circular materials is the ease of implementation in current processes and products[1].

In this perspective, we have started to investigate bis(2-hydroxyethyl) terephthalate (BHET), a low molecular weight diol as the main product of the glycolysis of polyethylene terephthalate (PET), as a promising circular component in the formulation of more sustainable ready-to-market polyurethanes[2]. This approach is particularly appealing considering that the end-of-life of a preeminent thermoplastic polymer on a global scale (i.e. PET) would serve as feeding for the most prevalent thermosetting polymer worldwide[3] (i.e. PUs), thereby offering an alternative route for closing the loop on a not negligible portion of PET waste.

In this contribution, we explored an innovative approach to implement BHET as a secondary raw material in the formulation of NCO-terminated prepolymer tailored for thermosetting resins. BHET was seamlessly integrated into the prepolymer formulation, removing the need for modifications to the industrial process, and demonstrating outstanding compatibility with other components within the mixture. The impact of BHET concentrations and its relative ratio with polyether and polyester constituents of the prepolymer on the final resins were systematically evaluated, showcasing the feasibility of fine-tuning the physical, chemical, and mechanical properties of polyurethanes while preserving market-level properties. In conclusion, we proved the successful incorporation of a significant amount of BHET (up to 20% w/w) into novel, eco-friendly prepolymers using a solvent-free methodology, without necessitating additional steps in the industrial workflow.

Acknowledgements.
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OR-26

Dual-Action Approach for Wastewater Purification: Synergistic Impact of Hydrodynamic Cavitation and Electrical Discharge (Cold) Plasma

[1] Federico Verdini, [1] Emanuela Calcio Gaudino, [1] Giancarlo Cravotto

[1] *University of Turin, Department of drug science and technology, Via P. Giuria 9, 10125-Turin, Italy*
(federico.verdini@unito.it)

The rising pollution of water bodies from toxic and non-biodegradable organic pollutants demands innovative wastewater treatment solutions. Due to the inefficiency of current green methods in removing contaminants of emerging concern (CECs), cavitation-based technologies like ultrasound (US) and hydrodynamic cavitation (HC) are gaining attention as sustainable, greener alternatives within advanced oxidation processes (AOPs) [1]. In recent years, HC processes have been coupled or hybridized with several AOPs to enhance their efficiency and versatility. A catalyst- and oxidants-free process has been developed by the hybridization of HC with the electrical discharge (ED) plasma in a new pilot-scale hybrid reactor (HC/ED plasma reactor, Figure 1). The synergistic production of hydroxyl radicals, hydrogen peroxide, ozone, UV light, and oxygen radicals has been studied for the fast and effective degradation of tetracyclines (TCs)[2], furosemide (FUR)[3], rhodamine B (RhB) and for the purification of a real pharmaceutical industry effluent (PIE)[4]. The treatments have been carried out working in flow-through with different inlet pressure values (45 to 70 bar) on 5 L or 10 L solutions and an average flow rate of 300 L/h. Near quantitative TCs (>95%), RhB (>95%) and FUR (90%) degradations were documented after only 15, 10, and 5 min, of treatment, respectively. The effect of HC/ED plasma technology has also been investigated in the presence of hydroxyl radical quenchers (t-BuOH and methanol) and compared to other pilot-scale cavitation-based reactors. A real PIE characterized by a starting chemical oxygen demand (COD) of 485 g/L was also treated inside the hybrid reactor, with a consequent highest COD reduction of 54% after only 10 minutes of treatment. Based on the results obtained, the combined HC/ED plasma process can be considered as a valuable, sustainable and industrially scalable alternative to conventional oxidation wastewater processes.

Figure 1. Hybrid HC/ED plasma pilot-scale reactor

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OR-27

Effect of activation conditions on properties of biomass derived biochar for H_2 storage

Marco Nicosia[1], Andrea Fasolini[1], Francesco Basile[1], Francesca Liuzzi[1], Anna Saotta[1], Alfonso Policicchio, Giuseppe Conte, Raffaele Agostino, Stefania Albonetti.

[1] *Department of Industrial Chemistry, Università di Bologna, Viale del Risorgimento 4, Bologna, BO, Italy.*
[2] *Department of Physics, University of Calabria Via Ponte P.Bucci - Cubo 31C Arcavacata di Rende CS, Italy*
(marco.nicosia4@unibo.it)

Introduction. Various chemical and physical techniques for storing hydrogen currently exist and their development will be a crucial point in enabling the large-scale deployment of this energy source. Among the various existing techniques, physical adsorption on a solid surface can be mentioned. The materials used for this application must have a high surface area and their production must be economical and have a low environmental impact; for these reasons, numerous studies have been carried out in recent years on carbon-based porous materials derived from waste or biomass. [1,2] In this study, the focus was on the production of Activated Carbons (ACs) from miscanthus, a perennial grass that can be cultivated on marginal lands, corn and hemp via pyrolysis. **Results.** Pyrolysis was carried out both using untreated biomass and previously activated biomass by impregnation with a solution containing potassium bicarbonate ($KHCO_3$). The influence of raw biomass and synthesis parameters on the porosity formation was investigated. Then, H_2 adsorption properties were evaluated through volumetric apparatus both at low temperature and room temperature. The experimental results show an improvement of both textural and adsorption properties as function of raw materials and thermal treatment conditions, developing adsorbent materials with high fraction of micropores (≃80-90 %), specific surface area (≃1500 m2/g) and hydrogen uptake of wt% at 77 K and 1 bar.

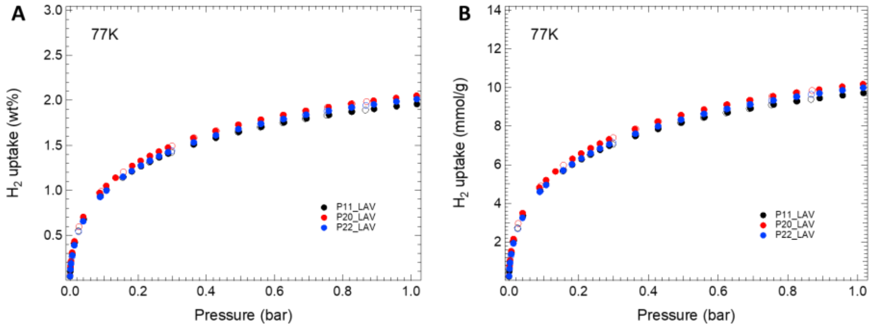

Figure 1. Hydrogen adsorption/desorption isotherms reported as (A) wt% and (B) mmol/g at T = 77 K and pressures up to 1 bar. (P11 – miscanthus 900°C, P20 – hemp 850°C, P22 – corn 850°C)

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OR-28

Hydroxyapatite from Eggshells: A Green Approach to Nanofertilizers

[1] Giordana Alessia, [1] Castellini Letizia, [1] Cerrato Giuseppina, [1] Operti Lorenza

[1] *Dipartimento di Chimica, Università degli Studi di Torino, Via P. Giuria 7, Torino.*

(alessia.giordana@unito.it)

Eggshells (ES) are an abundant and widespread waste that can be used to produce high-value goods. To fulfill the cradle-to-cradle sustainability concept, the final products may need to be materials that can either degrade or serve as nutrients in soil. Hydroxyapatite nanoparticles (HAP, $Ca_{10}(PO_4)_6(OH)_2$) have been proposed as solid fertilizer, to promote a controlled release of phosphorous nutrient.[1] ES can be converted into different Ca-precursors to obtain HAP.
In recent decades, several methods have been proposed to obtain HAP starting from ES. These include mechanochemical, wet precipitation, hydrothermal, and sol-gel. Most of the studies in the literature involved a preliminary thermal treatment (at $T \geq 800°C$) to convert ES in CaO.[2,3] This step is energy-intensive and produces large amounts of CO_2 from carbonate decomposition.
To reduce the environmental impact of HAP synthesis, we decided to use ascorbic acid. This nontoxic and cost-effective reagent dissolves ES and traps the produced CO_2 as oxalate ions[4]. The composition, crystallinity and morphology of the obtained product were compared to HAP obtained by a classical precipitation method and by dissolution of EG with nitric acid.
We study the dissolution of the obtained HAP, and the results indicate that nanoparticles obtained using ES and ascorbic acid are promising nanofertilizer, releasing high amount of P and K.

Acknowledgements.
A. Giordana benefits from funding REACT-EU within the program PON Asse IV "Istruzione e ricerca per il recupero " 2014–2020 (PON R&I), Action IV.6 "Contratti di ricerca su tematiche Green".

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OR-29

Isoselective Polymerization of 1-Vinylcyclohexene and (S)-4-Isopropenyl-1-Vinylcyclohexene: Synthesis and Copolymerization with Styrene and Terpenes

[1] Ilaria Grimaldi, [1]Assunta D'Amato, [1]Mariarosaria C. Gambardella, [1]Antonio Buonerba, [2] Raffaele Marzocchi, [2]Finizia Auriemma and [1]Carmine Capacchione

[1] Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università degli Studi di Salerno, Via Giovanni Paolo II, 84084 Fisciano, SA, Italy
[2] Dipartimento di Scienze Chimiche Università di Napoli Federico II, Complesso Monte S. Angelo, Via Cintia, 80126, Napoli, Italy
(ilagrimaldi@unisa.it)

The growing focus on environmental sustainability is promoting the use of renewable resources in industrial processes, including polymer production. Significant advancements have been made by utilizing renewable monomers to produce polyolefins, reducing reliance on traditional petrochemical-based materials. This shift addresses concerns about the finite nature of fossil fuel resources. A key development in synthesizing polyolefins from renewable monomers involves the use of metal complexes with OSSO-type ligands, which exhibit high catalytic activity and selectivity in polymerizing bio-based monomers, leading to efficient and high-quality polyolefin production.[1,2]

This study assesses the catalytic efficiency and stereoselectivity of two titanium complexes with OSSO-type ligands in the polymerization of a bio-based monomer, yielding highly regio- and stereoregular polymers. We successfully polymerized (S)-4-Isopropenyl-1-vinyl-1-cyclohexene (IVC), a naturally derived monomer synthesized from perillaldehyde, which is predominantly found in the herb perilla.[3] Previously, a similar study was conducted using 1-vinylcyclohexene (VCH) as a model monomer due to its structural similarity to IVC, differing only in the isopropenyl substituent. Furthermore, the copolymerization of these monomers with styrene and two terpenes, β-myrcene and β-ocimene, was also achieved. This demonstrated not only the remarkable versatility of [OSSO]-type titanium complexes in copolymerization reactions but also expanded the range of sustainable polymeric materials suitable for practical applications.

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OR-30

Merging biocatalysis and flow chemistry for efficient, sustainable and productive processes

[1] Martina Letizia Contente

[1] *Department of Food, Environmental and Nutritional Sciences (DeFENS), University of Milan, via Celoria, 2, 20133 Milan (Italy)*
martina.contenter@unimi.it

Today a lot of chemical commodities are produced using biocatalytic approaches, either by fermentation or enzyme-mediated synthesis. These goods range from food and beverage, cleaning products, cosmetics and pharmaceuticals[1] leading to the development of smart and efficient strategies for process optimization and large scale production. In this context flow biocatalysis represents an emerging technology which improves reaction productivity minimizing waste and energy consumption.[2] The integration of biocatalysts, both whole cells and cell-free enzymes, into continuous flow reactors usually involves immobilization techniques which not only enhance the catalyst stability but also enable its convenient isolation and reuse, thus improving the cost-efficiency of the process.[3]

Valuable molecules such as pharmaceuticals, aroma-compounds, and food ingredients have been successfully prepared merging the advantages of flow reactors with the specificity and benign conditions of biocatalysts thus contributing to advances in modern chemistry.

Figure 14. The joint effort of enzyme technology and flow chemistry to bring biocatalytic processes to the next level of sustainability, efficiency and productivity

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OR-31

Green chemistry approaches within the wastewater treatment

[1] Prisco Prete, [1] Felice Di Nardo, [2] Marco Visconti, [1] Raffaele Cucciniello

[1] Dep. Chemistry and Biology, University of Salerno, Via Giovanni Paolo II, 132 – 84084 Fisciano (SA), Italy.
[2] Cannon Artes, Via Resistenza, 12 – 20068 Peschiera Borromeo (MI), Italy
(pprete@unisa.it)

The degradation of water pollutants has become increasingly important due to the rising presence of refractory harmful substances, known as contaminants of emerging concern (CECs) [1]. Advanced oxidation processes (AOPs), which rely on the generation of free radicals (reactive oxygen species, ROS), offer a promising strategy for the removal of these pollutants. Among AOPs, the photo-Fenton process ($h\nu/H_2O_2/Fe^{2+}$) is one of the most investigated and promising. However, its practical application has been limited, as optimal conditions are typically achieved under acidic pH [2].

To enhance the feasibility of these processes, alternative catalytic systems using soluble iron complexes have been developed. The design of new catalysts for photo-Fenton-like processes is an area of great interest for both academic and industrial researchers. Despite this, there remain gaps in knowledge regarding how to improve the sustainability of these catalysts in line with the 12 Principles of Green Chemistry [3] and the Safe and Sustainable by Design framework [4].

To address this, two metal complexes (Cu-IDS and Fe-IDS) based on Iminodisuccinic acid (IDS), a biobased biodegradable ligand, have been synthesized and tested as sustainable catalytic systems in photo-Fenton-like processes for treating urban and industrial wastewater [5,6]. Additionally, the Fe-IDS catalyst has demonstrated the ability to be activated by visible and monochromatic light, rather than the more hazardous UV-C irradiation typically used in photo Fenton-like, thus enhancing the overall sustainability of the process.

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OR-32

Biomass-Derived Catalytic Architectures by Mechanochemical Extrusion

[1] Daily Rodríguez-Padrón, [1] Alvise Perosa, [1] Maurizio Selva,

[1] *Department of Molecular Science and Nanosystems, Ca' Foscari University of Venice, Venice, Italy*
(daily.rodriguez@unive.it)

This contribution focuses on utilizing waste streams from the fishery industry—amounting to millions of tons annually—as a valuable source of biopolymers. The primary aim is to develop a flexible biorefinery model that integrates waste management, chemical treatment of residues, and scalable catalyst production. Chitin, the second most abundant biopolymer on Earth, has been directly employed as a precursor for catalyst supports. While innovative applications of chitin are essential for designing sustainable protocols, they are often hindered by chitin's poor solubility in most solvents, with the exception of task-specific ionic liquids. In this work, various valorization pathways have been explored using mechanochemical approaches to transform chitin into advanced catalytic supports. Our research group has recently demonstrated the successful use of high-chitin bio-waste (shrimp shells) for synthesizing metal-free catalysts for CO_2-fixation reactions.[1] Additionally, we have developed new families of noble-metal and non-noble-metal nanoparticles supported on chitin, which have shown promising results in selective alcohol oxidation, reductive amination, hydrogenation, and C-C cross-coupling reactions.[2][3][4]

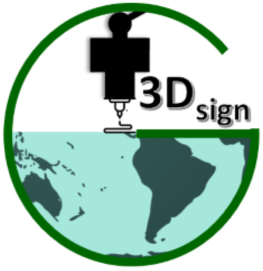

Figure 15. Green-3Dsign: a Marie Skłodowska-Curie - COFUND project.

Acknowledgements.

D.R.-P. acknowledges the project H2020-MSCA-COFUND-2019 "Global at Venice—Research and Training for Global Challenges

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OR-33

From micellar catalysed Hydroformylation and Hydroaminomethylation to solid waste-based sustainable processes

[1] Giulia Romagnoli, [1]Simone Zurzolo, [1]Elisabetta Monciatti, [1]Francesca Migliorini, [1]Maria Laura Parisi, [1]Matthias Vogt, [1]Elena Petricci

[1] Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via Aldo Moro 2, 53100 Siena, Italy.
[2] Fakultätfür NaturwissenschaftenII, Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Str.2, 06120 Halle, Saale, Germany.
(giulia.romagnoli1@student.unisi.it)

Hydroformylation reaction (HF) is the most applied catalytic process in industry worldwide, being an efficient atom-economic reaction for the synthesis of linear aldehydes from olefines.[1] We have recently reported sustainable and generally appliable protocols for the regioselective HF[2] and hydroaminomethylation (HAM)[3,4] of terminal alkenes in water, taking advantage from both micellar and microwave catalysis. Moving from Green Chemistry[5] to Circular chemistry,[6] a more sustainable solution has been proposed by replacing PEG-based surfactants with solid waste materials (SWMs). We report here a bio-based methodology for the HF in water of terminal olefins, using Sardinian White Wool (SWW) as waste-derived biomass, obtained as powder using mechanochemistry,[7] as an additive to regioselectively produce valuable linear aldehydes.[8] In a circular economy approach, SWW can be valorized, otherwise treated as special waste. The process is generally applicable to various terminal alkenes producing a library of linear aldehydes. The catalyst, the ligand, together with the biomass and H_2O, can be recovered and reused without a reliable decrease in conversion into the desired product and without using organic solvents, further reducing the environmental impact of the proposed methodology. Life Cycle Assessment (LCA) analyses confirm the efficiency and sustainability of this approach by comparing the new protocol with traditional HF methods. This proof of concept demonstrates the potential for SWMs to be used in the development of low impact catalytic processes, promoting a zero-waste approach.

Acknowledgements:
Thanks to MIUR for the grant Piano Operativo 644 Nazionale (PON) Green Innovation 2021.

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OR-34

Microcrystalline cellulose from Aloe plant waste: preparation, chemical functionalization and application in 3D printing

[1] Maria Chiara Cabua, [1] Annalisa Chiappone, [1] Francesco Secci

[1] *Università degli Studi di Cagliari, Cittadella Universitaria Monserrato – 09042 Monserrato (CA).*
(mariachiara.cabua@unica.it)

The development of new technologies for the synthesis of materials with low environmental impact is one of the most considered issues to face the current pollution phenomena. Cellulose deriving from agricultural waste, with its high degree of polymerization, represents a versatile building block for the design and preparation of alternative and biodegradable materials.
In this work, waste collected from local South Sardinia grown Aloe Vera was employed to prepare microcrystalline cellulose (MCC). Cellulose was purified from anthraquinones, lignin, and hemicellulose through hydrolytic procedures using eco-friendly solvents[1]. Anthraquinone biocomponents were quantified as well as lignin and hemicellulose and intended for other valorisation processes. At the same time, the cellulose fraction was further converted into MCC and characterized by NMR, infrared spectroscopy, and X-ray analyses. TGA-IR and SEM microscopy analyses were performed to investigate the structural changes of MCC. After proper functionalization, MCC derivatives were characterized and finally used as crosslinkers in the photopolymerization and light-induced 3D printing of acrylic monomers and hydrogels[2].

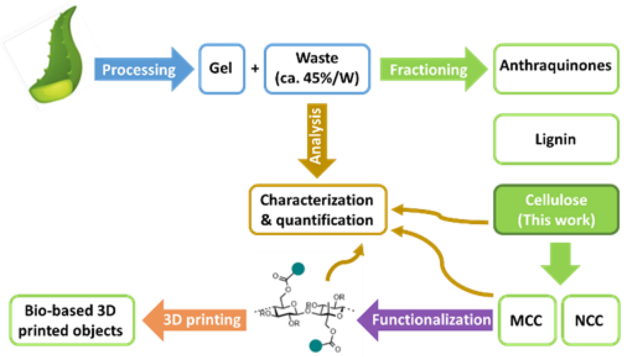

Figure 16. From Aloe Vera waste to 3D printed objects

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OR-35

Biomass valorisation towards new materials

[1] Alice Cappitti, [1] Stefano Fabbri, [1] Samuele Visi, [1] Monica Tonelli, [1] Debora Pratesi, [1] Camilla Matassini, [1,2] Donatella Giomi, [1,2] Antonella Salvini

[1] *Department of Chemistry "Ugo Schiff" University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino*
[2] *Laboratorio congiunto VALORE", via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italia)*

(alice.cappitti@unifi.it)

In recent years, the exploitation of renewable materials from biomass has become a strategic objective for the chemical industry, aimed at reducing the depletion of fossil resources while simultaneously addressing waste disposal challenges. Lignocellulosic biomass is abundant in nature and its use as a raw material offers the advantage of not competing with food or feed production[1]. Furthermore, there are numerous types of waste lignocellulosic biomass, whose valorisation represents a significant benefit.

On this basis, the study of new high-value-added materials derived from waste biomass is particularly interesting. Specifically, cellulose and other polysaccharides can be recovered from waste biomass using specialized protocols, optimized according to the varying composition of the biomass[2]. Mechanical, physical, and chemical treatments must be tailored to the specific type of biomass under investigation.

However, to achieve sustainable production processes, even with waste materials, it is crucial to minimize the stages that involve high energy consumption or the use of large quantities of reagents and solvents, while striving to maximize the full recovery of the biomass. The aim of this research was therefore to develop a low environmental impact biorefinery protocol for the extraction and/or valorisation of cellulose from the fibers of lignocellulosic biomass, with the goal of utilizing it in the production of biobased products such as gels, films, and insulating panels, which can be applied in various industries, including construction.

The primary biomass used in this study is *Posidonia Oceanica* Sea Balls (egagropili), a photosynthetic biomass commonly found along the coasts of the Mediterranean Sea, often destined for disposal. The goal is to extend the optimized procedures to other types of waste lignocellulosic materials as well.

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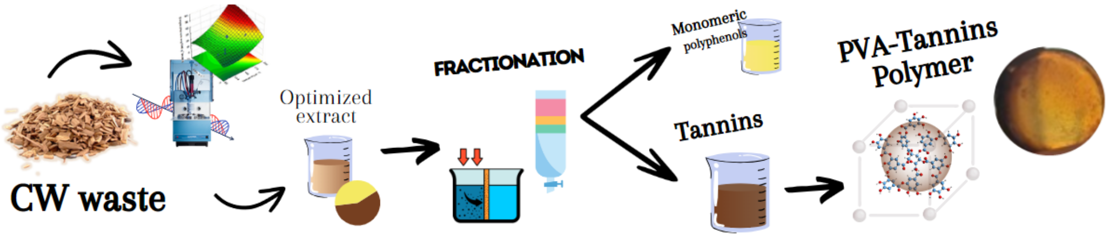
FL – 1

Chestnut Wood Valorization: A Green Strategy for Extraction, Fractionation, and Biopolymer Design

[1] Clelia Aimone, [1] Giorgio Grillo, [1] Giorgio Capaldi, [1] Salah Chaji, [1] Giancarlo Cravotto.
[1] Dipartimento di Scienza e Tecnologia del Farmaco, Via P. Giuria 11, Torino, 10125.
Univerisità di Torino
(clelia.aimone@unito.it)

In line with the principles of Circular Economy and Green Extraction, this study focuses on the extraction of chestnut wood (CW) waste (*Castanea sativa*, Mill.), which is rich in active metabolites with antimicrobial, antioxidant, and antiproliferative properties[1]. To assess the potential of sustainable and environmentally conscious extraction and fractionation methods, Microwave-Assisted Subcritical Water Extraction (MASWE) together with green and scalable downstream techniques have been exploited to isolate enriched extracts (characterized by simple polyphenols and tannins) from CW residues. Central Composite Design (CCD) was employed to identify the optimized extraction conditions (174 °C, 14 min, S/L ratio 1:20), to maximise the recovery of metabolites while balancing monomeric polyphenols and tannic fraction. The produced extract was then submitted to a crucial downstream process, comprising membrane filtration (Ultrafiltration and Nanofiltration with different cut-offs). The *tannin-rich* "heavy" fraction was used to develop a new biopolymer, based on Polyvinyl Alcohol (PVA). Several analyses have been performed on specimens to evaluate the cross-linking grade and mechanical characteristics, along with the biodegradability of the material.



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FL – 2

Ultrasound-Assisted Procedure for the Preparation of Ru- and Pd-Iron Oxide Catalysts

[1] Chiara Bruschetta, [1] Maela Manzoli, [1] Giancarlo Cravotto

[1]*Department of Drug Scienze and Technology, University of Turin, Via P. Giuria 9, 10125 Turin, Italy*
(chiara.bruschetta@unito.it)

Metal oxide nanoparticles achieve the unique properties such as high surface area, excellent mechanical strength, unusual catalytic properties and better biocompatibility[1]. Different preparation methods such as wet impregnation[2], hydrothermal synthesis[3], thermal decomposition[4], spray pyrolysis[5] etc. have been used. Ultrasound (US)-assisted preparation is known as an alternative pathway to obtain novel materials avoiding high temperature and pressure or prolonged reaction times[6]. The effect of US as an energy source for chemical reactions deals with process intensification[7] due to an increase in both mass and heat transfer and to the generation of cavitation bubbles undergoing very short and violent collapse within the fluid, giving rise to local hot-spots with high energy. Indeed, low-frequency ultrasound (20–100 kHz) whereby other parameters such as power and duration affect the final composition and rheology of the material.[8]

In particular, when used in liquid systems, within the zone of extreme 'mixing' close to the ultrasonic source (i.e. the transducer) the cavitation promotes (i) degassing, (ii) surface cleaning and pitting (erosion) and (iii) an increase in bulk temperature, thus offering remarkable advantages such as de-agglomeration, particle size reduction, dispersion, homogenisation, emulsification, atomisation, molecular degradation, and an improvement of surfaces.[8] The aim of this work is to evaluate the effect of different US irradiation systems (common ultrasonic bath, ultrasonic probe) during the preparation of ferrite-based[9] Ru and Pd catalysts (*figure 1*).

The structural and morphological changes depending on the adopted procedure have been monitored by XRD and high-resolution STEM coupled with EDS. It was observed that the US-assisted co-precipitation process allowed to obtain a better dispersion of the metals than the application of US after co-precipitation process. These systems, chemically bonded with lignin previously modified with aminic functional groups, will be employed as bio-based catalysts for biomass valorisation.

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FL-3

Carbon nitride materials as sustainable photocatalysts in C-H bonds functionalization processes

[1] Camilla Callegari, [1] Giulia Draghi, [2] Sonia Zoltowska, [2] Paolo Giusto, [1] Davide Ravelli

[1] Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy
[2] Max Planck Institute of Colloids and Interfaces, Am Muhlenberg 1, 14476 Potsdam, Germany
(camilla.callegari01@universitadipavia.it)

Graphitic carbon nitride semiconductors (CNs) are inexpensive and reusable photocatalysts, which are actively studied in organic synthesis for their capability to trigger single electron transfer (SET) processes upon irradiation with visible light. Herein, building upon a previously reported Minisci-type coupling involving aliphatic substrates and heteroarenes,[1] we propose an innovative redox-neutral application of carbon nitride materials in a Giese-type reaction between different hydrogen donors (ethers, amides, *etc*.; **R–H**) and electron-poor olefins (see Figure 1a). The preparative studies have been supplemented as well by mechanistic experiments, intended to elucidate the corresponding mechanism, presumably involving a proton-coupled electron transfer (PCET) mechanism.[2] Furthermore, recalcitrant substrates have been successfully functionalized by implementing a heterogeneous *indirect* hydrogen atom transfer process (*i*-HAT),[3] where an additive is activated by the CN and then takes care of **R–H** cleavage in the chosen substrate through the action of photogenerated $\mathbf{X}^{\bullet}$, working as a hydrogen abstractor species (see figure 1b).

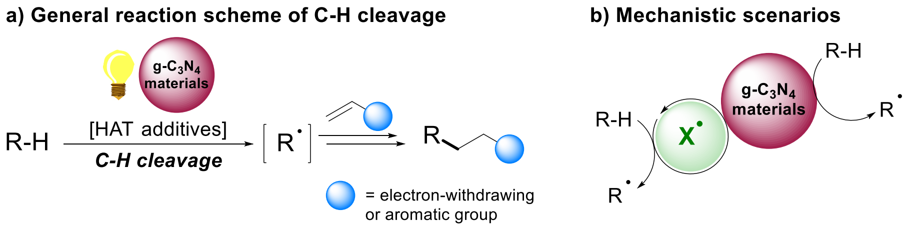
a) General reaction scheme of C-H cleavage
b) Mechanistic scenarios

Figure 17. Carbon nitride materials as heterogeneous photocatalyst in C–H bonds functionalization: a) General reaction scheme; b) possible mechanistic scenarios.

Acknowledgements. Financial support through the HORIZON-EIC-2021-PATHFINDEROPEN-01 project CATART (GA 101046836) entitled “Reaction robot with intimate photocatalytic and separation functions in a 3-D network driven by artificial intelligence” is gratefully acknowledged.

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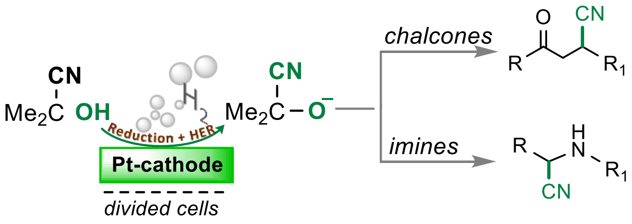
FL-4

Electrocatalytic activation of acetone cyanohydrin with hydrogen evolution: synthesis of β-cyano ketones and α-aminonitriles

Laura Palombi,[1]

[1] Dipartimento di Scienze Fisiche e Chimiche Università di L'Aquila
Via Vetoio, 10 Coppito, 67100 L'Aquila, Italy
(laura.palombi@univaq.it)

Cyanation reactions are crucial in organic synthesis, as they allow for quick structural diversification by transforming the nitrile group into a variety of other functionalities.[1] The inherent toxicity and volatility of hydrogen cyanide (HCN) have driven the research of more manageable reagents while concurrently developing safer processes with alternative techniques: mechanochemistry, continuous flow, photocatalysis, electrocatalysis, and combined strategies.[2]
Herein is reported an electrochemical procedure based on the Hydrogen Evolution Reaction (HER) of acetone cyanohydrin (ACN) at a Pt cathode enabling the cyanation of α,β- unsaturated carbonyl and imines. Catalytic current, along with a correspondingly reduced quantity of supporting electrolyte, facilitates the scalability of the procedure, ensuring brief electrolysis times while maintaining a simple electrochemical design.[3]



- Catalytic current (0.02 F/mol)
- Catalytic supporting electrolyte (0.04%)
- Slight excess of cyanating agent (1.5 eq)

Figure 18. Reduction with HER of ACH enabling cyanation of electrophilic carbons

Acknowledgements. European Union-NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041-VITALITY-CUP E13C22001060006.

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FL-5

Flotation Technique for Recycling Black Mass from Spent Lithium-ion Batteries

[1] Alireza Safdari, [2] Andrea Grassi, [2] Cristiano Bacco, [1] Mirko Magni

[1] Department of Environmental Science and Policy, Università degli Studi di Milano, Via Golgi 19, Milan
[2] Engitec Technologies SpA, Via Paolo Borsellino e Giovanni Falcone 31, 20026 Milan
(alireza.safdari@unimi.it)

The rapid increase in the adoption of lithium-ion batteries (LIBs) in consumer electronics and electric cars has highlighted the need for efficient recycling methods. This study, within the framework of the European Battery Innovation - EuBatIn initiative, aims to develop a sustainable and industrially scalable hydrometallurgical process for recycling spent LIBs. One of the many challenges to face in is to get an efficient separation of the components of the black mass (BM) – a fine, powdery material comprising cathode and anode active substances (typically metal oxides and graphite), as well as metallic collectors such as copper and aluminum, and residual plastics – produced from the shredding of batteries. This research specifically investigates experimental conditions for an effective flotation process for separating BM components, particularly focusing on two key objectives: i) the isolation of graphite from the cathode active material, and ii) the separation of distinct cathode active materials (*e.g.*, nickel manganese cobalt oxide (NMC), lithium iron phosphate (LFP)) in case of mixed-chemistry battery batches. The flotation process hinges critically on the surface and charge properties of the materials involved, making the determination of the point of zero charge (PZC) a crucial step for optimizing separation efficiency. Given the limited availability of data on the PZC, especially for representative samples of BM of spent LIBs, this study aims to fill this knowledge gap to design robust and effective flotation protocols. A systematic comparison was conducted using three commonly employed methods for PZC determination (drift method, titration, and mass titration) to assess the results consistency and/or limitations. Experiments invariably revealed notable differences in PZC (~2.5 pH units*)* for pristine battery-grade LFP and NMC samples, indicating that charge-driven surface manipulations could be leveraged to enhance the efficiency of separation by flotation. Furthermore, PZC measurements for cathode and anode materials collected from spent LIBs have been performed to highlight the role of particles dimension and of matrix interferences.

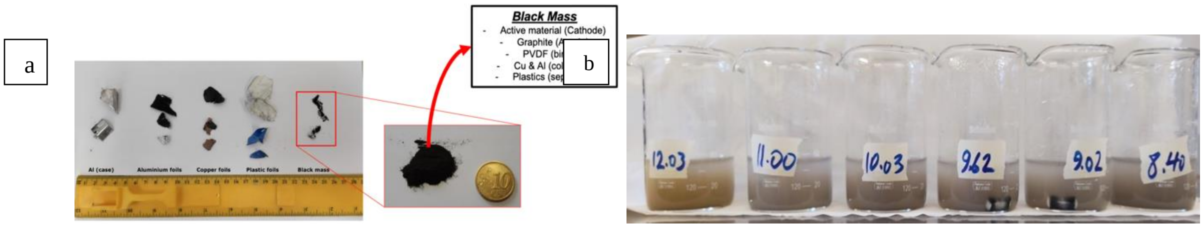

Figure 1. a) Main components of a LIB, sorted after shredding; b) picture of a typical run for the measurement of PZC through the drift method.

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FL-6

Sustainable Polymers obtained by Schiff Base-Based Zn and Mg Complexes

[1] Tufano Federica, [1] Santulli Federica, [1] Galotto Maria Vittoria,[1] D'Elia Alfredo,
[1] Vitiello Sabrina, [1] Mazzeo Mina, [1]Lamberti Marina

[1] *Università degli Studi di Salerno-Fisciano (SA), Italy*
(ftufano@unisa.it)

Nowadays, plastic has become one of the most used materials in many fields thanks to its lightness, versatility, resistance and low cost[1]. However, problems related to related both to the employment of non-renewable raw materials and the disposal of these materials has given rise to great interest in the development of alternative polymers. Among them, aliphatic polyesters and aliphatic polycarbonates have attracted significant attention as they are biodegradable and obtainable from renewable resources; moreover, their mechanical properties make them ideal candidates in different types of applications, such as biomedical field andh packaging[2]. Different synthetic methods can be exploited to obtain these categories of polymers: among them, the Ring-Opening Polymerization (ROP) of lactones and cyclic carbonates has emerged as one of the most efficient ways to produce aliphatic polyesters and aliphatic polycarbonates, respectively, under mild conditions, with good control over molecular weight. To ensure that the sustainability criteria are respected throughout the entire life cycle of the polymer, the use of high performance and selective catalysts is required: a possible strategy involves the use of biocompatible metals, which eliminates the difficulty of removing trace amounts of residues from the produced polymers. Herein, we report a class of heteroleptic Mg and Zn complexes, supported by naftoxy-imine ligands, bearing an additional pyridine moiety. The synthesized complexes have been fully characterized by NMR spectroscopy and then tested as catalysts in the ROP of different monomers: both lactones, as lactide and ε-caprolactone, and cyclic carbonates, such as trimethylene carbonate. The complexes resulted active in the ring-opening polymerization of both classes of cyclic monomers, showing high activity, even under green and industrially relevant conditions. Moreover, the study has been also extended to the synthesis of polycarbonate-polyester copolymers for the production of well-defined sustainable block copolymers with adjustable properties.

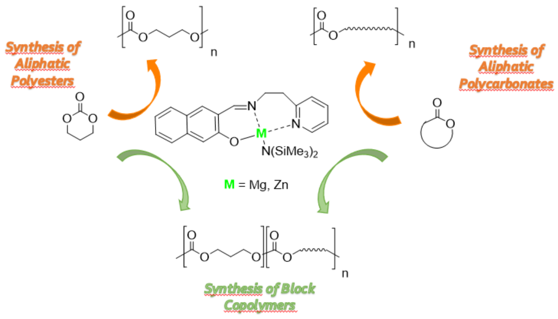

Fig. 1: ROP of lactones and cyclic carbonates.

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P – 7

Renewable diphenolic acid synthesis in batch and continuous reactor: an eco-friendly substitute for bisphenol A

[1]B. Bertini, [1]D. Licursi, [2]F. Taddeo, [3]A. Sessa, [4]N. Scotti, [3]R. Cucciniello, [2]V. Russo, [1]A.M. Raspolli Galletti, [1]C. Antonetti

[1]*Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, 56124 Pisa, Italy*
[2] *Department of Chemical Sciences, University of Naples Federico II, Via Cintia, IT-80126 Naples, Italy*
[3]*Department of Chemistry and Biology, University of Salerno, Via G. Paolo II 132, SA 84084 Fisciano, Italy*
[4] *CNR-SCITEC "Giulio Natta", Via C. Golgi 19, 20133 Milano, Italy*
(claudia.antonetti@unipi.it)

Diphenolic acid (DPA) is emerging as a promising "green" alternative to bisphenol A for the production of epoxy resins and polycarbonate plastics[1]. The DPA synthesis involves a condensation reaction between phenol (PhOH) and levulinic acid (LA), catalyzed by Brønsted acid catalysts, in particular mineral ones, which lead to significant corrosion issues and difficult catalyst recycling. Therefore, it is paramount to move towards heterogeneous systems, especially those derived from renewable resources. In this specific domain, the PRIN 2020 LEVANTE project focuses on synthesizing a fully renewable *p,p'*-DPA. This approach requires the renewability of all the reaction components, in particular LA, PhOH and the catalyst. LA is commonly obtained by C6-rich feedstocks, particularly cheap or, even better, waste lignocellulosic biomasses[2], whereas PhOH, as well as other phenolic derivatives, can be obtained from renewable lignin through pyrolysis or reductive depolymerization. The possibility of using a biomass-derived catalyst offers the opportunity to make the entire DPA synthesis fully renewable. To achieve these goals, new *ad hoc* acid catalysts have been synthesized by sulfonating xylose- and glucose-derived hydrochars, and tested for the selective production of *p,p'*-DPA and *p,p'*-DPAC (the DPA derivative from catechol) in batch and continuous reactors. The effects of the main reaction parameters on the *p,p'*-DPA/*p,p'*-DPAC yield have been investigated and optimized in both reactor configurations. In particular, both homogeneous and heterogeneous catalysts were tested in flow to check their performance. Under the best reaction conditions, *p,p'*-DPA yields reached about 20 mol%, with ongoing progress towards achieving real feasibility for the *p,p'*-DPAC. At the same time, LCA (Life Cycle Assessment) evaluation is in progress to compare environmental impacts associated to the newly developed preparation of DPA with those of the consolidated process which involves mineral acids as catalysts.

Acknowledgements.
The authors would like to thank the Italian Ministero dell'Istruzione, dell'Università e della Ricerca for funding the PRIN 2020 LEVANTE project "LEvulinic acid Valorization through Advanced Novel TEchnologies" (Progetti di Ricerca di Rilevante Interest Nazionale Bando 2020, 2020CZCJN7).

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P – 8

PHENOCYCLES: Exploiting the Multifuctional Proprierties of Polyphenols from Waste to High Value Products

[1] Giorgio Capaldi, [1] Giorgio Grillo, [1] Federico Verdini, [1] Emanuela Calcio Gaudino, [1]Marina Gallarate, [1]Silvia Tabasso, [1]Simona Sapino, [1]Daniela Chirio, [1]Elena Peira, [2] Alessandra Bianco Prevot, [2]Enzo Laurenti, [2]Silvia Berto, [2] Chiara Riganti, [2] Joanna Kopecka, [2] Davide Palma, [2] Giuliana Magnacca, [3]Giovanna Gautier di Confiengo, [3]Maria Giulia Faga, [4]Maria Luisa Testa, [4]Marco Russo, [4]Valeria La Parola, [5]Massimo Guaita, [5]Silvia Motta, [5]Antonella Bosso, [1]Giancarlo Cravotto

[1] Dipartimento di Scienza e Tecnologia del Farmaco (Università di Torino, Via Pietro Giuria 9, Torino).
[2] Dipartimento di Chimica (Università di Torino, Via Pietro Giuria 7, Torino).
[3] Ist. di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) (CNR, Str. delle Cacce 73, 10135 Torino)
[4] Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), (CNR, via U. La Malfa 153, I-90146 Palermo)
[5] Centro di Ricerca Viticoltura ed Enologia (CREA-VE, via P. Micca 35, 14100 Asti)
(giorgio.capaldi@unito.it)

The PHENOCYCLES project aims to develop innovative applications for polyphenols (PPs) extracted from agro-industrial wastes, like grape, apple, and berry pomace, as well as medicinal weeds. Through interdisciplinary collaboration across Europe, South America, and Central Asia, the project fosters knowledge transfer and supports sustainable development. By valorizing agro-waste, PHENOCYCLES addresses key environmental challenges in line with the EU Green Deal and UN Sustainable Development Goals. The waste-extracted bioactive compounds are fractionated using advanced membrane filtration systems, these to maximize their multiapplication potential across diverse sectors, including human health, environmental protection, agriculture, and material sciences. In human health, PHENOCYCLES will develop polyphenol-based drug delivery systems using nano- and micro-scale carriers to treat non-communicable diseases, as well as creating hypoallergenic cosmetics and nutraceuticals. For environmental protection, PPs will be combined with nanomaterials—such as carbon dots and metal-organic frameworks (MOFs)—to enhance water treatment, focusing on pollutant removal and advanced oxidation processes. In agriculture, the same PPs nanomaterials will be applied to create multifunctional biopesticides and biostimulants, promoting both crop protection and plant growth. This comprehensive approach represents significant progress, particularly in green chemistry and non-food materials, offering high-value applications for the agri-food and environmental sectors. By closing the loop on food waste and integrating eco-friendly practices, PHENOCYCLES will contribute to a zero-waste economy while advancing both scientific and socio-psychological sustainability perspectives.

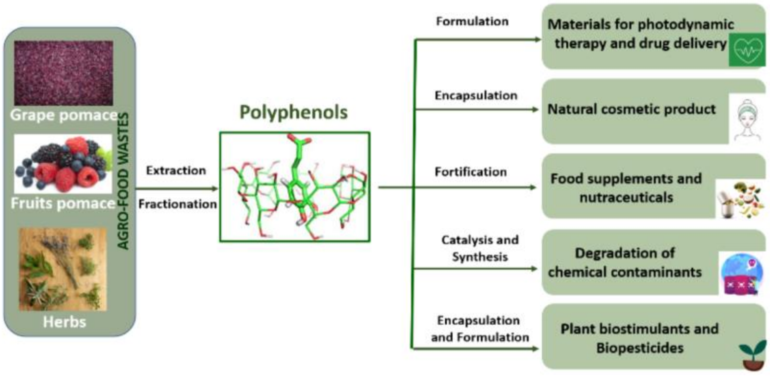


Figure 19. Phenocycles' strategy and objectives

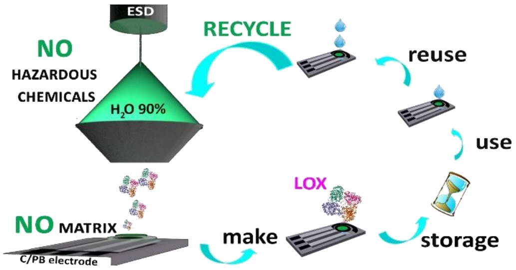
P – 9

GREEN TECHNOLOGY FOR LACTATE OXIDASE-BASED BIOSENSOR FABRICATION

A. Cartoni,[1] D. Rossi[1], V. Scognamiglio,[2] V. Frisulli,[2] M.T. Giardi,[2,3] E. Tempesta,[4] J. Chiarinelli,[5]
M. Parracino,[5] L. Avaldi, [5] M. C. Castrovilli[5]

[1]Department of Chemistry, Sapienza University, P. le Aldo Moro 5, 00185 Roma, Italy.
[2]Institute of Crystallography, National Research Council, Area Della Ricerca di Roma 1, Via Salaria Km 29.300, 00015, Monterotondo, Italy.
[3] Biosensor Srl, Via Degli Olmetti 4, 00060, Formello, Rome, Italy.
[4] CNR-Institute of Environmental Geology and Geoengineering (CNR-IGAG), Area della Ricerca Roma1, Via Salaria km 29.300, 00015, Monterotondo, Italy
[5] Istituto di Struttura della Materia-CNR, (ISM-CNR), Area della Ricerca di Roma 1, 00015, Monterotondo, Italy

In the field of biosensors, there is a growing need for environmentally friendly and reusable sensors and biosensors. Current methods of immobilizing enzymes on electrodes often involve the use of entrapment matrices and hazardous chemicals, which can be harmful to the environment and limit the reuse and storage capabilities of the biosensors. Therefore, there is a need for a new approach that is sustainable and non-toxic, while also allowing for prolonged reuse and storage at room temperature [1234]The aim of this research is to develop a lactate oxidase (LOX) biosensor using a green and reusable approach [5]. This research utilizes the ambient ESD technique to fabricate the biosensor. The technique allows for the immobilization of the LOX enzyme on the PB/C-SPE electrode without the need for entrapment matrices or hazardous chemicals. The study demonstrates that the ESD technology enables the biosensor to be stored at room temperature and pressure for up to 90 days without affecting the enzymatic activity. The biosensor can also be reused for up to 24 measurements on both freshly prepared electrodes and electrodes that are three months old. The linear range of lactate detection is between 0.1 and 1 mM, with a limit of detection of 0.07±0.02 mM. Importantly, the biosensor does not exhibit any memory effects. The immobilization process does not involve the use of entrapment matrices or hazardous chemicals, making it environmentally sustainable and non-toxic compared to current methods. Furthermore, the application of an electrospray deposition cycle on previously used biosensors rejuvenates their performance, making them comparable to freshly made biosensors. This highlights the excellent recycling potential of the technique, eliminating the waste associated with disposable devices (scheme 1).



Scheme 1

References:

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P – 10

μ-FTIR reflectance spectroscopy coupled with multivariate analysis: rapid and robust method for identifying the extent of photodegradation on microplastics

[1]Eleonora Conterosito, [1]Maddalena Roncoli, [1]Chiara Ivaldi, [1] Marysol Ferretti, [2] Beatrice De Felice, [2]Marco Parolini, [3]Stefano Gazzotti, [3]Marco Aldo Ortenzi and [1]Valentina Gianotti

[1] Dipartimento per lo Sviluppo Sostenibile e la Transizione Ecologica, Università del Piemonte Orientale, Piazza S. Eusebio 5, 13100 Vercelli, Italy
[2] Department of Environmental Science and Policy, University of Milan, Via Celoria 26, I-20133, Milan, Italy
[3] LaMPo, Department of Chemistry, Università degli Studi di Milano, via C. Golgi 19, 20133, Milan, Italy
(eleonora.conterosito@uniupo.it)

Understanding the origins of microplastics (MPs) and evaluating the consequences of plastic pollution requires precise chemical information. Moreover MPs undergo chemical and physical changes, due to photoaging, which could impact their toxicity. μ-FTIR is one of the key techniques for the screening of microplastics, coupling the possibility of collecting optical images of the particles with the chemical information provided by the IR spectra. While reflectance μ-FTIR spectroscopy's sensitivity to particle thickness and photodegradation complicates automated spectral matching, it can also provide valuable information. In this study, we developed a method for the identification and the determination of the degree of photo-oxidation of microplastics, performing principal component analysis (PCA) on μ-FTIR data. We studied four types of microplastics: two conventional (PE and PS) and two compostable bioplastics (PLA and PBAT). which underwent artificially accelerated photoaging. PCA was able to classify the polymers and show degradation trends, highlighting even subtle changes in the spectra. Particular attention was given to the preprocessing of the dataset, which has great impact on the outcome of the analysis. The issue of reflection spectral "artifacts" obtained from particles thicker than 100 μm, which often hinder the recognition of the polymer by spectral matching, was also addressed.

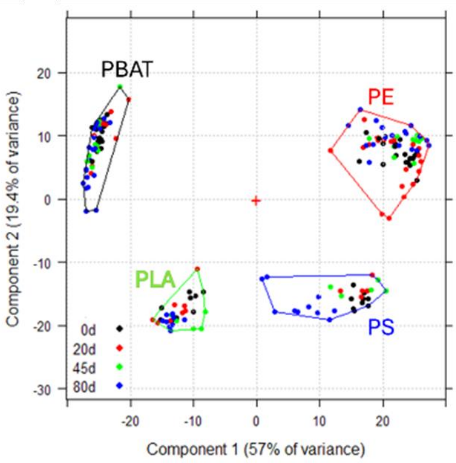

Figure 20. PCA scores plot of the μ-FTIR data.

Acknowledgements.
Eleonora Conterosito holds a researcher position supported by Next Generation EU–MUR.

P – 11

Solid Phase Peptide Synthesis using side-chain unprotected arginine and histidine, with Oxyma Pure/TBEC in green solvents.

[1] Ilaria Di Stefano,[1] Tommaso Fantoni,[2] Andrea Orlandin,[2] Marco Macis,[1] Alessandra Tolomelli,[2]
Antonio Ricci,[1]* Walter Cabri,[1]* and Lucia Ferrazzano

[1] Affiliation 1 (Università di Bologna via Gobetti 85, 40129-Bologna, Italy).
[2] Affiliation 2 (.R&D, Fresenius kabi, via San Leonardo, Villadose(RO), Italy)
(Ilaria.distefano3@unibo.it)

The elimination of side-chain orthogonal protective groups of arginine and histidine is critical to improve Solid Phase Peptides Synthesis (SPPS) sustainability through the increase of the peptides atom economy (AE) and the decrease of impurities generated during the final cleavage step. [1] In this work the combination of oxyma pure and tertbutyl ethyl carbodimmide (TBEC) in the correct ratio allowed us to use side-chain free arginine and histidine in green solvents.[2] Etelcalcetide and vasopressin intermediates as well as critical key fragments of liraglutide and semaglutide have been succesfully synthetized with SPPS using the optimized conditions. In addition, the oxyma pure/TBEC protocol in NBP/DMC was succesfully applied to a sequence containing side-chain unprotected arginine, histidine, tryptophane and tyrosine.

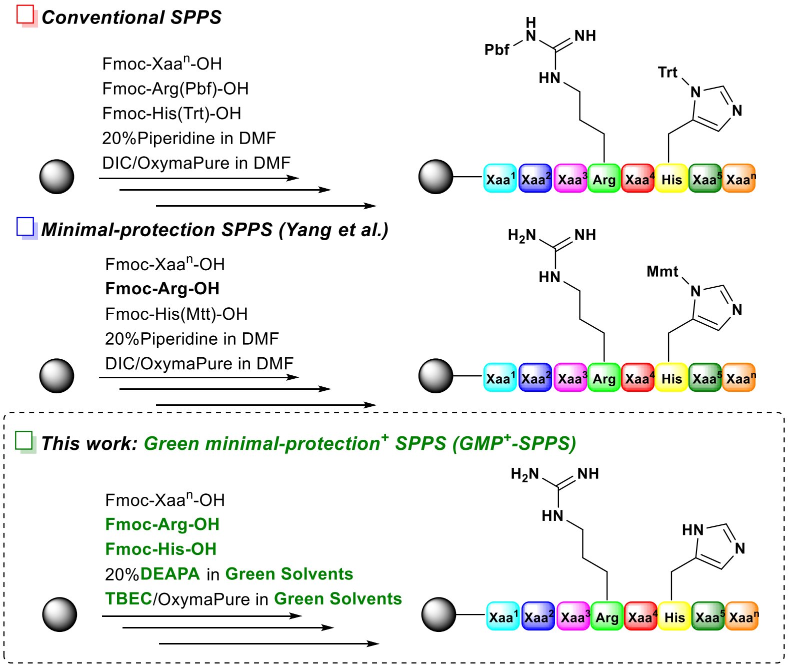

Figure 21. Minimal Protection (MP) in SPPS.

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P – 12

Synthesis of Block and Multi-Block Copolymers Based on Polyesters from ROCOP of Phthalic Anhydride and Epoxides from Renewable Sources

S. Esposito[a,b], S. Guerra[c], L. Tadiello[c], L. Giannini,[c] and C. Capacchione[a,b]

[a]*Department of Chemistry and Biology "Adolfo Zambelli", University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano, SA, Italy*

[b]*Consorzio InterUniversitario Reattività e Catalisi (CIRCC) Via Celso Ulpiani, 27 – 70126 Bari, Italy*

[c]*Pirelli Tyre S.p.A., Viale Piero e Alberto Pirelli, 25, I-20126 Milan, Italy*

saresposito@unisa.it

Polyesters are amongst the most widely applied oxygenated polymers. Most of commercial polyesters is prepared by polycondensation, they are found in applications spanning packaging, fibres, rigid plastics and engineering materials. Other routes, like ring-opening polymerization (ROP) of lactones and ring-opening copolymerization (ROCOP) of epoxides and cyclic organic anhydrides, have been explored to synthetize polyesters[1] coming from renewable source. With ROCOP the properties of the resulting materials can be easily manipulated by facile substitution of just one of the monomers and it may enable new materials based on aliphatic or semi-aromatic polyesters which are inaccessible using ROP due to thermodynamic reasons and this is interesting to increase thermal and mechanical properties.

In this context, block and multi-block copolymers possessing polyester blocks with different rigidity have been synthesized by ROCOP of phtalic anhydride and epoxides like cyclohexenoxide (CHO) and vinyl-cyclohexenoxide (vCHO) and others from renewable sources like epoxy methyl undecenoate (EMU) and glycidyl geraniol ether (GGE) respectively from fatty acids and terpene alcohols. Polymerizations were conducted resorting to insertion coordination transition metal catalysts like [OSSO]-type-Fe(III) with PPNCl, a catalytic system already demonstrated capable of promoting the synthesis of polycarbonates through ROCOP of epoxides and CO_2[2]. Different synthetic strategies have been explored, monomer conversions were monitored by NMR spectroscopy, and, in all cases, block copolymers are obtained due to the different polymerization rate of the epoxides. Furthermore, to modify the thermal properties of the polymers, copolymerization tests were carried out by varying the ratios between the epoxides which influence the formation of blocks with different rigidity. The polymers were characterized by Nuclear Magnetic Resonance techniques (^{1}H-NMR, ^{13}C-NMR, HSQC e DOSY), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and their ability to separate into microphases was investigated by Atomic Force Microscopy (AFM).

For a possible application these new synthesized polymers can be investigated within the properties of TPEs.

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P – 13

Organocatalytic Keratin Sponges for the Chemical Fixation of CO_2 into Cyclic Carbonates

[1] Alessandro Massi, [2] Marco Bottin, [3] Daniele Ragno, [4] Graziano Di Carmine

[1] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari, 46 – 44121 Ferrara (Italy).
(alessandro.massi@unife.it)

The fabrication of a novel macroporous organic material from keratin wool fiber waste is herein described together with its utilization as a heterogeneous matrix for the immobilization of organocatalysts, namely methyl imidazolium iodide, TBD, and a combination thereof. Additional features of the cross-linked keratin sponges include their insolubility in water and common organic solvents, as well as their exposure to the surface of isocyanate groups for organocatalyst immobilization. The one-component multifunctional keratin sponge bearing hydrogen bond donor, nucleophilic, and CO_2 activating sites effectively promotes the cycloaddition of CO_2 to epoxides free of solvent and co-catalysts, producing five-membered cyclic carbonates in high yields (79-94%) at moderate temperature (35 °C) and pressure (10 atm), with satisfactory recyclability (five runs) and the possibility of complete biodegradation in 2 days by enzymatic treatment (protease XIV).[1],

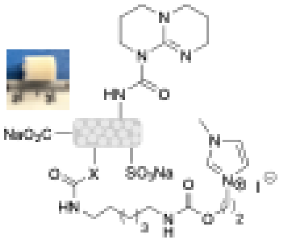

Figure 22. Multifunctional organocatalytic keratin sponge

Acknowledgements.
PRIN 2022, grant number: 2022JM3LZ3; PRIN 2022, grant number: 20225X2FS5; PRIN 2022 PNRR, grant number: P20224TTZF) and the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 1.5 – Next Generation EU, Call for tender n. 3277

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P – 14

In-situ and ex-situ thermocatalytic pyrolysis of plastics: a comparison of two different approaches

[1] Michele Offidani,[1] Loris Giorgini, [1] Tiziana Benelli, [2] Mirco Nodari, [2] Mattia Melloni,
[2] Angelo Ferrando, [1] Fabrizio Cavani and [1] Tommaso Tabanelli

[1] Dipartimento di Chimica Industriale "Toso Montanari" and Center for Chemical Catalysis-C3,
Università di Bologna, viale del Risorgimento 4, 40136 Bologna, Italy
[2] Research Center "C. Buonerba", Versalis s.p.a., 46100 Mantova, Italy
(michele.offidani2@unibo.it)

Plastic is considered one of the greatest technological innovations of the past century and its production has grown exponentially, exceeding that of many other man-made materials, indeed, in 2019 global plastic production was estimated to be around 460 million tons[1]. Pyrolysis is one of the most promising techniques that can be employed to minimize incineration and landfill disposal by upgrading the waste polymeric fraction that cannot be recycled otherwise. The pyrolysis oil can readily be employed as a starting material to produce new monomers and therefore new virgin polymers[2]. Nevertheless, there are some criticalities with purely thermal pyrolysis such as poor control over the oil yield and composition and challenging management of pollutants and unwanted compounds present in the plastic waste. The implementation of a catalytic system in the *in-situ* or *ex-situ* configuration can be the key to minimize some of those drawbacks. Among all the different catalyst tested in the pyrolysis of plastic wastes, mordenites seems to show promising results. Here we reported the catalytic performances of a mordenite with a silica over alumina ratio (SAR) equal to 90. Figure 1 shows the results of the tests performed in both the in-situ and ex-situ approach compared with a reaction conducted without a catalyst (blank). It is possible to see that the catalyst in the in-situ configuration was able to dramatically enhance the oil yield to over 83% and, the produced oil showed also a better composition. In addition to zeolites, other catalytic systems based on metal oxides (e.g. ZnO) have been tested on a PET-containing matrix to address the problem of terephthalic acid formation, by promoting decarboxylation reactions.

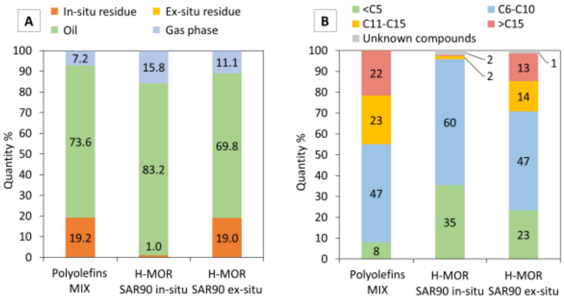

Figure 23. Catalytic performance of H-MOR SAR 90 in the in-situ and ex-situ configuration. A) Weight percentages of residue, oil and gas phase, B) Distribution of compounds based on the number of carbon atoms.

Acknowledgements

The authors are grateful to Italian Ministero dell'Università e della Ricerca and to Versalis for the Ph.D granted to M.O. through the PNRR D.M. 352/2022.

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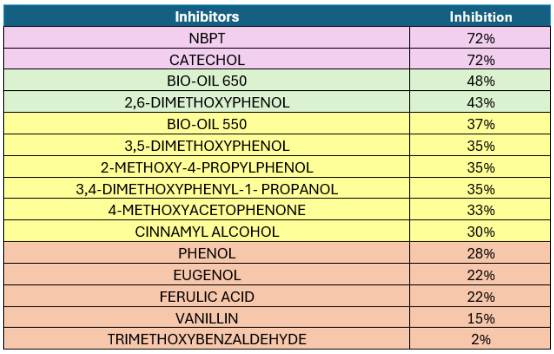
P – 15

Natural urease inhibitors from lignocelluloses

Spadavecchia Vanessa*,[1] Paola Galletti,[1] Chiara Samorì[1]

[1] *Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Piero Gobetti 85, 40129 Bologna.*
**vanessa.spadavecchi2@unibo.it*

Urea is the main source of N in worldwide crop production, but its rapid hydrolysis catalyzed by soil urease resulted in a substantial decrease in fertilization efficiency. Also, the rising pH impacts plant germination or early growth. Overall, the main problem remains ammonia volatilization, considering the compound itself and contributing to atmospheric pollution by reacting with acid pollutants (e.g., SO_2, NO_x)[1].
Using urease inhibitors as N-stabilizers has been implemented to counterbalance these negative aspects. One of the most used for agronomic purposes is N-(n-butyl) thiophosphoric triamide (NBPT), often co-formulated with urea for a controlled release of both the fertilizer and the urease inhibitor. Catechol and catechol-like molecules have been widely studied as alternatives but many of these compounds have safety issues[1].
In the present work, different aromatic molecules obtainable from lignocelluloses were investigated to understand any possible structure activity regarding urease inhibition and find sustainable and safe substitutes for commercial urease inhibitors.
The inhibition experiments were performed on Jack bean urease as well as urease naturally present in soil samples. Preliminary results indicate that the phenolic compounds here tested have a wide range of inhibition activity (from 2 to 48%) but no one of them reach the performance of catechol. The best inhibition results were obtained with a bio-oil obtained by pyrolysis of wood at 650°C and 2,6-dimethoxyphenol (Table 1).



Inhibitors	Inhibition
NBPT	72%
CATECHOL	72%
BIO-OIL 650	48%
2,6-DIMETHOXYPHENOL	43%
BIO-OIL 550	37%
3,5-DIMETHOXYPHENOL	35%
2-METHOXY-4-PROPYLPHENOL	35%
3,4-DIMETHOXYPHENYL-1- PROPANOL	35%
4-METHOXYACETOPHENONE	33%
CINNAMYL ALCOHOL	30%
PHENOL	28%
EUGENOL	22%
FERULIC ACID	22%
VANILLIN	15%
TRIMETHOXYBENZALDEHYDE	2%

Table 1. Inhibition of the activity of soil urease achieved by various aromatic compounds, in comparison to NBPT and catechol.

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P – 16

Upcycling of chitin to cross-coupling catalysts: tailored supports and opportunities in mechanochemistry

[1] Oscar Trentin, [2] Daniel Ballesteros-Plata, [2] Enrique Rodríguez-Castellón, [1] Leonardo Puppulin, [1] Maurizio Selva, [1] Alvise Perosa, [1] Daily Rodríguez-Padróna

[1] Department of Molecular Science and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, 30175 – Venezia Mestre, Italy
[2] Department of Inorganic Chemistry, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, Spain.
(oscar.trentin@unive.it)

In this study, chitin derived from shrimp shells was used in the design of heterogeneous Pd-based catalysts for Heck and Suzuki-Miyaura cross-coupling reactions. Pd nanoparticles supported on N-doped carbons were synthesized using three different approaches, including a sustainable mechanochemical method with a twin-screw extruder (Figure 1). The catalytic systems were then characterized using a multitechnique approach involving XPS, XRD, SEM, TEM, ICP-MS, and N_2-physisorption. Additionally, the effects of nanoparticle size, N-doping on the support, and their synergistic interactions on conversion were confirmed using Kelvin Probe Atomic Force Microscopy (KPFM), which provided valuable insights into charge transfer and metal-support interactions. All catalysts were tested in both reactions, and a complete parametric analysis was conducted to optimize experimental conditions, considering factors such as reaction time, temperature, solvent, base, and catalyst amount. The catalytic performance of the samples was evaluated in cross-coupling reactions under both batch and semi-continuous flow solvent-free conditions, resulting in a quantitative yield and an excellent productivity of 8.7 mol/(gPdh) respectively.[1]

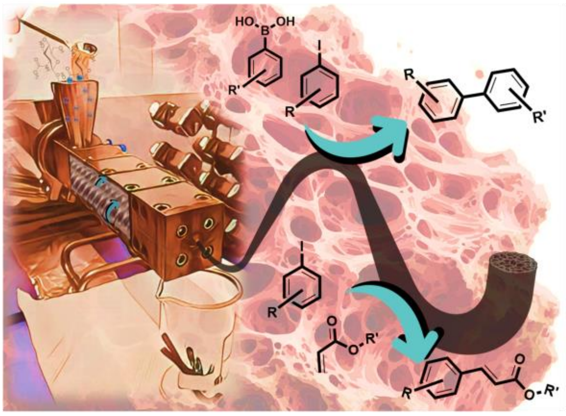

Figure 24. Schematic representation of the mechanochemical process employing a twin-screw extruder.

References:

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P – 17

Green retrofitting of a vintage reaction: production of acetone from renewable sources via pyrolysis of acetates

[1] Federica Zimbardi, [2] Cristian Torri

[1] Dipartimento di chimica Giacomo Ciamician (Università di Bologna, Via Francesco Selmi, 2, Bologna).
(federica.zimbardi2@unibo.it)

CO_2 emissions have exceeded pre-pandemic levels and continue to increase[1], suggesting a need to develop technologies that can exploit CO2 as a source. There is also a need to decarbonize chemical industries by employing alternative chemical synthesis that are GHG-free sources[2].

The aim of the study was to demonstrate that it is possible to obtain high-purity acetone by the thermal ketonization of acetates resulting from gas fermentation. Acetate is one of the main products of fermentation and anaerobic bioconversion and is the simplest platform chemical that can be generated from CO_2.[3]

A series of pyrolysis was performed in a bed fixed reactor system at 450°C using sodium acetate and salts from Carbon Capture and Fixation system (CCF) as feedstock. Pyrolysis was conducted in CO_2 atmosphere and three different retention time were tested. The bio-oil obtained showed an organic content of more than 70%, of which 95% was acetone. Impurities content was negligible and mostly characterised by Isophorone whose quantity did not exceed 1%w/w. Results confirmed pure acetone can be produced from renewable sources.

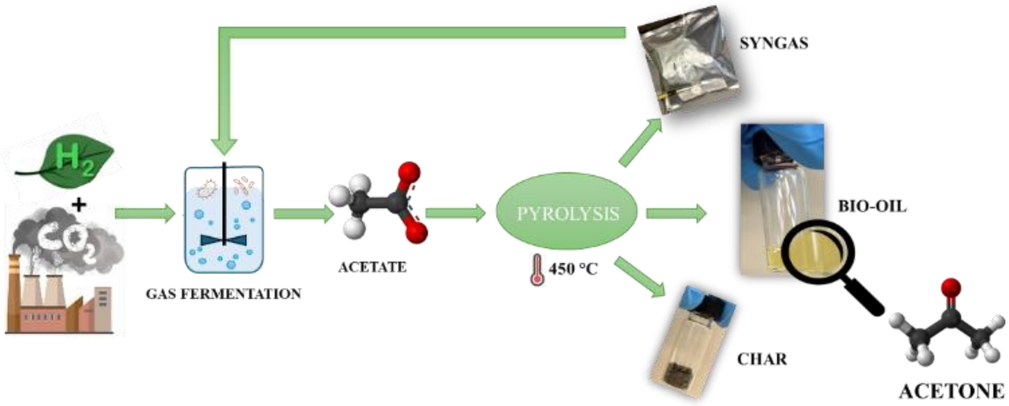

Figure 25. Scheme of the conversion of gas fermentation products into high-purity acetone.

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Lista contatti partecipanti

Nome	Cognome	Indirizzo e-mail
Clelia	Aimone	clelia.aimone@unito.it
Francesca	Annunziata	francesca.annunziata@unimi.it
Claudia	Antonetti	claudia.antonetti@unipi.it
William	Bertoluzzo	william.bertoluzzo@studenti.unipd.it
Elza	Bontempi	elza.bontempi@unibs.it
Chiara	Bruschetta	chiara.bruschetta@unito.it
Fabio	Bucciol	fabio.bucciol@unito.it
Maria Federica	Buonsanti	federica.buonsanti@bracco.com
Maria Chiara	Cabua	chiara.cabua@gmail.com
Emanula	Calcio Gaudino	emanuela.calcio@unito.it
Callegari	Camilla	camilla.callegari01@universitadipavia.it
Carmine	Capacchione	ccapacchione@unisa.it
Giorgio	Capaldi	giorgio.capaldi@unito.it
Alice	Cappitti	alice.cappitti@unifi.it
Vito	Capriati	vito.capriati@uniba.it
Carla	Carfagna	carla.carfagna@unibo.it
Massimo	Carraro	mcarraro@uniss.it
Antonella	Cartoni	
Mattea Carmen	Castrovilli	matteacarmen.castrovilli@cnr.it
Fabrizio	Cavani	fabrizio.cavani@unibo.it
Noemi	Colozza	noemi.colozza@mlib.ism.cnr.it
Martina Letizia	Contente	martina.contenter@unimi.it
Eleonora	Conterosito	eleonora.conterosito@uniupo.it
Matteo	Corradini	matteo.corradini7@studio.unibo.it
Giancarlo	Cravotto	giancarlo.cravotto@unito.it
Marta	Da Pian	m.dapian@elsevier.com
Graziano	Di Carmine	graziano.dicarmine@unife.it
Ilaria	Di Stefano	ilaria.distefano3@unibo.it
Sara	Esposito	saresposito@unisa.it
Maurizio	Fagnoni	maurizio.fagnoni@unipv.it
Giulia	Fiorani	giulia.fiorani@unive.it
Sara	Fulignati	sara.fulignati@unipi.it
Alessia	Giordana	alessia.giordana@unito.it
Giorgio	Grillo	giorgio.grillo@unito.it
Ilaria	Grimaldi	ilagrimaldi@unisa.it

Lorenzo	Guazzelli	lorenzo.guazzelli@unipi.it
Alexandra	Jorea	alexandra.jorea01@universitadipavia.it
Giulia	Licini	giulia.licini@unipd.it
Domenico	Licursi	domenico.licursi@unipi.it
Federico	Locardi	federico.locardi@unige.it
Maela	Manzoli	maela.manzoli@unito.it
Alessandro	Massi	alessandro.massi@unife.it
Andrea	Mezzetta	andrea.mezzetta@unipi.it
Stefano	Nejrotti	stefano.nejrotti@unito.it
Marco	Nicosia	mnic41999@gmail.com
Michele	Offidani	michele.offidani2@unibo.it
Federica	Palmeri	f.palmeri@uniroma1.it
Laura	Palombi	laura.palombi@univaq.it
Emilia	Paone	emilia.paone@unirc.it
Fabrizio	Passarini	fabrizio.passarini@unibo.it
Sveva	Pelliccia	sveva.pelliccia@unina.it
Prisco	Prete	pprete@unisa.it
Salvatore	Princiotto	salvatore.princiotto@unimi.it
Stefano	Protti	stefano.protti@unipv.it
Carlo	Punta	carlo.punta@polimi.it
Venanzio	Raglione	venanzio.raglione@mlib.ism.cnr.it
Monica	Rigoletto	monica.rigoletto@unito.it
Silvia	Rizzo	silvia.rizzo12@unibo.it
Daily	Rodriguez-Padron	daily.rodriguez@unive.it
Giulia	Romagnoli	giulia.romagnoli1@student.unisi.it
Vincenzo	Russo	v.russo@unina.it
Alireza	Safdari	alireza.safdari@unimi.it
Antonella	Salvini	antonella.salvini@unifi.it
Chiara	Samori	chiara.samori3@unibo.it
Michela	Signoretto	michela.signoretto@unive.it
Vanessa	Spadavecchia	vanessa.spadavecchi2@unibo.it
Silvia	Tabasso	silvia.tabasso@unito.it
Leana	Travaglini	ltravaglin@wiley.com
Oscar	Trentin	oscar.trentin@unive.it
Federica	Tufano	ftufano@unisa.it
Federico	Verdini	federico.verdini@unito.it
Gabriele	Viada	gabriele.viada@unito.it
Federica	Zaccheria	federica.zaccheria@scitec.cnr.it
Federica	Zimbardi	federica.zimbardi@studio.unibo.it
Daniele	Zuccaccia	daniele.zuccaccia@uniud.it

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