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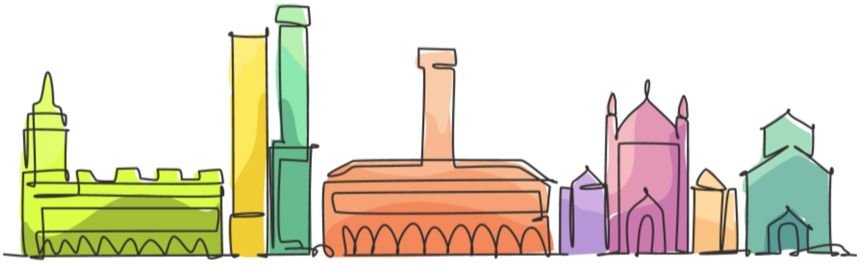

- BOOK OF ABSTRACT -

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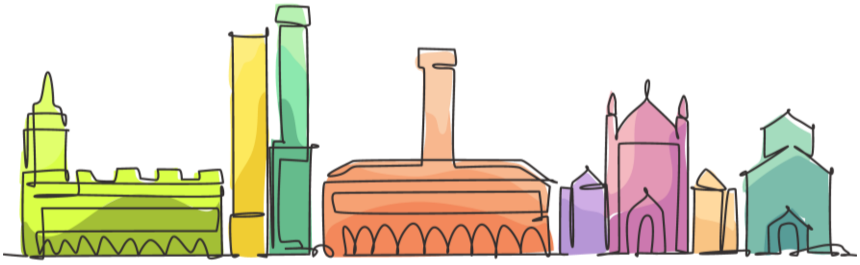

- PREMI ALLA RICERCA -

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An insight into the relationship between deep eutectic solvents and ionic liquids for sustainable applications

Mezzetta Andrea[1]

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Deep eutectic solvents (DESs) and ionic liquids (ILs) are two classes of media which have the potential to drive the ecological transition in several different research areas. Although different entities, DESs and ILs share some attractive features, the most astonishing being their designer solvent nature. This denomination is often used to describe the possibility to tailor the properties of these materials for a specific application, which is a unique trait when compared to classical organic solvents.
When first appeared in the literature, DESs were presented as new ionic liquids, and have then been called this way for quite some time. However, the relationship between ILs and DESs deteriorated over time, being DESs called first a "kind" of ionic liquids and finally alternative to ionic liquids (Figure 1).

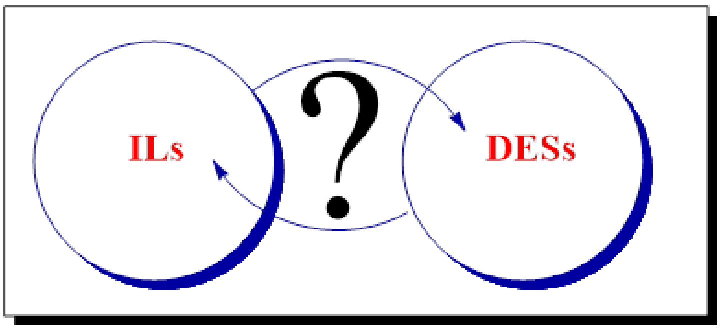

Figure 1. Deep eutectic solvents and ionic liquids: to what extent are they actually related?

Recently, we started to look into the relationship between ILs and DESs, highlighting similarities, clear differences and complementarity in some aspects [1]. Herein, examples will be shown with the aim of underlining pros and cons of both classes of solvents in relevant applications keeping in mind the goal of sustainable development.

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I tried to be a "green" industrial chemist

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The roots of innovation aimed at developing a **more sustainable industrial chemistry**, within the activities carried out in the Bologna group founded by Prof. Ferruccio Trifirò in 1976, can be identified in the study aimed at rationalizing - both from the point of view of process schemes and energy costs - the synthesis of some basic chemical compounds, for example starting from fossil-based alkanes, instead of alkenes. In the field of catalytic oxidations, the transformation of once-through processes operating with air, into recycling processes operating with oxygen, the latter being characterised not only by lower gaseous emissions but also by greater selectivity. All these process modifications require the development of **new or improved catalysts**.

The theme of sustainability in the chemical industry has then experienced a new era with the "**green chemistry**" and "**green engineering**" principles, driving, for example, the abandonment of fossil fuels as raw materials, and the study of new processes from renewables (e.g., biomass).

The **bio-refinery paradigm** is located in this context, and the use of new types of building-blocks, obtained for example from lignocellulose instead of petroleum, or from organic by-products of the manufacturing industry - in response to the requirements of **Circular Economy** - has stimulated the development of new synthetic routes and therefore of new catalysts.[1] These must possess multifunctional characteristics, to be able to catalyze in a single step the defunctionalization and refunctionalization of bio-based platform molecules.

During my lecture I will present some of the research studies conducted with the aim of making industrial chemistry less impactful on the environment.

Acknowledgements. My deepest thanks go to Prof. Ferruccio Trifirò, my mentor, who explained to me the chemical industry and the importance of scientific collaboration with the industrial environment. Thanks also to all my students, collaborators, colleagues, and to my family.

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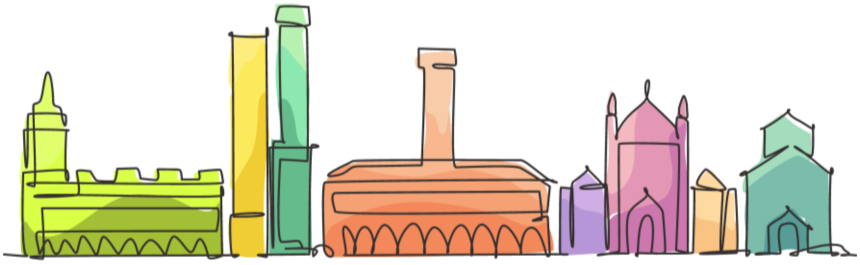

- PREMI DI DOTTORATO CINZIA CHIAPPE –

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Premio *"Cinzia Chiappe"* Ed. 2025

Massimo Melchiorre

Titolo Tesi di Dottorato

Sustainable solvents and chemicals: synthesis and applications in catalysis, storage energy devices, and cultural heritage

Corso di Dottorato

Scienze Chimiche

Tutor

Prof. Francesco Ruffo

Prof.ssa Maria E. Cucciolito

Università degli Studi di Napoli Federico II, Dipartimento di Scienze Chimiche

Sintesi della Tesi

I solventi sono composti fondamentali per la chimica e trovano ampio impiego nell'industria. Tuttavia, molti solventi comuni derivano da fonti fossili ed hanno una certa tossicità, e il loro utilizzo contribuisce all'impatto ambientale di prodotti e processi chimici. Le strategie per evitare o ridurre l'uso di solventi pericolosi sono principalmente tre: l'utilizzo di condizioni *solvent-free*; l'utilizzo di solventi acquosi; l'utilizzo diretto di solventi organici o sistemi molecolari di origine rinnovabile e a basso profilo di rischio. Nonostante le prime due strategie risultino particolarmente interessanti per molte applicazioni, esse non possono coprire l'intero spettro d'uso dei solventi; pertanto, anche la terza strategia è necessaria per sostituire i solventi organici più problematici (es. DMF, NMP).

Questo progetto di dottorato si inserisce in quest'area di ricerca e mira a introdurre i 4-oxo-diossolani (DOX) come una nuova classe di solventi dipolari aprotici. In una prima fase è stata sviluppata una strategia conveniente per la preparazione di DOX tramite chetalizzazione di α-idrossiacidi di origine rinnovabile (es. acido lattico) catalizzata da acidi di Lewis (es. sali di Fe(III)). [1] Successivamente sono stati preparati, caratterizzati e testati sei diversi DOX come mezzi di reazione per processi di *cross-coupling* catalitici (es. coupling di Mizoroki–Heck promosso da Pd) e reazioni stechiometriche (es. reazione di Menšutkin). [2] Tra i DOX ottenuti, il candidato solvente con la polarità più elevata, il 5-metil-1,3-diossolano-4-one, è stato utilizzato per la preparazione di elettroliti adatti a dispositivi di accumulo energetico. Nell'ambito di questa ricerca, è stato inoltre studiato in modo comparativo il γ-valerolattone (GVL) come solvente per sistemi di accumulo ad alta potenza, ad alta energia, e ibridi. [3] Infine, alcuni DOXs insieme ad altri solventi organici di origine rinnovabile (es. GVL, solketal, etil lattato, 2-etilesil pelargonato), sono stati applicati nel restauro di beni culturali, sostituendo i solventi tradizionalmente impiegati (es. acetone, etanolo e isoottano). [4]
Un riassunto grafico complessivo del lavoro è riportato nella **Figura 1**.

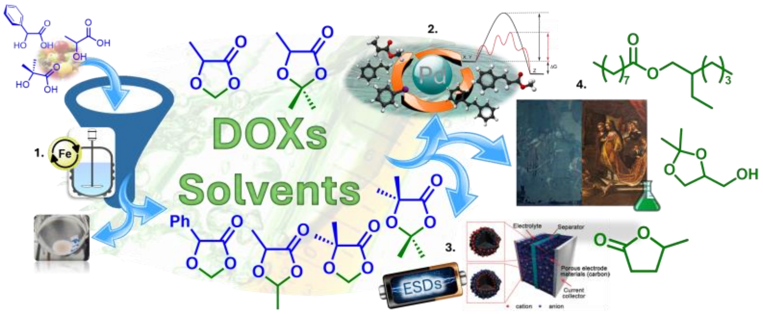

Figura 1: Introduzione dei DOXs come solventi aprotici polari per diverse applicazioni.

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Acknowledgment

Massimo Melchiorre thanks the MICS Extended Partnership and received funding from the European Union Next-Generation EU (PNRR–MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 –D.D. 1551.11- 10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

Premio “*Cinzia Chiappe*” Ed. 2025

Federico Verdini

Titolo Tesi di Dottorato

New Hybrid Technologies for Chemical Process Intensification

Corso di Dottorato

PhD in Pharmaceutical and Biomolecular Sciences

Tutor

Prof. Emanuela Calcio Gaudino

Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino

Sintesi della Tesi

In the present PhD thesis, various enabling technologies—whether employed individually, such as microwaves (MW), ultrasound (US), and hydrodynamic cavitation (HC), or combined synergistically, such as HC coupled with non-thermal electrical discharge (ED) plasma—have been effectively utilized to enhance specific chemical processes. The focus has been specifically on two pivotal domains of green and sustainable chemistry: (I) wastewater remediation and (II) valorisation of residual lignocellulosic biomass within the circular economy.

SECTION I: A novel hybrid HC/ED plasma advanced oxidation process (AOP) was developed to intensify wastewater purification processes in quaternary treatments, achieving fast degradation of emerging organic contaminants without the use of external oxidizing chemicals in a pilot-scale reactor. The hybrid HC/ED process generated more reactive oxidative species (H_2O_2, •OH, •O, •H) than HC alone and other typical AOPs such as Fenton and ozonation, with UV light enhancing the oxidative effect. This reactor enabled a complete degradation of several pharmaceutical contaminants such as tetracyclines [1], metronidazole, and furosemide [2] at very high starting concentrations (>10 mg/L) in deionized and tap water (> 5 L) within only 15 minutes at a flow rate >280 L/h, with moderate energy consumption (~10 kWh/m^3). Moreover, the hybrid HC/ED reactor demonstrated remarkable efficiency in decontaminating harshly polluted real pharmaceutical industrial effluent (PIE) [3] when combined with activated carbon adsorption, effectively reducing the extremely high initial PIE chemical oxygen demand (COD > 480 g/L) to levels below Italian legal limits for river or groundwater disposal (COD < 160 mg/L), presenting a promising solution for treating highly polluted effluents.

SECTION II: The hybrid HC/ED plasma reactor was integrated into a biorefinery framework for complete biomass valorization. Residual biomass (wheat straw, WS) was delignified with MW to recover lignin, which was depolymerized using the HC/ED reactor without catalysts or solvents, producing monolignols (4-vinylphenol, anisole, etc.). Anisole was further converted to platform chemicals via MW-assisted hydrogenation (80°C, 30 bar H2, 2 h). Additionally, WS served as cellulose- and hemicellulose-rich biomass, while corn straw underwent MW-assisted alkaline hydrolysis (2 min; 200°C; 0.1 M HCl) to yield C5/C6 sugars. Fermentation with MMC bacteria from dairy sludges produced polyhydroxyalkanoates (PHA), with yields of 41.4% (lab-scale) and 76.3% (pilot-scale, 3 L) [4].

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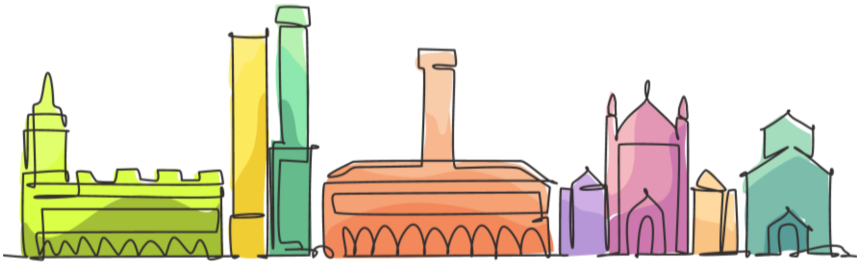

- CHEMSUSCHEM LECTURE –

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Biomass-Derived Catalytic Architectures: Chitin valorisation for the synthesis of modified N-doped carbons

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This study investigates the potential of utilizing fishery industry waste, which amounts to millions of tons annually, as a valuable source for biopolymers. The primary objective is to develop a flexible biorefinery model that integrates waste management, chemical processing of residues, and the scalable production of catalysts. Chitin, the second most abundant biopolymer on Earth, has been explored as a precursor for catalyst supports. Despite its potential, the use of chitin in innovative applications is often limited by its low solubility in most solvents, except for specific ionic liquids. In this work, we explore various valorization pathways using mechanochemical approaches to transform chitin into advanced catalytic supports. Our research team has recently demonstrated the successful conversion of chitin-rich bio-waste (shrimp shells) into metal-free catalysts for CO_2 fixation reactions.[1] Furthermore, we have developed new families of both noble and non-noble metal nanoparticles supported on chitin, which have shown promising catalytic activity in selective alcohol oxidation, reductive amination, hydrogenation, and C-C crosscoupling reactions.[2-4]

Acknowledgements.
DRP gratefully acknowledges the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie Cofund Grant Agreement no. 945361.

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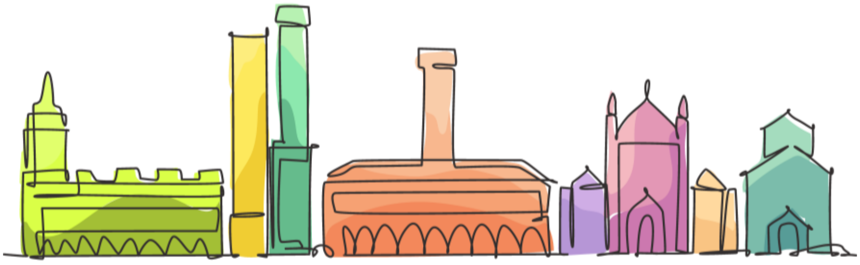

- KEYNOTES -

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Unlocking the potential of oleochemistry in biorefinery development

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To achieve the goal of a successful biorefinery, that is producing a wide range of high value-added products and materials, one of the key tools offered by chemistry is the ability to fully exploit the diverse and versatile structures found in biomass-derived sources. During the last years we gained a strong experience in the transformation of oils and fats, that are important actors in bioderived streams and that fully represent the two-faced essence of biomass managing: chemical richness on one hand and complexity on the other. The carbon skeleton of triglycerides, combined with the presence of double bonds and ester moieties (Figure 1) make them suitable substrates for several transformations able to prepare a wide variety of chemicals and materials. By way of example, the use of oils with different fatty acid compositions, including used cooking oil, allowed us to obtain thermosetting resins with tunable properties [1]. The valorisation of the oil extracted from rice bran, a waste of rice manufacturing, has been employed for the preparation of emulsifiers [2] and free fatty acids has been exploited to prepare biobased surfactants in combination with sugars. An overview of these and other applications of oils and fats studied within different biorefinery projects will be presented.

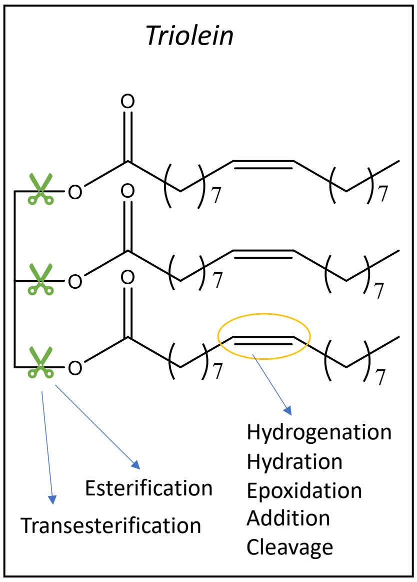

Figure 1. Simplified triglyceride and main possible reactions at glance

Acknowledgements

Thanks are due to the Extended Partnership PE00000004 “Made in Italy Circolare e Sostenibile” (MICS) project, funded by the European Union-Next Generation EU and to Futuraw Project (le materie prime del futuro da fonti non-critiche, residuali e rinnovabili) for financial support.

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The Intriguing Case of CO_2-Switchable Solvents Extractions, Separations, Reactions

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CO_2 addition can convert an apolar solution mixture of amine and hydroxyl compound into a polar carbonate salt liquid phase (CO_2-triggered polarity switch). The change can be reverted through CO_2 removal (Fig. 1)[1]. Lipophilic substances soluble in the first phase become unsoluble in the second one; vice versa for hydrophilic substances. Depending on the presence of water or not, these solvents systems are called: Switchable Hydrophilicity Solvents SHS or Swithchable Polarity Solvents SPS,

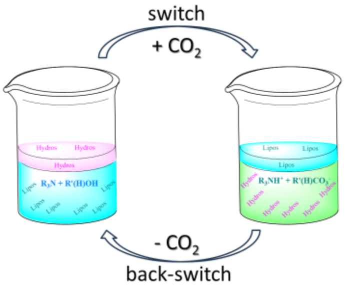


Figure 1. CO_2-triggered solvent switch and back-switch

This intriguing behaviour allows straightforward solute recovery and easy and energy-saving solvent recycling, fostering chemical sustainability.

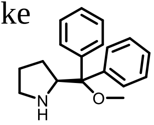
We exploited some of these facinating solvent systems for different purposes:

Extraction of valuable substances from biomass.

We extracted useful lipids (trigycerids, hydrocarbons) from alagal biomass of *Botryococcus braunii*, *Nannochloropsis gaditana* and others using bot SPS, like DBU + 1-Octanol, or SHS like N,N-Dimethylcyclohexylamine (DMCHA).[2]

Separations of different components of multilayered packaging materials.

We exploted DMCHA for separation, collection and recovery materials from mutilayered packaging wastes, expecially those composed of aluminum layer and different polymer layers No degradetion of properties of both organic polymers and the metal was obseved. Full solvent recycling and reuse could be achieved for 7 cycles.[3]



Reactions performing asymmetric catalysis could be carried out in SHS systems, like DMCHA, exploiting chiral amine organocatalysts. The organocatalyst, in priciple, follows the SHS solvent in the switch/back-swiths process and can be recycled together with the solvent. The organocatalyst/SHS system, however, proved to be unreliable, giving reise to many unforeseen drawbacks, whose fixing is still ongoing.

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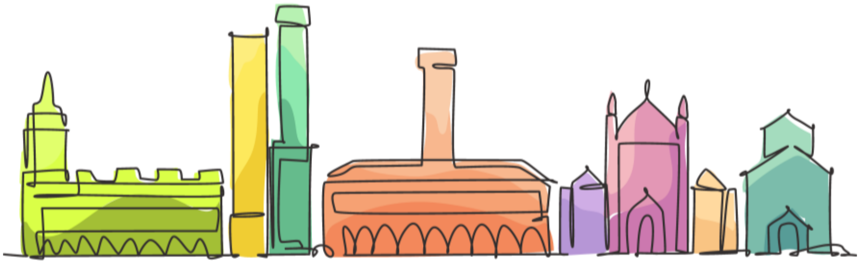

- PRESENTAZIONI ORALI -

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Sustainable ABA copolymers: tuning thermal and mechanical properties by chemical composition

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In this contribution, the synthesis via ARGET-ATRP of bio-based ABA copolymers with tunable thermal- and mechanical properties is discussed. ARGET-ATRP is a convenient technique for the synthesis of sustainable polymers as it requires low amounts (as low as ppm levels) of catalysts based on benign and abundant metals (Cu, Fe), thus avoiding the purification steps and significantly reducing the environmental impact of the process[1,2]. All ABA triblocks feature a soft central chain B consisting of poly(lauryl methacrylate) (PLMA, a fatty-acid-derived polymer with a low T_g) and hard, glassy segments A based on methacrylic derivatives of, alternatively, dihydro-eugenol (DEuMA), carvacrol (CaMA) or syringaldehyde (SyMA). A bifunctional PLMA macroinitiator was employed in the ARGET process and the molar fraction of the glassy monomers was varied (Figure 1).

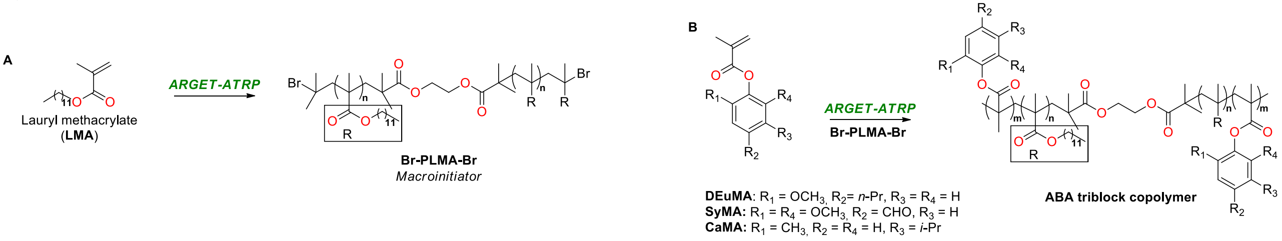

Figure 1. Two-step synthesis of bio-based ABA copolymers by ARGET-ATRP

Thermal properties of copolymers showed that the lowest T_g was not drastically influenced by the M_w of the central PLMA, while the nature of the hard blocks strongly impacted both the higher T_g and mechanical properties of materials. In fact, copolymers containing SyMA and DEuMA exhibited T_g higher than those with CaMA. Moreover, the DEuMA conferred plastic behavior to copolymers, while CaMA blocks prevalently led to elastomeric properties. Interestingly, thermoplastic and elastomeric behaviors could be modulated varying the weight fraction of SyMA. More in general, the stress-strain tests supported the possibility that ABA structures may lead to advanced bio-based materials with a wide range of mechanical properties, the latter spanning from elastomeric- to thermoplastic depending on the nature and amount of A.

Acknowledgements. All the authors acknowledge financial support by "Fondi di Ateneo per la Ricerca" (FAR) 2023 and Prometeon Tyre Group for the support in performing thermal- and mechanical analyses

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From water to oil resistance: exploring the potential of cellulose nanofibers-based coating agents

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The increasing environmental concerns associated with non-biodegradable, fossil-derived packaging materials have led to growing interest in sustainable alternatives. Although these materials offer excellent barrier properties against water, water vapor, oxygen, and oil, their persistence in the environment poses significant ecological risks. In contrast, cellulose-based materials have gained attention due to their biodegradability, renewability, and non-toxicity, showing potential for the development of eco-friendly packaging solutions. However, their intrinsic poor barrier properties limit their application, necessitating surface coatings to enhance their performance, particularly against water and oil migration. Nevertheless, the hierarchical structure of cellulose enables the extraction of nanoscale constituents with outstanding properties, such as high surface area and capability for hydrogen bonding, making them promising candidates as additives for the improvment of paper barrier properties.[1]

In this work, cellulose nanofibers (CNF) are extracted from eucalyptus-derived cellulose through two different approaches for comparison. The first approach involves TEMPO-mediated oxidation, a regioselective chemical treatment that converts C6 primary hydroxyl groups of cellulose into carboxyl groups.[2] The second method is a enzymatic hydrolysis with endoglucanase which cleaves the glycosidic bonds, leaving the chemical structure unmodified.[3] Both treatments are followed by a combination of mechanical processes, including ultrasonication, refining, and homogenization, to effectively achieve nanosizing. Different formulations containing CNF, both individually and in combination with other biopolymers are tested after being applied on different paper matrices through spray coating. Furthermore, hydrophobization of CNF is performed by chemically modifying their surface, resulting in novel formulations capable of improving water resistance. Finally, oil resistance of treated paper is evaluated performing KIT test while, water resistance performances are tested through $Cobb_{60}$ test and measuring water contact angle. Outstanding results, both in terms of oil and water resistance are obtained, even with minimal coating loads (< 5 g/m^2), highlighting the potential of CNF-based coating agents.

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The ESCAPE model application approach for the eco-design of cellulose nanocrystals

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Sustainability is increasingly acknowledged as a key guiding principle in the design of materials and processes. In this context, cellulose emerges as a promising renewable resource for the development of advanced materials, due to its biodegradability, renewability, and favorable mechanical properties. The hierarchical structure of cellulose can be deconstructed to yield nanocellulose, among which cellulose nanocrystals (CNC) have garnered considerable attention for applications in packaging, cosmetics, energy storage, and nanocomposites.

This work compares two CNC production routes on the bases of an early-stage sustainability assessment: the conventional sulfuric acid hydrolysis[1] and an alternative method based on the extraction by a deep eutectic solvent[2] (DES) composed of oxalic acid and choline chloride. As-obtained CNC were extensively characterized in terms of morphological and physicochemical properties.

While full life cycle assessment (LCA) is generally not easily performed for technologies at low technological readiness levels, the "ESCAPE"[3] model offers a simplified and accessible tool for preliminary evaluation.

For the first time, the ESCAPE methodology was applied as an eco-design tool at lab-scale for CNC production, to assess the overall sustainability of each process and identify environmental hotspots. Sustainability was quantified in terms of embodied energy (EE) and carbon footprint (CF), incorporating both local and international energy mixes, and considering the temporal progressive variation of the same mix in the last 15 years in favor of renewable sources. The DES-based process demonstrated improved sustainability, mainly attributable to shorter purification steps and higher material recovery. Targeted optimizations in these stages further reduced environmental impacts without compromising the morphology of the final CNC products.

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Sustainability and Paper Production

An Integrated Approach to Minimizing Environmental Impact

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The production of paper and paperboard is a highly energy-intensive process that involves significant use of chemicals. These chemicals are used to impart various functionalities to cellulose-based materials, such as mechanical properties, moisture resistance, and barrier properties, as well as to facilitate their production through the use of additives known as process products. In recent years, the high environmental impact of this sector has prompted constant efforts by industry stakeholders to provide technological and chemical alternatives as a commitment to more sustainable production.

One effective strategy for the use of chemicals is to optimize their usage through the development of more efficient products that reduce their use and improve their retention on cellulose fibre, thus limiting their presence in wastewater.

Looking to the future, the vision of more sustainable paper and paperboard production also involves replacing traditional fossil-based chemicals with raw materials of vegetable origin, particularly cellulose-based.

Investment in research and continuous optimization of products are key components of a sustainability strategy focused on the product and staff training. In a nutshell, we contribute on various fronts to minimizing the impact of chemicals in paper production through immediate actions and long-term vision.

Life Cycle Assessment (LCA) of Ceramic Pigments: The Case of $CoAl_2O_4$

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To facilitate the ceramic industry's shift towards digital decoration via inkjet printing, it is crucial to develop more environmentally friendly pigments. Although cobalt-aluminium spinel ($CoAl_2O_4$) is widely used as a blue pigment, its environmental impact has not been evaluated through Life Cycle Assessment (LCA), potentially missing opportunities for more environmentally sustainable alternatives. This study provides the first comparative environmental LCA of four different synthetic methods for producing $CoAl_2O_4$ and several lower-cobalt alternatives. It also examines two hybrid pigments, three M^{2+}-doped spinels ($M_{1-x}Co_xAl_2O_4$, where M = Zn^{2+}, Mg^{2+}), cobalt olivine (Co_2SiO_4), and its lower-cobalt variants, including Co^{2+}-doped willemite (Zn_2SiO_4). The findings highlight the key substances and processes contributing to the environmental impacts of cobalt-based blue ceramic pigments and suggest strategies to mitigate these impacts. Hybrid pigments emerged as promising candidates with vibrant blue hues and lower environmental impacts compared to traditional CoAl2O4, while $Co_{0.05}Zn_{1.95}SiO_4$ showed the lowest environmental impacts among the pigments studied. The reliability of these results was confirmed through Monte Carlo (MC) simulations. Potential environmental impacts were compared with CIELAB colour parameters to identify pigments that offer desirable blue hues while being environmentally sustainable, supporting their practical application.

Life cycle assessment of an ammonia production process via electroreduction of nitrates in aqueous solution

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Nowadays, ammonia is one of the most common chemical products (150 Mt produced worldwide annually) as it is mainly employed as an intermediate to produce nitrogen fertilizers (around 85% of the total).[1] Alternative technologies to the energy-intensive Haber-Bosch process are gaining recent interest among researchers, e.g., the Nitrate Reduction Reaction (NO3RR) aimed at synthesising ammonia via electrochemical reduction of nitrates, a widespread waste product and water pollutant. In this study, Life Cycle Assessment (LCA) methodology is applied to evaluate the environmental profile associated with a laboratory scale NO3RR technology. The aim is to assess the environmental feasibility of the process by identifying hotspots—materials and processes that significantly contribute to the system's overall burdens—and to support upscaling in line with ecodesign principles. The analysis was subdivided in two levels, to focus both on the production of the flow cell (level I, FU=1 cell) and on the production of NH_3 (level II, FU=10 mg NH_3). Results indicate that polytetrafluoroethylene and iridium (a CRM) used in the assembly of cell components are the primary contributors to the total environmental impacts of the electrochemical cell. Regarding the laboratory reaction, data reveal that higher electricity consumption, driven by longer reaction times, results in increased cumulative impacts associated with the system. These insights are essential for a sustainable technology development.

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Life Cycle Assessment (LCA) of Curcumin-stabilized Silver Nanoparticles (Cur-AgNPs)

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Silver nanoparticles functionalized with curcumin (Cur-AgNPs) have recently attracted growing interest as antimicrobial agents[1], combining the well-known antimicrobial properties of silver nanoparticles (AgNPs) with bioactive properties of curcumin. Although many studies have demonstrated the remarkable antimicrobial activity of Cur-AgNPs[2,3], their potential environmental impacts have yet to be assessed with Life Cycle Assessment (LCA) methodology. LCA provides a comprehensive overview of the impacts associated with each stage of a product or process, from raw material production through to end-of-life and is one of the most highly regarded tools for sustainable decision-making. This study focuses on the assessment of Cur-AgNPs with LCA methodology. Cur-AgNPs were synthesised at a laboratory scale in water using a low-energy microwave-assisted approach. Additionally, the study compared the potential environmental burdens of two distinct curcumin supply lines: chemical synthesis from vanillin and extraction from *Curcuma longa* rhizomes cultivated in India. The environmental impacts of each stage, from cultivation and drying through to extraction, was assessed. The results of the LCA identified the critical substances and processes that contribute to the environmental footprints of CUR-AgNPs as well as curcumin production via synthesis and ethanol-based extraction. Finally, this analysis provided guidelines for more sustainable production of CUR-AgNPs for antimicrobial applications.

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Cascade Valorization of Enological Waste

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Waste minimization is a key pillar of the circular economy, driving interest in the valorization of agri-food residues. Lignocellulosic biomass, such as grape stalks, offers a low-cost feedstock rich in bioactives and biopolymers suitable for biorefinery applications.

This work proposes a sequential biomass valorisation protocol featured by a multidisciplinary strategy, exploiting microwave technology and subcritical water as green solvent, where physical/chemical treatments work in synergy with biological ones. The early stage encompassed the sequential fractionation of grape stalks, achieving several product streams, enriched in polyphenols, hemicellulose and pectins, lignin and cellulose.

The polyphenolic fraction successfully inhibited the growth of *Brettanomyces bruxellensis* and *Acetobacter pasteurianus*, microorganisms responsible for major wine off-flavors.

The pectic fraction was investigated for its prebiotic activity with *Lactobacillus acidophilus* CECT 1529 and *Enterococcus faecium* NCIMB 10415.

The cellulose-rich residue from the cascade treatment was exploited as a fermentation substrate for the last step, producing lactic acid by harnessing engineered *Clostridium thermocellum* strains LL1111 (Δ*adhE, ldh*^{S161R}), an hyperproducer of lactic acid, and LL1630, a mixed culture directly evolved from LL1111 characterized by a higher tolerance to lactic acid (up to 35 g/L)[1]. Globally, this study represents a proof-of-concept of a 2nd generation biorefining process based on locally available biomass.

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Green Extraction of Ginger's Polyphenols under Hybrid Techniques and Biphasic NaDES

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In the context of green extraction and circular economy, a new approach for ginger valorisation was developed. The process employed a hybrid reactor that works simultaneously with ultrasound and microwaves to increase efficiency. Natural Deep Eutectic Solvents (NaDES), which are both hydrophilic and hydrophobic, were used as green solvents to enhance the recovery of metabolites, focussing on polyphenols and in particular gingerol as compounds of interest.

The optimisation of the protocol included the selection of a suitable NaDES, the adjustment of extraction parameters (temperature, solid-liquid ratio, time) and the evaluation of synergistic effects achieved by the hybrid setup. The optimised extract was subjected to a purification step using resins that allowed the isolation of up to 80% of the polyphenols while the DES was recovered.

To further improve the extraction efficiency, a two-phase solvent extraction approach was introduced for the selective fractionation of gingerols from the hydrophilic polyphenols. Malic acid:Glucose[1] (hydrophilic DES) and Menthol:Eucalyptol (hydrophobic DES) were used in sequential and simultaneous procedure. The simultaneous approach proved to be the most effective as it concentrated the gingerol predominantly in the hydrophobic phase and achieved similar yields in a single step. Compared to the sequential approach, this method halved the time, solvent consumption and energy consumption. As both the hybrid extraction system and the biphasic NaDES approach can be extended to a wide range of biomasses and solvents, this strategy provides a flexible and adaptable platform for the selective separation of compounds into different phases, enabling more efficient and sustainable downstream processing.

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Simultaneous extraction of calcium phosphates and collagen from fish processing by-products and their application in cosmetic

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One of the most promising sectors for waste recovery is fish processing. Fish bones have great potential for the extraction of valuable compounds, as they are largely composed of a mineral fraction (calcium phosphates, CaPs) and organic material (mainly collagen, Col). Their applicability in fields such as medicine and cosmetics, combined with the fact that fish-derived materials pose no religious or social restrictions, makes them an attractive alternative to mammalian sources. A major limitation of conventional extraction protocols is that they typically allow recovery of only one of the two phases. This study introduces an alkaline hydrolysis method for the simultaneous extraction of CaPs and Col proteins from fish bones of various species.[1] CaPs and Col were characterized for morphology, structure and composition. A Design of Experiments approach was applied to optimize the process. Results showed efficient recovery of Col, mainly in the α-1 form, with species-specific differences, and a biphasic mineral phase composed of hydroxyapatite and β-tricalcium phosphate after calcination. Functional testing demonstrated that CaPs can act as SPF boosters in sunscreen formulations, increasing protection by up to 90% and allowing for reduced UV filter content. Additionally, the organic extracts containing peptides below 10 kDa exhibited high antioxidant activity. This dual-extraction process provides a sustainable strategy for valorizing fish waste, yielding high-value ingredients for safer sunscreens and anti-aging cosmetic products.

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New sustainable materials from agriculture and for agriculture

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Currently, materials based on conventional plastics derived from fossil fuels and non-degradable in the environment pose a major threat to the sustainability of our planet. Therefore, the development of new sustainable materials is crucial. This work, carried out within the Horizon Europe AgriLoop project, aims to obtain materials from agro-residues while adding new functionalities. Cutin, a natural biopolyester extracted from agricultural residues with interesting properties such as antibacterial and barrier properties, and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) copolymers produced by microorganisms, were used. Cutin was supplied by TomaPaint and INRAE. The materials studied also include PHI003, a commercial PHBV from NaturePlast (with 1.5 mol% of HV units), and new PHBV samples with 16 and 57 (w/w)% HV content, provided by Sapienza University of Rome. Characterization of the copolymers revealed that increasing the HV content leads to a significant decrease in crystallinity, resulting in materials that tend to be amorphous after melting. Cutin was used to prepare blends with commercial PHBV at PHBV/cutin ratios of 95/5, 90/10, and 80/20 (w/w) % using a twin-screw extruder. Notably, the presence of cutin improved the processability of the polymer and enabled the production of homogeneous blends in the form of films. Furthermore, cutin addition lowered the melting temperature and crystallinity of the samples. Increasing cutin content also led to more flexible and ductile blends. These materials have potential for agricultural applications, including mulching films designed to biodegrade in soil. Cutin was additionally applied as a coating for PHBV films. Barrier tests showed reduced water vapor permeability upon cutin application. Oxygen permeability and antimicrobial activity will be investigated further. Using PHBVs with higher HV content may further enhance these properties. Ongoing studies aim to optimize both blend and coated film properties in order to obtain even more promising materials.

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Experimental Study and Hill-Based Kinetic Modeling on Beeswax Dispersion in Hydrophobic DESs

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Deep eutectic solvents (DES) are an emerging class of unconventional solvents used in various fields as *green* solvents[1]: from synthetic organic chemistry to technological and extraction processes, in the pharmaceutical industry and also in the field of cultural heritage restoration[2,3] offering advantages in terms of safety, sustainability, versatility and costs.

This study focuses on the evaluation of the solubility and dispersion kinetics of beeswax, a hydrophobic coating widely used in conservation, within a series of natural hydrophobic DES (hNADES).

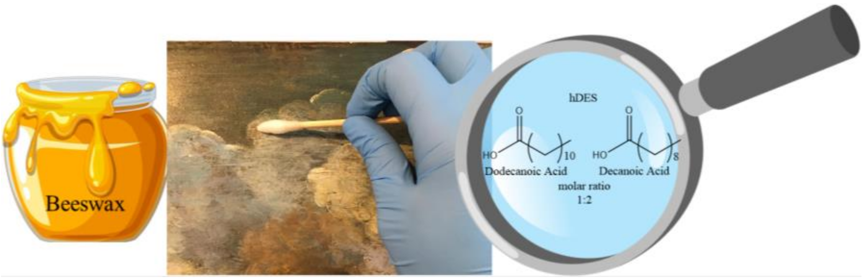

Figure 1

The compatibility of several hNADES with beeswax was identified using both theoretical and experimental approaches including turbidimetric, gravimetric and wax height reduction measurements over time.

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Glycerol-derived solvents as non-innocent reaction media for additive-free Pd- and Au-catalysed transformations

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Solvents represent a key issue in sustainable organic synthesis, as alternatives to the toxic, flammable and non-renewable volatile organic compounds are constantly being sought.[1] Notably, some of these novel unconventional solvents can play an active role in the reaction, thus replacing a normally required reagent or catalyst. Here, we propose the application of a family of eco-compatible solvents, based on glycerol derivatives,[2] for transition metal-catalysed reactions. The use of glycerol-derived ionic liquids with a carboxylate anion allows to perform Pd-catalysed direct C–H arylations of thiophene derivatives, avoiding super-stoichiometric amounts of base, for the synthesis of conjugated scaffolds for optoelectronics and imaging. On the other hand, Au(I) catalysis is pivotal to the synthesis of complex molecular architectures, but expensive Ag co-catalysts are generally required, which can also negatively interfere with the reaction.[3] Here we show that glycerol mono- and diethers, when used as solvents, are effective activators for Au(I) pre-catalysts, enabling Ag-free Au(I) catalysis.

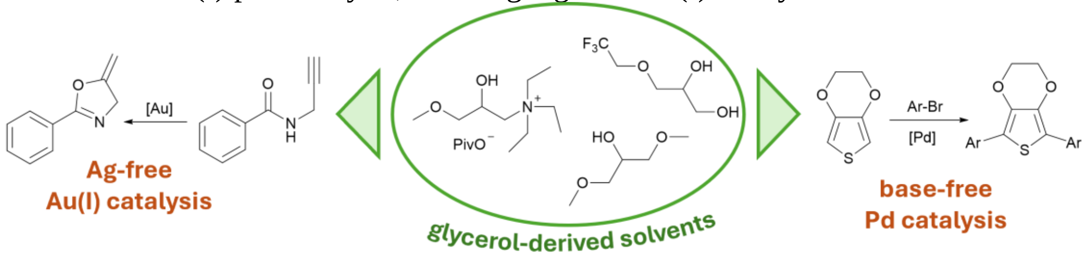

Figure 1. Advantageous application of active glycerol-derived solvents in synthesis.

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A new approach to the etherification of bio-based furanic compouds via continuos flow.

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The main goal of Biorefinery is the transition from a fossil-fuel-based model to a more sustainable system focused on renewable raw materials, in line with circular economy principles.[1,2] In this context, the so-called Bio-Based Platform Chemicals play an important role. Among them, 5-hydroxymethylfurfural (HMF) and 2,5-bis(hydroxymethyl)furan (BHMF) - achieved by HMF hydrogenation - are two of the most studied representatives. Etherification of these compounds with different alcohols yields 5-(alkoxymethyl)furfurals (AMFs) and 2,5-bis(alkoxymethyl) furans (BAMFs) respectively, both demonstrating potential application as fuel additives.[3] In addition, HMF, when subjected to self-etherification, leads to 5,5′-[oxybis(methylene)]bis-2-furfural (OBMF), another bio-based monomer of growing interest.[4]

From this premises, the present talk will focus on the etherification of HMF and BHMF using a commercially available ion exchange resin - Purolite CT275DR, using a continuous flow apparatus. The reaction conditions were optimized by evaluating several key parameters, including catalyst type and quantity, reaction media, temperature, and flow rate for the etherification of BHMF with ethanol and then extended to achieve a library of BAMFs. HMF self-etherification to form OBMF was carried out employing both heterogeneous (CT275DR) and homogeneous acid (methanesulfonic acid - MSA) catalysts using dimethyl carbonate (DMC) as green solvent, with the latter being the most efficient. Lastly, green metrics were calculated for the optimized etherification of BHMF with ethanol and the values were compared to previously published procedures.

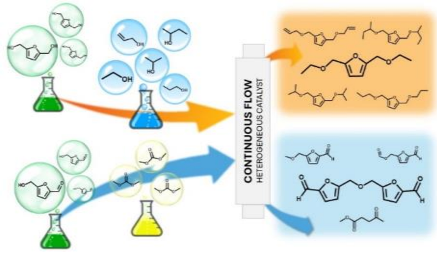

Figure 1: Etherification of furanics via Continuous Flow

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Mechanochemistry: A New doorway for Rapid, Greener and Efficient Synthesis and Catalysis

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As researchers pursue more suitable and environmentally friendly approaches, mechanochemistry is proving that many chemical transformations can take place with little or no environmental impact. The IUPAC has listed mechanochemistry as one of the top ten innovative methodologies with the potential to transform global sustainable development.[1] Complexes containing N-ligands have been widely studied in the literature with regard to their applications in catalysis,[2] medicine[3] and other fields. However, despite the importance of these complexes, an efficient, sustainable approach remains unexplored.

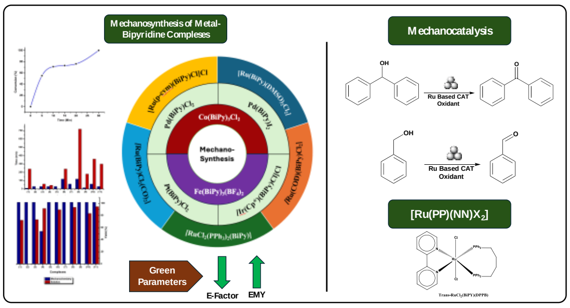

Figure 1: Mechanosynthesis andMechanocatalysis in this work

Herein,[4] we present mechanochemistry as a new, environmentally friendly tool for synthesising metal-bipyridine complexes (e.g. Ru, Pt, Pd, Ir, Fe and Co with 2,2'-bipyridine) that does not require air-sensitive procedures, purification steps or bulk solvents. The mechanosynthesis of these metal-bipyridine complexes was found to be highly efficient and rapid. For most of our complexes, we observed optimal values, i.e. E-factor ≅ 0 and EMY ≅ 100. Furthermore, mechanochemistry was utilised for both the synthesis of $[Ru(PP)(NN)X_2]$ catalysts (where PP = diphosphine ligands, NN = dinitrogen ligand and X = Cl or acetate) and their subsequent use as catalysts for the aerobic oxidation of alcohols.

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Solvent-free 1,3-dipolar cycloadditions: exploring a more sustainable synthesis of glycomimetics

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1,3-Dipolar cycloadditions of nitrones are key reactions to access five-membered heterocycles[1], useful intermediates in the synthesis of biologically relevant glycomimetics when nitrones are derived from carbohydrates or other polyhyrohydroxylated natural compounds. Due to high atomic balance and stereoselectivities, these reactions are good candidates for the development of green protocols. We have optimized these reactions by avoiding the use of organic solvents and considering starting materials derived from the biomass. Reactions involving acyclic and cyclic nitrones (**2** and **4**, respectively) as dipoles and levoglucosenone (**1**) as the dipolarophile have been investigated (Figure **1**). Levoglucosenone (**1**) is a highly functionalized chiral synthon that can be produced by pyrolysis of cellulose-containing industrial residual materials such as waste paper and it is a promising 1,6-anhydrosugar for obtaining highly added-value chemicals in various applications[2]. Performing selected 1,3-dipolar cycloadditions in neat conditions showed reduced reaction times, maintaining similar selectivity and yields of isoxazolidine adducts **3** and **5** with respect to the classical protocols. In addition, the use of microwave irradiation was also exploited to increase the sustainability of the synthetic protocols.

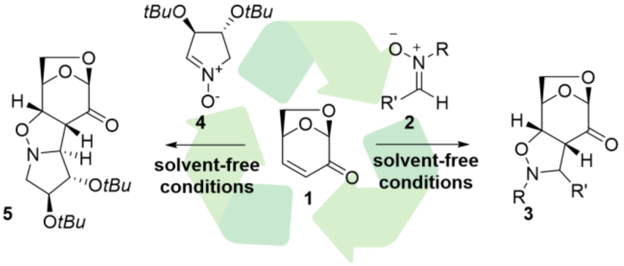

Figure 1. 1,3-Dipolar cycloaddition in solvent-free conditions of levoglucosenone (**1**) and nitrones.

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Sustainable Mechanochemical Oxidation Of Benzylic Alcohols

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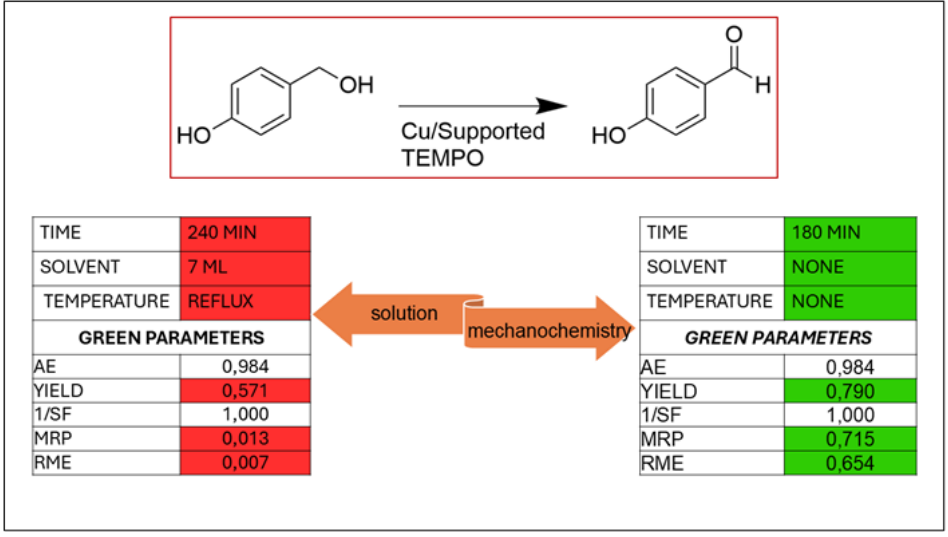
The aim of this work is to develop a new sustainable protocol for oxidizing alcohols into carbonylic compounds through a mechanochemical catalysed reaction. Selective oxidations are pivotal reactions in the chemical industry; however, they produce large amounts of waste and perform poorly in terms of green metrics [1]. Mechanochemistry is a tool used by chemists to achieve more sustainable chemical processes[2] and to facilitate catalytic activation of reactions [3].

In this work, preliminary studies have shown that p-OH-benzyl alcohol can be selectively oxidised into the corresponding aldehyde using a mechanochemical protocol with different copper-supported catalysts and TEMPO. The reaction proceeds in 3 hours achieving approximately 80% conversion (Figure 1). The procedure is straightforward: first, the solid alcohol is placed in the milling vial along with TEMPO and a copper-supported catalysts and then the mixture is subjected to ball milling. After that, the aldehyde can be easily extracted with a small amount of solvent.

Compared to the solution-phase synthesis, this method requires less time and energy and generates no byproducts. In addition, the green assessment [4,5] reveals that the mechanochemical route exhibits improved metrics compared to the solution-phase synthesis using the same reagents.



TIME	240 MIN
SOLVENT	7 ML
TEMPERATURE	REFLUX
GREEN PARAMETERS	
AE	0,984
YIELD	0,571
1/SF	1,000
MRP	0,013
RME	0,007

TIME	180 MIN
SOLVENT	NONE
TEMPERATURE	NONE
GREEN PARAMETERS	
AE	0,984
YIELD	0,790
1/SF	1,000
MRP	0,715
RME	0,654

Figure 1. Comparison of solution synthesis and mechanochemical synthesis.

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Lignin extraction from wood sawdust: batch *vs* cyclic approach

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Lignin is an abundant, underutilized biomass component rich in aromatics, making it a valuable renewable feedstock for sustainable chemicals, fuels, and materials. Catalytic depolymerization enables its conversion into useful monomers, supporting biorefineries and reducing reliance on fossil resources—an approach aligned with circular bioeconomy principles.[1] Deep eutectic solvents (DES) offer a promising method for lignin extraction, being low-cost, biodegradable, and non-toxic. They enable mild extraction conditions that help preserve lignin's structural integrity. Recent studies show DES effectively extract lignin from various biomass sources, including wood, straw, and agricultural residues,[2] and could result good at preserving labile linkages such as β-O-4 bonds, crucial for downstream processing. Here, we extract lignin from wood sawdust using a DES composed of lactic acid and choline chloride, comparing the conventional batch method to a novel cyclic extraction approach that improves both extraction yields and retention of labile bonds.

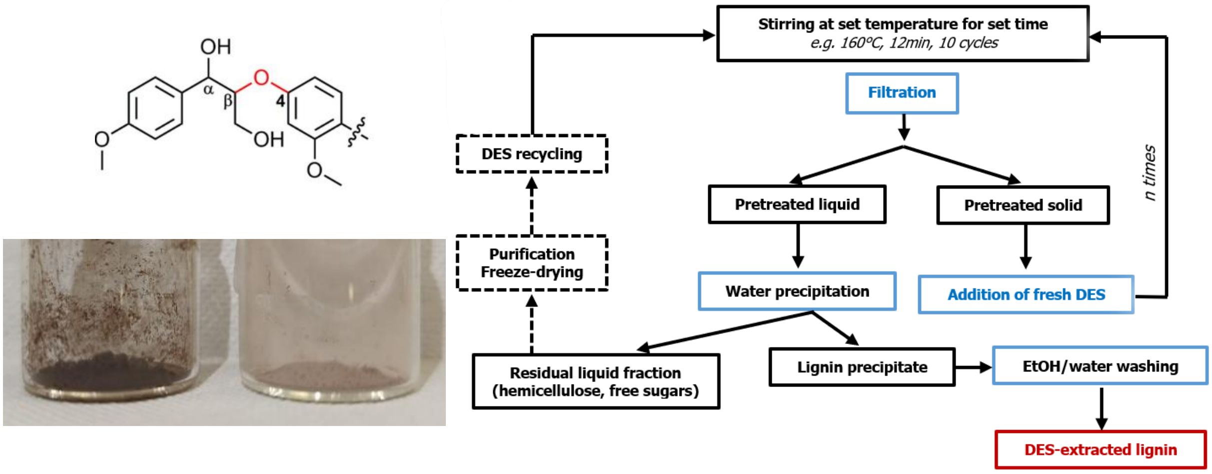

Figure 1. Lignin extracted with the batch method (left), and with the cyclic method (right). General scheme of the cyclic extraction approach, and structure of the labile β-O-4 motif bond.

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., F. S. A., and E. C. fellowships).

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Catalytic lipophilization of natural antioxidants

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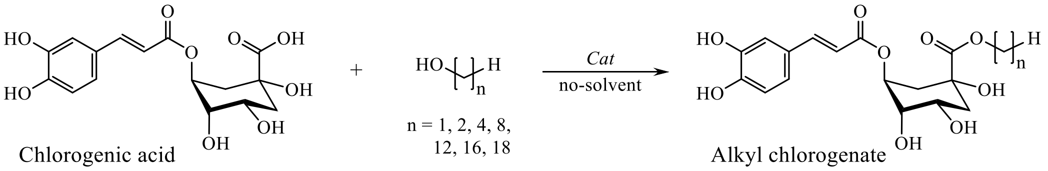
The valorization of agro-food byproducts is a pillar of circular economy. These residues are rich in valuable bioactive compounds, especially antioxidants. Among them, chlorogenic acid (CGA), a natural widespread polyphenol, displays several pharmacological and biological activities including anti-aging effects. However, its highly hydrophilic structure hinders the use into oil-based products like cosmetics and nutraceuticals. To overcome this drawback, CGA was lipophilized through a sustainable, one-pot, direct esterification with a serious of fatty alcohols in the presence of the solid catalyst Amberlyst® 15 under no-solvent conditions (Scheme 1).[1]



Scheme 1

Alkyl chlorogenates, isolated with yields of up to 93%, exhibited a higher anti-radical activity than unsubstituted CGA (Figure 1). Moreover, preliminary studies have highlighted that ethyl chlorogenate protects human fibroblasts from oxidative stress-induced aging.

The lipophilisation of CGA is a model strategy that can be extended to other valuable hydrophilic antioxidants, such as gallic and caffeic acids.

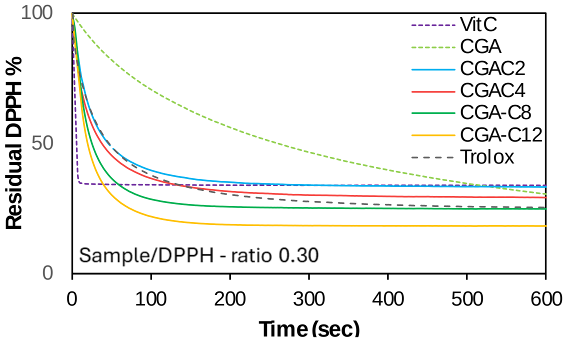


Figure 1

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Vinavil's approach to sustainability

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Often defined as the right balance between the environment, equity, and economy, Sustainability is one of the key topics for today and forthcoming years. Through legislations such as Eu Green Deal, Taxonomy and Chemical Sustainability Reporting Directive, EU is trying to steer the way to a more sustainable society: to adhere to them the chemical companies are taking initiatives to reduce the environmental impact of their products-processes, at the same time having to ensure that all disclosed data, communication and information are transparent, reliable and verifiable.

Mass balance schemes are typically directed to replace a portion of fossil input material with a biogenic alternative. This management system offers the advantage that companies can protect the environment and decrease their emission values (i.e. Carbon FootPrints, CFPs), by using the existing supply chains, at a reasonable extra cost.

We will provide practical examples on Vinavil's path towards sustainability and show its experience with ISCC PLUS certification, a voluntary scheme to assess and certify the sustainable content (recycled and bio-based materials) of its finished products.

At the end we will illustrate our voluntary communication through another tool, the Life Cycle Assessment (LCA) methodology, for measuring environmental impact indicators., to show a possible comparison between bio-based and fossil-based products.

Design of a Photo-Catalyzed Strategy for the Synthesis of C-Glycosides *via* Giese Reaction with Karady-Beckwith Dehydroalanine and Bisphosphonate Alkene

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We present the selective photo-catalyzed Giese reaction using pyranosyl/furanosyl bromide derivatives to access C-Glycosides. For decades, researchers have acknowledged the significance of C-glycosides as stabilized biological isosteres in pharmaceutical and biological studies. Their presence in natural compounds, and their valuable role as key components in complex molecule synthesis, further highlight their importance in scientific exploration.[1] Following previous work by the group,[2] in which a photo-catalytic generation of glycoside radicals was carried out to form C-C bonds with dehydroalanines as reaction partners to access C-glycosyl α-amino acids, we decided to develop a methodology that would make use of completely organic photocatalysts (TADF) without the presence of metals both in homogeneous (4CzIPN) and heterogeneous phases (4CzIPN-POP), as well as the use of chiral Karady−Beckwith dehydroalanines and bisphosphonate alkene as acceptors of the Giese reaction to give rise to products of pharmaceutical interest (Figure 1). This methodology has allowed us to obtain the products with high diastereoselectivity and excellent yields, also demonstrating an excellent tolerance to the main hexose and pentose monosaccharides as well as to disaccharides. Furthermore, the possibility of making the photocatalyst heterogeneous provides an additional advantage, such as the easy removal of the catalyst at the end of the reaction. This also opens up the possibility of its reuse and its application in flow chemistry.

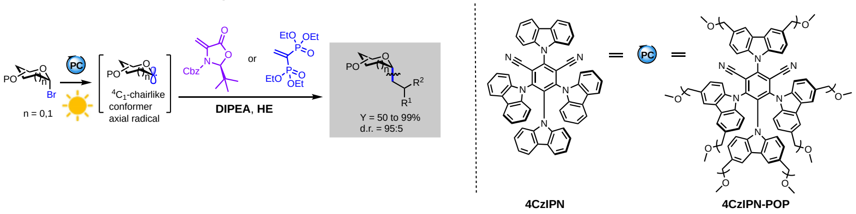

Figure 1. General reaction scheme.

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Improved Reductive Catalytic Fractionation of Lignocellulosic Biomass through the Application of a Recyclable Magnetic Catalyst

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Valorization of lignin into low molecular weight lignin oil through Reductive Catalytic Fractionation (RCF) has been an area of extensive research. Noble metal catalysts with carbon-based supports, were found to be active for the RCF process; however, the inefficient catalyst recovery from the fibrous cellulose pulp impacts the economic sustainability of the process at its scale-up.[1] In this work, have developed a novel magnetically recoverable 5 wt.% $Ru/\Upsilon\text{-}Fe_2O_3$ catalyst for the RCF, with an efficient recovery of 90%.[2] The magnetic catalyst was compared to a commercial 5 wt.% Ru/C catalyst in terms of delignification of cellulose, lignin oil yield and catalyst recovery. Preliminary recyclability tests have proven the stability of our catalyst for at least 3 RCF cycles. The catalyst shows great potential to produce high quality cellulose pulp along with relatively low molecular weight lignin oil.

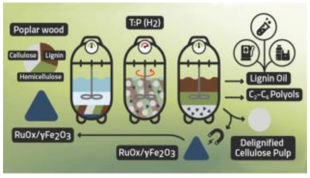

Figure 1. Enhanced RCF process in the presence of a magnetic recyclable catalyst.

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Investigating the mechanism of reductive catalytic fractionation with alternative magnetic catalysts: a model molecule approach

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The sustainable valorization of lignocellulosic biomass requires catalysts capable of selectively cleaving lignin linkages while suppressing undesired recondensation. Herein, we used model molecules like eugenol, vanillin, and 2-phenoxy-1-phenylethanol (2P1P) to investigate the catalytic behavior of RuOx/γ-Fe_2O_3, a recyclable magnetic catalyst proven to be effective in the reductive catalytic fractionation of poplar sawdust[1]. Contrary to the conventional view that metal nanoparticle size and dispersion primarily dictate activity[2], we demonstrate that the support could play a critical role in adsorption geometries and product selectivity. Upon in situ reduction, RuOx/γ-Fe_2O_3 forms Ru/Fe_3O_4, which is able to cleave β-O-4 bonds preserving aromaticity, yielding over 40% in monomers such as phenol, ethylbenzene and 1-phenyl-ethanol (Figure 1). In contrast, Ru/C promotes over-hydrogenation, leading to saturated dimers and higher H_2 consumption. Despite larger Ru particles, Ru/Fe_3O_4 exhibits higher selectivity, likely due to oxyphilic interactions that favor orthogonal adsorption via hydroxyl groups, a hypothesis supported by ongoing DFT studies. These findings reveal how catalyst supports can partially override particle size effects and guide selective lignin depolymerization strategies aligned with a green chemistry approach.

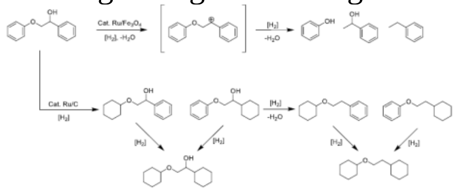

Figure 1. 2P1P hydrogenation/hydrodeoxygenation pathway over either RuOx/γ-Fe_2O_3 (active species Ru/Fe3O4) or Ru/C.

Acknowledgements.

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Tetrabutylammonium Hexatungstate as an Efficient Photocatalyst for the Sustainable Decarboxylative Functionalization of Acids

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In recent years, the polyoxometalate tetrabutylammonium hexatungstate ($[TBA]_2[W_6O_{19}]$) has attracted considerable interest in sustainable organic chemistry due to its remarkable thermal catalytic activity.[1,2] A rare dated example on its use as photocatalyst regards the dehydrogenative conversion of alkanes to non-thermodynamic alkenes showing an excellent photoredox activity.[3]

In this work we investigated a photocatalytic system comprised of $[TBA]_2[W_6O_{19}]$ and biphenyl (BP), for the decarboxylative derivatization of carboxylic acids **1** at room temperature. As shown in **Figure 1a**, the excited photocatalyst oxidizes **BP** to the radical cation $\mathbf{BP}^{\bullet+}$, which, in turn, converts the carboxylate $\mathbf{1}^-$ (generated from **1** under basic conditions), to carbonyloxy radical $\mathbf{1}^{\bullet}$. The latter intermediate spontaneously decarboxylates to give the carbon radical $\mathbf{1}'^{\bullet}$, that, upon trapping by an electron-poor olefin **2** followed by reduction by the reduced form of the tungstate led the alkylated olefin **3**.

The hexatungstate anion demonstrated to be a highly efficient catalyst, enabling the smooth functionalization of several classes of acids (***Figure 1b***) including bicyclo[1.1.1]pentane derivatives, valuable building blocks in medicinal chemistry.

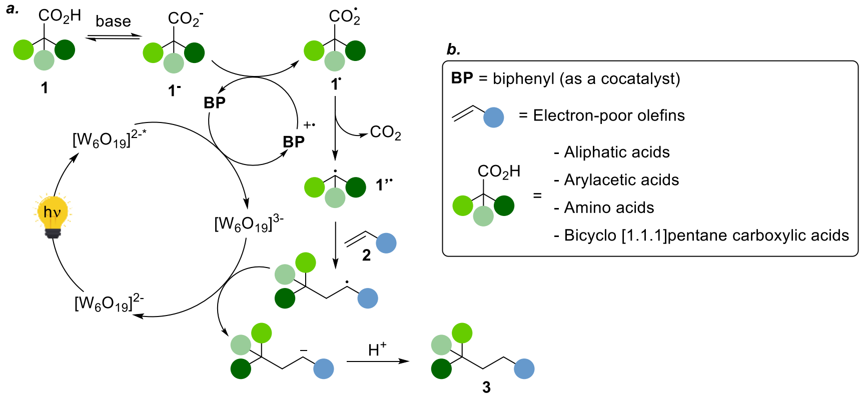

Figure 1. a. Proposed mechanism **b.** Substrates studied.

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Metal nanoparticles supported by nanoporous polymer matrix for highly efficient and selective production of hydrogen via formic acid decomposition

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Formic acid (FA) is one of the most promising candidates as an H_2 carrier. FA dehydrogenation (FAD) ($HCOOH \rightarrow H_2 + CO_2$) requires the use of efficient catalysts, capable of operating at low temperatures and with selectivity to avoid the collateral decomposition reaction to carbon monoxide and water.

This contribution reports on developing a new catalytic system based on gold and/or copper nanoparticles (NPs) supported by poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as catalysts for FAD. PPO is a commercially available polymeric material with high chemical, mechanical, and thermal resistance, also due to the high glass transition temperature of 220°C.[1-3] Furthermore, it has a complex crystalline polymorphism, and the presence of nanometric-sized pores (micropores) confers to this polymer support a high permeability to small molecules. The AuNPs-PPO system has been proven highly selective in the FA decomposition reaction with activities, expressed as turnover frequency (TOF), of 600 $mol_{FA}\ mol_{Au}^{-1}\ h^{-1}$. The AuNPs-PPO catalytic system has been proven to operate at low temperatures (60-120°C), in water as solvent or even without solvent, and in the absence of bases, typically required in this reaction (Figure 1).

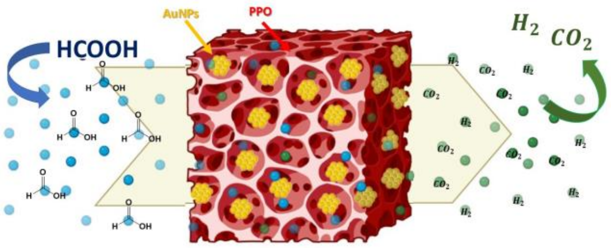

Figure 1. AuNPs supported by PPO for the catalytic decomposition of formic acid to H2 and CO2

Acknowledgements.
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XII Workshop Gruppo Interdivisionale Green Chemistry – Chimica Sostenibile

Bologna – 3-4 Luglio 2025

Oxidized Thiourea Derivatives: Uncovering New Frontiers with Resonant Acoustic Mixing (RAM)

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Nitrogen-containing compounds play a crucial role in the development of active pharmaceutical ingredients. However, their conventional synthesis often relies on environmentally unfriendly methods, requiring high temperatures, prolonged reaction times, hazardous reagents, and large solvent volumes for both synthesis and purification.[1] Mechanochemistry has recently emerged as a powerful, solvent-free alternative that significantly enhances process sustainability. By utilizing mechanical energy, typically generated by ball mills or twin-screw extruders, reactions can proceed efficiently with minimal waste. A novel approach in this field is Resonance Acoustic Mixing (RAM), which promotes reactivity without the need for grinding media. This technology operates via vertical oscillations at a constant frequency (60 Hz), adjusting the G factor up to 100 G to optimize reaction conditions.[2]

In this study, RAM was employed to investigate the reactivity of thiourea trioxide (TTO), an oxidized derivative of thiourea. Unlike commercially available thiourea dioxide (TDO), TTO lacks reducing properties and does not degrade into dithionite, making it an attractive alternative for oxidation-driven transformations. Specifically, we utilized TTO in the synthesis of 2-aminobenzoxazoles via a liquid additive method with water. The target compounds were obtained in good yields by simple extraction with ethyl acetate and filtration, demonstrating the efficiency and sustainability of this approach.

This work highlights the potential of RAM in mechanochemical synthesis, paving the way for greener methodologies in pharmaceutical development. [3]

Figure 1. 2-Amino-benzoxazole synthesis thought the use of Resonance Acoustic Mixing (RAM).

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XII Workshop Gruppo Interdivisionale Green Chemistry – Chimica Sostenibile

Bologna – 3-4 Luglio 2025

Novel Captopril-inspired broad-spectrum metallo beta-lactamase inhibitors using sustainable Joullie'-Ugi and continuous flow implementation

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ESKAPE pathogens (*Enterococcus faecium*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, and *Enterobacter spp*) have become highly resistant to most available antibacterial drugs by exploiting different mechanism of resistance.[1] One of the main mechanisms of resistance is the expression of metallo beta-lactamases (MBL), bacterial enzymes able to cleave the beta-lactam ring of the antibiotics. Since no clinically relevant MBL inhibitors have yet been approved, the quest for novel compounds with a broad-spectrum activity against several MBL, represents an urgent need. Captopril, an angiotensin converting enzyme inhibitor used for the treatment of hypertension, showed weak inhibitory activity against some MBL isoforms. Therefore, we rationally modify the structure of the captopril using a Joullié-Ugi multicomponent reaction protocol for the synthesis of two indoline-based subseries, implemented by a convenient continuous flow protocol. Two synthesized compounds (Figure 1) showed broad-spectrum inhibition against three MBL isoforms (NDM-1, VIM-1, and IMP-7). Furthermore, activity in clinical isolates in synergy with beta-lactam antibiotics was assessed for the best performing compounds, thus paving the way to a further optimization campaign.

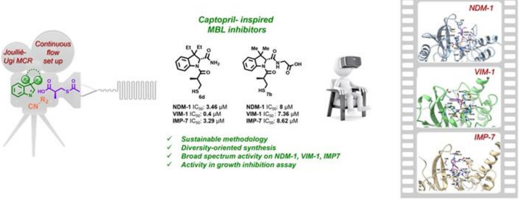

Figure 1. Novel captopril-inspired broad-spectrum MBL inhibitors

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Bio-Sourced Nitrogen-doped graphitic Carbon Quantum Dots (N-gCQDs) as Additives for Dendrite-Free Zinc Batteries

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As the global demand for energy grows, efforts must be made to meet the need for efficient energy storage devices, while minimizing the critical resources depletion and promoting an ecological transition towards sustainably sourced materials. Zn-batteries already offer a safer, low-cost and greener alternative to Li-based systems, thanks to the non-toxic nature of Zn and its compatibility with aqueous electrolytes.[1] However, challenges such as dendrite growth, side reactions, and limited cycling stability still hinder their broader adoption.

Here, some citric acid-based N-doped graphitic Carbon Quantum Dots (N-gCQDs)[2] were synthesised as a model material and applied for dendrite suppression in Zn-batteries, demonstrating remarkable improvements in overall performance.

N-gCQDs effectiveness was proven through in-situ visualisation and electrochemical measurements. The promising strategy was then extended to synthesise comparable nanomaterials from chitin and, ultimately, directly from crab shells. These materials effectively promoted uniform Zinc deposition and prevented dendrite growth at current densities up to 20 mA/cm² for 4 hours. This approach, using sustainable sources like bio-waste to replace fine chemicals in advanced materials synthesis aligns with circular economy principles and paves the way for greener solutions to reduce dependence on endangered and environmentally impactful materials for safer and scalable Zn-based energy storage systems.

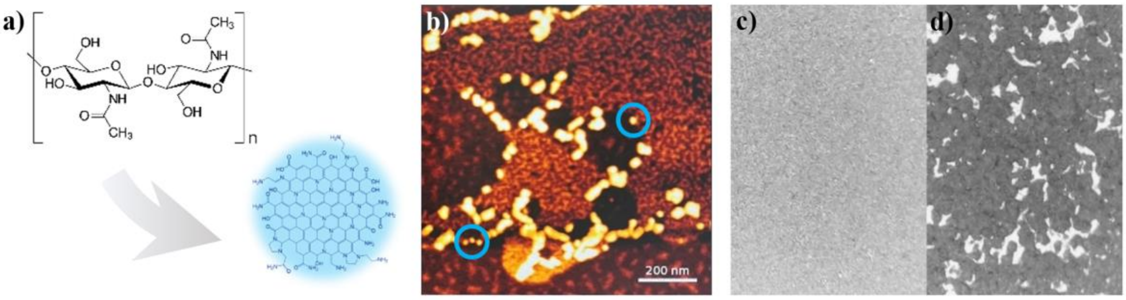

Figure 1. a) Dots synthesis from Chitin. b) AFM of dots on mica. Zn-plating c) with and d) without dots.

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Low Molecular Weight Polyesters From 4-Vinyl Guaiacol

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The identification and application of renewable and more sustainable raw-materials for biopolymers production have enormous importance.[1] In addition, the use of sustainable catalytic polymerization processes is pivotal to replace current commodity plastics with new biopolymers. For example, functional monomers can be prepared from bio-based molecules allowing the application of controlled polymerization techniques such as ring-opening (co)polymerization [RO(CO)P].[2] In this scenario, 4-vinyl guaiacol (4-VG) is a promising bio-based platform molecule for the production of new biopolymers.[3] The 4-VG can be obtained via biocatalytic processes from ferulic acid,[4] which is recovered from several renewables such as bagasse, lignin, and wheat bran. Despite 4-VG potential applications in polymer chemistry, its functionalization and controlled polymerization is relatively underexplored,[5] so we envisaged the possibility to obtain polyesters by ROCOP of new 4-epoxy guaiacol esters with cyclic anhydrides (Figure 1).

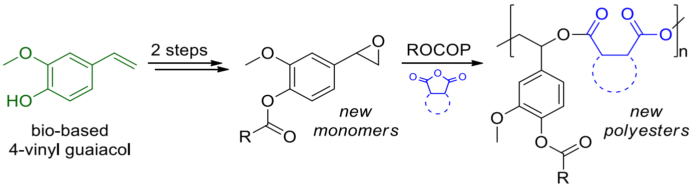

Figure 1. General structure of new monomers polyesters obtained from 4-vinyl guaiacol.

We used a two-step procedure for the synthesis of new 4-epoxy guaiacol esters (4-EGEs) monomers obtained in good yields. Following, we studied the ROCOP of 4-EGEs with several cyclic anhydrides by varying different parameters (e.g., temperature, solvent, and organocatalyst), to obtain a series of new structurally different polyester polyols with low molecular weights ($M_n < 6$ kDa) and narrow distributions ($Đ < 1.3$) in short times and high yields. Overall, the obtained results demonstrate a concrete starting point for the production of new 4-VG-based bio-polymers with potential applications in polymer industry, such as in thermoplastic or polyurethanes formulations.

Acknowledgements.
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XII Workshop Gruppo Interdivisionale Green Chemistry – Chimica Sostenibile

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Eco-Friendly Farming *via* Automated Iminosugar Syntheses: Next-Generation Agrochemicals

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In response to the growing demand for sustainable agricultural solutions, we are collaborating with Syngenta to develop next-generation agrochemicals based on iminosugars, glycomimetics known for their biological activity and structural versatility. These compounds are obtained from commercially available carbohydrates by using straightforward synthetic routes which allow the insertion of a nitrogen atom providing a piperidine[1] or a pyrrolidine[2,3] skeleton. At Syngenta, iminosugar libraries were designed using key molecular characteristics (e.g. molecular weight, logP) and synthesized through an automated laboratory, which significantly minimizes waste and boosts efficiency.[4] This automated process ensures high throughput, precise control over reactions and faster production, reducing human error and resource consumption.

A set of carboxylic acids from Syngenta's collection was used to generate libraries *via* amide coupling with piperidine- or pyrrolidine-based iminosugars, removing the basic feature of the nitrogen atom. In a second set of libraries a spacer was also introduced between the iminosugar and the acid, facilitating further diversification while retaining the basic characteristic of the glycomimetic. The new compounds were tested against a panel of plant pathogens present in Syngenta, resulting in the identification of a promising antifungal candidate. Optimization work at the University of Florence is now focused on enhancing its efficacy and selectivity, while ensuring low toxicity and environmental safety, with the aim of contributing to the development of sustainable crop protection solutions, meeting the demand for eco-friendly agrochemicals.

Acknowledgements.
We thank #NEXTGENERATIONEU (NGEU) and the Ministry of University and Research (MUR), National Recovery and Resilience Plan (NRRP), DM 352/2022, for a PhD fellowship.

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Valorisation of Spent Brewer's Yeast for the Development of Sustainable Bio-Composites Based on Poly(butylene succinate)

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This work is part of the activity of the Centro Nazionale Agritech, Spoke 8, which aims to valorize agro-industrial residues to obtain new materials in alignment with circular economy principles, focusing on waste reduction and the replacement of fossil-based materials[1]. Spent Brewer's Yeast (SBY), a major by-product of beer production, is rich in proteins, polysaccharides (mainly β-glucans), and bioactive compounds, making it a suitable candidate not only for food applications (Cfr. PNRR ONFOODS) but also, in a novel approach of valorization for bio-composite applications[2].

SBY was recovered from a local brewery and subjected to a series of treatments aimed at obtaining solid fractions with different composition and properties. These powders were then used as fillers in poly(butylene succinate) (PBS) matrices through twin-screw extrusion, with loadings up to 30 wt%.

The biocomposites were analyzed in terms of thermal and mechanical properties; even new functionalities, for example UV-blocking capability and antrimicrobial and antioxidant properties, were assessed. The resulting materials offer a cost-effective and eco-friendly alternative to neat PBS,

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New Trends In Peptide Synthesis Using Side-Chain Unprotected Amino Acids

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Improving the sustainability of solid-phase and liquid-phase peptide synthesis (SPPS and LPPS) is a key objective in modern peptide chemistry.[1] A significant advancement in this area involves the elimination of orthogonal side-chain protective groups for arginine, histidine, tryptophan, and hydroxyl-containing amino acids.[2] This approach enhances peptide atom economy (AE) and minimizes impurity generation during the final cleavage step, thereby streamlining the synthesis process.[3] While the well-established coupling reagents, such as DIC/Oxyma, provide exceptional performance in SPPS,[4] their application to peptide synthesis involving unprotected amino acids or in LPPS is significantly limited. In contrast, TBEC and EDC·HCl have demonstrated exceptional performance, even if in ‟orthogonal” methodologies.[5] Specifically, TBEC effectively minimizes racemization and eliminates the need for side-chain protecting groups in SPPS, while EDC·HCl has proven invaluable for methodologies requiring aqueous work-up. However, both coupling agents have notable drawbacks: EDC·HCl exhibits poor solubility in organic solvents and a higher tendency for racemization, whereas TBEC presents challenges in purification during peptide elongation in LPPS. To address these limitations, we have developed a novel carbodiimide named TBDC – and its corresponding urea – that is soluble in both organic and aqueous media. This innovation maintains stereochemical fidelity, demonstrates high reactivity, and reduces the reliance on protective groups. As proof of concept, this newly commercialized coupling agent has been successfully applied to the synthesis of peptides containing unprotected amino acids in both SPPS and LPPS.

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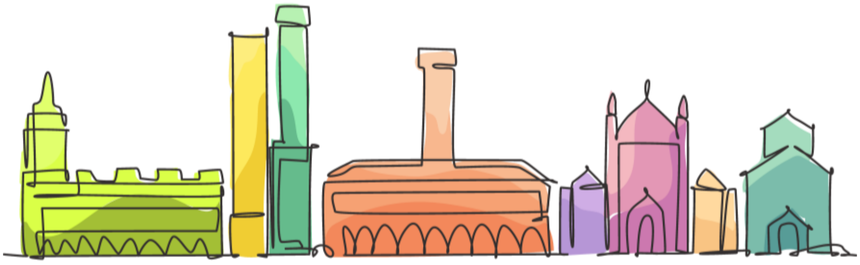

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MILESTONE HELPING CHEMISTS

Microwave-Enhanced, Additive-Free C-H Amination of Benzoxazoles Catalysed by supported Copper

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Among nitrogen-containing heterocyclic compounds, 2-aminobenzoxazoles are of great importance because of their many applications, such as a scaffold in the design of new drugs. Selective C-N bond formation is usually performed by reactions such as Buchwald-Hartwig or Ullmann and Goldberg couplings, but still some disadvantages need to be solved for better agreement with green chemistry criteria. Many transition metals have been exploited as catalysts for these transformations, but the use of copper has increased due to its low cost, high functional group tolerance, high environmental abundance and safety, and low overall toxicity.[1, 2]

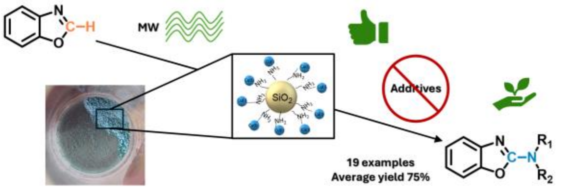

Figure 1. **Graphical representation of microwave assisted C-H amination of benzoxazole**

This work presents a facile, green and efficient C-H amination catalyzed by CuCl and $CuCl_2$ in acetonitrile without acidic, basic or oxidizing additives and accelerated by microwave (MW) irradiation.[3] The reaction was shown to take advantage of microwave irradiation and excellent results were obtained in the presence of a silica supported Cu(I) catalyst, which made the process cost effective and heterogeneous, thus simplifying the work-up and minimizing free copper in solution. The catalyst was found to be regenerable and reusable for up to eight cycles. The optimized method facilitated the synthesis of various benzoxazole derivatives, demonstrating its versatility and practical applicability.

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Turning textile waste into high-performance nanostructured cellulose-based aerogels for clean water

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The upcycling of textile waste into high-performance nanocellulose-based aerogels represents a sustainable and innovative approach for water remediation. The textile industry is a significant contributor to water pollution, releasing harmful dyes and heavy metals into aquatic ecosystems, necessitating efficient and eco-friendly purification strategies [1]. This study explores the production of nanocellulose-based aerogels derived from recycled cotton-based textiles through controlled oxidation and functionalization processes, such as TEMPO-mediated oxidation [2]. These aerogels exhibit high porosity and surface area, making them ideal candidates for the adsorption of heavy metal ions (Cu^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}) and organic contaminants.

A systematic pre-treatment of textile waste, including chemical purification and fibrillation, ensures the extraction of high-quality cellulose nanofibers (CNFs), which are then included as building-block for the production of aerogels *via* freeze-drying and thermal treatment [3]. The resulting materials demonstrate excellent adsorption capacities, efficiently capturing and removing pollutants from contaminated water. Structural and chemical characterizations confirm the aerogels' functionalization, stability, and adsorption efficiency, reinforcing their potential for large-scale application.

These findings highlight the viability of nanocellulose-based aerogels as a circular and eco-friendly solution for wastewater treatment, addressing environmental concerns while valorizing textile waste. This approach contributes to the development of a sustainable water purification strategy that aligns with circular economy principles and promotes resource efficiency in the textile industry.

Acknowledgements.

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Bologna – 3-4 Luglio 2025

Efficient ruthenium-catalyzed Guerbet reaction for the upgrading of Bioethanol to Higher Alcohols: a sustainable approach to biofuel production

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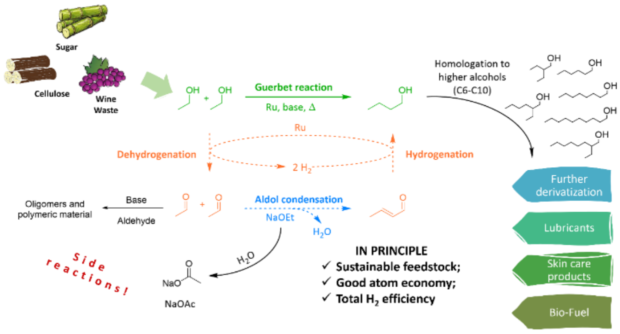
In 2022, global bioethanol production exceeded 100 billion litres, with 80% originating from the USA and Brazil. Besides being used as a biofuel, it can be utilized as renewable commodity to obtain several valuable chemicals. One of the possible transformations is the homologation of ethanol to form butanol and longer chain alcohols by means of the Guerbet reaction. This process consists of three key steps: initially, ethanol is converted into acetaldehyde then following an aldol condensation mechanism, crotonaldehyde is generated. Lastly, crotonaldehyde is transformed into butanol via hydrogenation.[1] To accomplish the dehydrogenation/hydrogenation steps, a redox catalyst is required. At prof. Mazzoni's lab we synthetised and tested a ruthenium homogenous catalyst (Ru-NHC)[2] obtaining good results on this transformation in terms of ethanol conversion and butanol selectivity. Adding benzoquinone as a co-catalyst (1.5 mol %) alongside the ruthenium catalyst significantly boosted selectivity for longer chain alcohols (+18%).[3] This catalytic pair was also tested on some upscaling experiments finding that by decreasing the headspace volume in the reactor a better carbon balance is observed.[4] Finally, using microwaves as a heating source reduced reaction time from 4 hours to just 10 minutes, enhancing process sustainability.



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Propargyl Derivatives of Isosorbide and Its Epimers: Novel Monomers for Thiol-Yne Polymerization

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In the last two decadeds, bio-based molecules, obtained from biomass, have found numerous applications as substitutes of petroleum-derived compounds.[1] Poignat examples include their exploitation as additives for biodiesels as well as for the production of bio-based polymers and green solvents.[2] Among these compounds, isosorbide has gained increasing interest due its unique structure and to the possible industrial applications of its derivatives. Isosorbide is obtained from the cyclization of D-sorbitol and presents a rigid structure with two hyroxyl functionalities bonded to two of the four chiral centres present in the molecule. These moieties have shown an unexpected reactivity towards alkylation and alcoxycarbonylation reactions.[3] From these premises, the present work is focused on the synthesis of new derivatives of isosorbide – and its two epimers i.e., isomannide and isoidide – incorporating termnal triple bonds. In particular, isosorbide dipropargyl carbonate (IDPC) is herein reported for the first time. Its synthesis proceeded in 2 hours by using a catalytic amount of a nitrogen superbase and an excess of dipropargyl carbonate (DPC). After the reaction, the latter was recoveded by distillation and reused for future experiments. The procedure was extended to the other epimers of isosorbide which could be isolated with yield varying from 70 to 80%. Finally, preliminary studies were performed on these family of compounds for the production of polymers via thiol-yne photopolymerization.

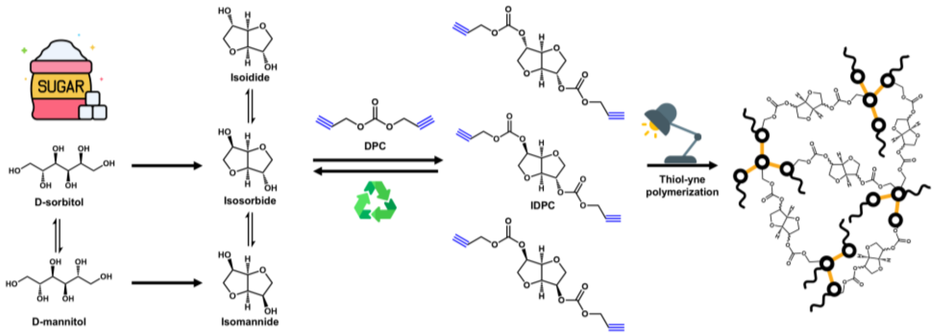

Figure 1. Synthesis and applications of isosorbide, isomannide and isoidide propargyl carbonate derivatives.

Acknowledgements.
This work was supported by the DoE 2023-2027 (MUR, AIS.DIP.ECCELLENZA2023_27.FF project).

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Metal-Free Graphitic Carbon Nitride/Carbon-Dots Composites: Unveiling Mechanochemical Synthesis Opportunities

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Environmentally friendly, metal-free photocatalysts offer a promising alternative to traditional metal-based semiconductors. Among them carbon dots (CDs), defined as spherical-like carbon particles,[1] are an emerging class of nanomaterials with unique optical properties, biocompatibility, low toxicity and highly functionalized surface. Notably, CDs can be synthesized inexpensively and on a large scale, often through a one-step process using biomass waste-derived sources.[2] Despite these advantages, CDs face limitations in practical applications, particularly due to challenges in recovering them after catalytic reactions, which restricts their reusability and increases operational costs, often making them single-use photocatalysts.[3] A promising approach to overcome this limitation involves the incorporation of CDs into carbonaceous materials,[4] such as graphitic carbon nitride (CN), which is a well-known photocatalyst, recognized for its layered structure, thermal stability, and suitable bandgap (2.7 eV) for visible light absorption. By supporting CDs on CN, it is possible to create composite materials that combine the strengths of both components. In this study, we synthesized CN/CD photocatalysts using two different methods: a hydrothermal approach[5] and an innovative solvent-free mechanochemical extrusion process. To the best of our knowledge, mechanochemistry, particularly reactive extrusion, has not been reported for the preparation of CN/CDs composites. Comprehensive characterization and photocatalytic testing, specifically in the UV-driven selective oxidation of benzyl alcohol, revealed that synthesis methods significantly impacted materials' morphological and optical characteristics, thereby influencing their photocatalytic performance. Additionally, light–matter interaction modeling provided further insights into the relationship between optical properties and catalytic behaviour, offering valuable understanding of the structure–function relationship in these novel photocatalysts.

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New insights into the key role of the thermal treatment of V/P/O catalysts for the selective oxidation of butane to maleic anhydride

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Maleic anhydride (MA) is a versatile molecule due to its three active sites, i.e. two carboxylic groups and a double carbon bond. It is considered an important building block in industrial chemistry, with several applications such as monomers for polyesters and alkyd resins, as well as an intermediate to produce fine chemicals (succinic acid, malic acid, and fumaric acid). Industrially, the production of MA remains solidly linked to the continuous-flow, gas-phase selective oxidation of petrochemical raw materials, Traditionally, benzene was the main substrate used in the production of MA, using vanadium and molybdenum containing catalysts. However, this method presents several drawbacks such as the carcinogenic nature of benzene itself, relatively low atom efficiency (i.e. two C atoms are lost in the form of COx), and high exothermicity. Therefore, benzene is gradually being replaced with *n*-butane (due to lower cost and higher atom economy), while vanadium and molybdenum catalysts have been replaced by vanadium phosphates (V/P/O), which are able to promote the selective oxidation of this linear alkane toward MA exhibiting best results in terms of conversion and yields.

This work explores the thermal treatment of V/P/O catalyst precursors to achieve active and selective catalysts for the oxidation of *n*-butane to maleic anhydride (MA) in a continuous-flow, fixed-bed reactor. Vanadyl pyrophosphate (V^{4+}, VPP), the key catalyst component, is produced together with suitable V^{5+} vanadium orthophosphate ($VOPO_4$) allotropic forms by thermally treating vanadyl hydrogen phosphate hemihydrate (VHP) in various atmospheres and temperature ramps[1]. The characterization conducted using X-ray diffraction, Raman spectroscopy, and reaction testing allowed the identification of optimal conditions for active and selective catalysts. Oxygen is necessary for obtaining VPP and affects the vanadium oxidation state, a crucial parameter for selectivity. Water enhances the crystallinity and conversion of VHP to VPP. An optimized calcination atmosphere (6:10:84 mol% of O_2:H_2O:N_2) ensures 70% MA selectivity at 50% butane conversion at 400 °C [2]. VHP precursors characterized by higher P/V ratios allow to obtain higher MA selectivity when treated at the same calcination conditions.

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Redesigning lignin-derived surfactants: from waste to health

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Quaternary ammonium compounds (QAC) are widely used in gene transfection and drug delivery due to their ability to insert hydrophobic alkyl chains into cell membranes and bind negatively charged phospholipids, facilitating cargo release.[1] However, petroleum-derived QACs suffer from poor safety profiles, environmental persistence, respiratory hazards, and have driven microbial resistance through their extensive use in disinfectants.[2] These drawbacks have been addressed by the adoption of lignocellulosic biomass as starting material, an abundant agro-industrial byproduct offering a cost-effective source of chemical building blocks,[3] thus facilitating a transition towards more sustainable processes. This work presents a circular approach to both non-ionic and cationic surfactants from lignin-derived aromatic compounds for advanced biomedical applications.

Lignin can undergo oxidative depolymerization to yield vanillin and vanillic acid,[4] versatile precursors for amphiphilic design. Hydrophobic tails were introduced via esterification with long-chain alcohols.[5] Head groups were added through two complementary strategies: (i) epoxidation, followed by ring-opening with diethyl- or diethanol-amine, and (ii) quaternization of the resulting amines with ethyl iodide to introduce cationic centers. The fusogenic helper lipid dioleoylphosphatidylethanolamine was added to the cationic surfactants and size and zeta potential were determined. Preliminary hemolysis assays indicated favorable biocompatibility for further biomedical applications.

By integrating green chemistry and circular economy principles, this work advances bio-based surfactants for innovative applications, offering reduced environmental impact without compromising functionality.

Figure 1. Lignin-derived bio-based surfactants for biomedical applications.

Acknowledgements. This work is funded by Fondazione CRT, project *BioTenMed*, Prot. n. 2024.AI864.U1076, RF = 108579 / 2024.0435.

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Functionalized Calcium Phosphate Nanoparticles for Sustainable Phosphorus and Nitrogen Delivery in Agriculture

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Modern agriculture aims to reduce nutrient losses while protecting ecosystems, limiting chemical inputs, and preserving environmental balance and resilience. Conventional fertilizers contribute to nitrogen and phosphorus leaching, contaminating water bodies, accelerating aquatic eutrophication, and degrading long-term soil health[1]. In this study, we investigated the urea-functionalization of two types of calcium phosphate (CaP) nanoparticles - crystalline hydroxyapatite (HAP) and amorphous calcium phosphate (ACP) – as a nano-fertilizer capable of simultaneously releasing phosphorus and nitrogen in a controlled manner. Both materials were synthesized via a green chemistry route. In a leaching test using a vermiculite column, ACP-Urea significantly slowed urea release compared to free urea and retained over 95% phosphorus after 48 hours. In contrast, HAP-Urea exhibited urea release behavior similar to free urea. In *Zea mays* greenhouse trials, ACP-Urea significantly outperformed both HAP-Urea and monocalcium phosphate (MCP), increasing biomass by 160% and enhancing chlorophyll content and nutrient uptake, while preserving rhizosphere microbial diversity and structure. These results highlight the promise of CaP nano-fertilizers to enhance nutrient use efficiency, improve soil quality, and reduce the ecological footprint of fertilization practices in agriculture.

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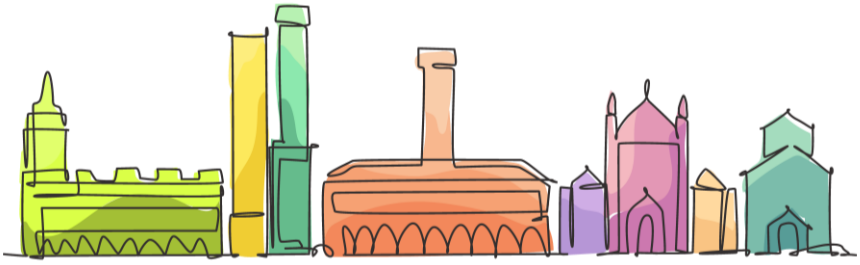

- PRESENTAZIONI POSTER -

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NaDES as solvent for extraction of astaxanthin from the cyanobacterium *Synechococcus* sp. PCC 11901

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Astaxanthin produced by the microalgae is one of the most powerful natural antioxidants. It has a huge market potential, and it is approved as generally recognized as safe (GRAS) food ingredient; however, its extraction is quite challenging since astaxanthin accumulates in highly resistant algal cysts and the use of too-harsh conditions can degrade the carotenoid structure[1].

Hydrophobic deep eutectic solvents (HDES) based on thymol and long-chain fatty acids have been recently proposed as efficient solvents for the extraction of astaxanthin from *Haematococcus pluvialis*, giving the additional benefit of an exceptional astaxanthin stabilization[2].

Herein, seven thymol-based HDES were prepared and used to extract astaxanthin from the cyanobacterium *Synechococcus* sp. PCC 11901 which was genetically engineered to synthesize the non-native astaxanthin, to facilitate its extraction and yield. Results were compared with a traditional solvent extraction (cyclohexane:acetone:ethanol 2:1:1 volume ratio); specifically, thymol was combined with urea (TU, 5:1 molar ratio); betaine (TB, 3:1); lauric acid (TL, 1.3:1.6); menthol (TM, 1:1); phenylacetic acid (TP, 2:1); oleic acid (TO, 3:1) and water (TW 0.5 g/L). The best extraction results were obtained after 24 h with TF (1.6%±1,14E-03) and TU (1.5%±1.97E-03) followed by TW and TL (1.4%±1,40E-03). All of these solvents extracted more astaxanthin than the mixture cyclohexane:acetone:ethanol. However, future research will be apply to elucidate the stability in time of astaxanthin in the HDES.

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BIPHASE CATALYSIS: SYNTHESIS OF FINE CHEMICALS

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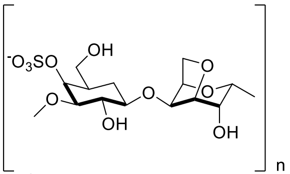
Catalytic biphasic reactions are widely used because of their advantages over conventional homogeneous catalytic syntheses as the easy separation and reuse of the expensive catalyst and the environmental aspects of the chemical process. In particular, the use of both water as co-solvent for biphasic reactions and easily recyclable catalysts are highly desirable for the realization of green processes with industrial prospectives. Recently, our research has focused on developing water-soluble catalysts by interacting metal salts with bio-based polymers such as carboxymethyl cellulose and chitosan [1, 2]. Building on this, we investigated the preparation and characterization of Pd(0) and Rh(0) nanoparticles stabilized by K-carrageenan, a sulfonated water-soluble galactan obtained primarily from the tropical alga Kappaphycus alvarezii, and their catalytic performance in hydrogenation of cinnamaldehyde and citral, two important substances for the synthesis of valuable fine chemicals.

K-carrageenan



We also evaluated the activity and selectivity of some heterogeneous catalysts with low precious metal content, such as Pd/Al_2O_3 (Pd 0.3% w/w) and Rh/Al_2O_3 (Rh 0.18% w/w), which were prepared using a method developed in our laboratory. These catalysts have demonstrated high activity in hydrogenation and hydroformylation reactions.[3-5] All the catalytic systems employed showed very good activity and recyclability. Regarding selectivity, this was strongly dependent on the catalyst. Specifically, in citral hydrogenation, water-soluble catalytic species favored the formation of citronellal, whereas Pd/Al_2O_3 predominantly produced menthol. As regards the hydrogenation of cinnamaldehyde, all catalysts favored the formation of 3-phenylpropanal but, by varying the reaction conditions, the preferential formation of 3-phenylpropanol can be obtained.

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Spent Coffee Ground valorization: polyphenols and nanocellulose extraction

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The waste coming from coffee industry includes coffee husk, silverskin and especially a large amount of spent coffee grounds (SCG). Approximately 20 million tons[1] of SCG are generated each year as a by-product of the brewing process. Identifying potential applications for SCG is of great importance in reducing the environmental impact of the entire coffee supply chain. As defined, SCG contain significant amounts of lipids (≈15%), polysaccharides such as cellulose and hemicellulose (≈45%) and bioactive compounds, such as polyphenols and diterpenes (≈3-5%). SCG can be used, treated or untreated, as a filler in polymer composites and, due to its composition, it is suitable for biorefinery approach. Among the other components, polyphenols are interesting for packaging, cosmetic, nutraceutical and pharmaceutical formulations.[2]

This work aims at enhancing the valorization of said waste through the recovery of different fractions. Polyphenols and fatty acids are recovered via Soxhlet extraction with a variety of possible solvents. Then, the solid residue can be used as a filler to increase the SCG share in polymer composites or it can be furtherly treated to obtain functionalized nanocellulose according to a recently licensed patent in collaboration with Coffeefrom Srl SIAVS.[3] Also nanocellulose can serve as an additive in cosmetics and food packaging and it can be used to tune and further enhance the mechanical properties of polymeric materials.

Figure 1. Representation of the valorization pathway.

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From lignocellulosic biomass to biomaterials

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In recent years, growing awareness of the economic and environmental issues associated with fossil resource exploitation has encouraged the search for more sustainable and environmentally friendly alternatives. Among these, lignocellulosic materials, especially those available as waste or by-products, have emerged as one of the most promising natural sources for developing high-value-added biopolymers and materials. Their biodegradability, renewability, recyclability, and wide availability make them attractive, particularly within the framework of eco-design.

This study investigates various strategies for the valorisation of lignocellulosic biomass aimed at creating innovative materials for different application sectors. One key approach involves producing biomaterials, such as composite panels and cellulose-based films, through pre-treatment techniques and solubilization of the cellulose fraction of natural or waste fibres. Additionally, lignocellulosic feedstocks can serve as the basis for designing new polymer formulations via the synthesis of biomonomers and their biopolymers. In particular, the presence of biomonomers derived from saccharides with polar and reactive functional groups can significantly enhance the performance of final materials, while also contributing to improved sustainability and recyclability. These monomers allow the development of various acrylic and vinyl copolymers, whose properties can be tailored to specific applications. Results of applicative tests confirm the potential of these copolymers in the creation of advanced adhesives and other polymer formulations opening up new opportunities in sustainable product design.

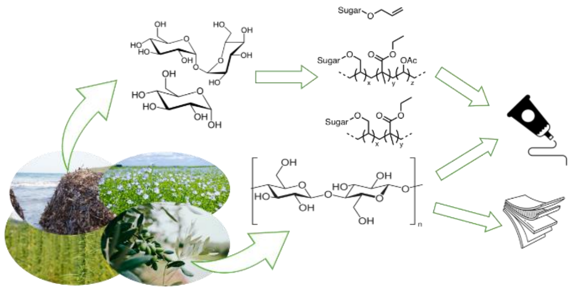

Figure 1. From biomass to new biomaterials.

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A new sustainable approach for the carbonylation of *β*-amino alcohols

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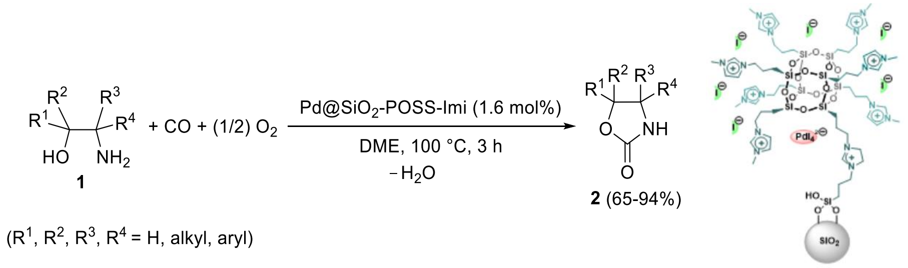
The direct synthesis of 2-oxazolidinones by the oxidative carbonylation of *β*-amino alcohols[1], allows obtaining high value added molecules with several biological applications. 2-Oxazolidinones are known, in particular, for antibacterial[2], and antitumor activities.[3]

We have now found that it is possible to perform this kind of transformation by supporting our PdI_4^{2-} catalyst (already widely applied in the development of oxidative carbonylation processes under homogeneous catalysis conditions[4]) on an hybrid material based on imidazolium modified polyhedral oligomeric silsesquioxanes (POSS-Imi) grafted on amorphous silica (SiO_2).

The newly developed heterogeneous catalyst has been shown to be effective with a wide range of *β*-amino alcohols **1** to give the 2-oxazolidinone derivatives **2** in high isolated yields (65-94%) as shown in Scheme 1.



Scheme 1

Pd@SiO_2-POSS-Imi

The recyclability of the catalysts has been successfully verified for three consecutive runs.

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Ethanol to gasoline and sustainable aviation fuel precursors: an innovative cascade strategy over Zr-based multifunctional catalysts in the gas phase

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The production of alternative fuels from biomass is a topic of significant interest for both academic and industrial research, driven by the urgency to reduce reliance on fossil resources and achieve a more sustainable circular economy. The aviation industry is particularly in focus due to its dependence on fossil-derived jet fuel. Greenhouse gas (GHG) emissions from international aviation have increased substantially over the past two decades, marking the largest rise in the transport sector. In response, industry associations, governments, and airlines are investing in alternative fuels, commonly known as sustainable aviation fuels (SAFs). Produced from renewable energy, biomass, or waste resources, SAFs offer comparable performance to conventional jet fuel but with a significantly reduced carbon footprint, thereby mitigating GHG emissions from aviation.[1] Various alcohols currently derived from renewable raw materials have been considered for SAF production, among which the greatest interest is in ethanol processes, since bioethanol is the most widely used renewable energy source in the world. Herein, the gas-phase, continuous flow catalytic upgrading of ethanol to blends with features close to those suitable for jet fuel is tackled through an innovative strategy based on the promotion of several reactions in cascade. Catalytic transfer hydrogenation, aldol condensation, dehydrogenative coupling, and ketonization reactions were combined in a one-pot approach over a relatively simple and cheap catalytic system consisting of copper nanoparticles supported on zirconium oxides. The resulting cascade reaction scheme led to the production of a blend of compounds in the C6-C14 range, including linear and branched esters, linear and branched alcohols, linear, branched and cyclic ketones, aldehydes, alkenes and aromatics, which showed similar properties to those of Jet A and A-1 fuels, the most widespread worldwide. By tailoring the features of the non-innocent support and/ or co-feeding hydrogen to the reactor, up to 40% selectivity for the jet fuel range fraction, with ethanol conversion above 85%, was achieved during the first 6 h of time on stream, simultaneously enhancing catalyst stability and lifetime.[2] Even though more work is needed to optimize the catalytic material, increasing its lifetime and fostering acetaldehyde conversion, the obtained blends could be potentially used as jet fuel or jet fuel additive after a few preliminary operations such as the distillation of the lighter compounds and a mild hydrogenation process in order to stabilize aldehydes and unsaturated compounds.

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What is hidden between amide-type solvents and acyl chlorides? Let's unveil it by NMR

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N,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF) are the most common used solvents in amidation reactions due to their exceptional solubilising properties and their compatibility with polar reactants[1,2]. Moreover, the amide-type solvent appears to be involved in the reaction mechanism. The aim of this study is to improve the understanding of this catalytic function by performing kinetic and NMR experiments. The amidation reaction taking place between sterically hindered anilines and an acyl chloride was conducted measuring kinetic constants (k) using DMAc, DMF and other non-amidic polar solvents. The results show that the presence of the amide (either as a solvent or additive) drastically increases the reaction rate. **Figure 1** illustrates a possible interaction between the amide solvent and acyl chloride. To support this hypothesis, we acquired proton NMR spectra of the mixture acyl chloride-DMAc (or DMF) and bi-dimensional NMR spectra (COSY, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC, ^{1}H-^{15}N HMBC) at different temperatures and molar ratios. The analysis of the NMR spectra indicates the presence of an intermediate species, whose structure can be represented by intermediate B (Fig. 1). Specifically, the chemical shift of C5 is more consistent with the structure of intermediate B than an iminium ion.

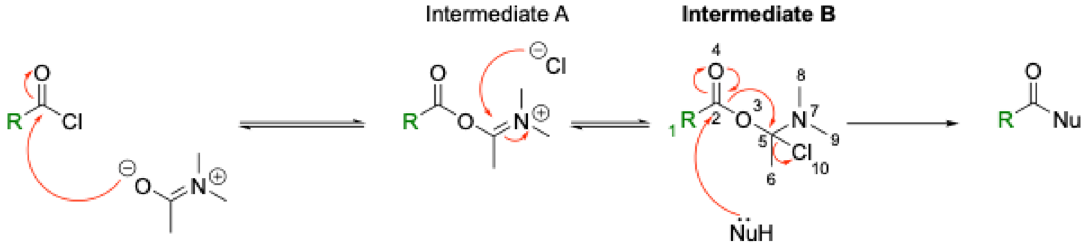

Fig. 1 Hypothesized mechanism between acyl chloride and N,N-dimethylacetamide

Acknowledgements
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Deep Eutectic Solvents as Green Solvents for Iodocyclization Reaction of 3-Alkynylthiophene-2-carboxamides

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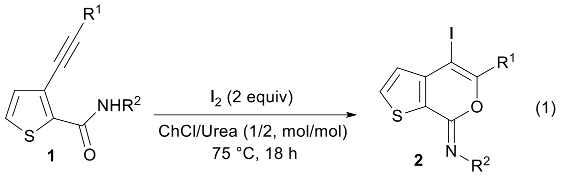
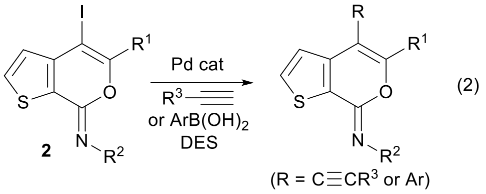
A green approach to a previously unknown class of iodine-containing heterocycles, namely 4-iodo-7H-thieno[2,3-c]pyran-7-imines **2**, by iodocyclization of readily available 3-alkynylthiophene-2-carboxamides **1** in a deep eutectic solvent as both solvent and promoter, has been developed (Eq. 1).



While the reaction with I_2 and K_2CO_3 as the base in a classical volatile organic solvent proceeded to a very limited extent, the iodocyclization was successful when performed in choline chloride/urea (1/2 molar ratio) in the absence of any external base. Moreover, the DES solvent could be efficiently recycled several times without a significant decrease in the product yield. The possibility to further decorate the newly synthesized iodinated heterocycles in a DES solvent (choline chloride/glycerol, 1/2 molar ratio, for Sonogashira reaction, and betaine/glycerol, 1/2 molar ratio, for Suzuki-Miyaura coupling) has been successfully assessed (Eq. 2).



The promoting effect by the DES has been studied in detail by computational methods while the structures of products have been confirmed by X-ray diffraction analysis.

Synergistic effects of Hydrodynamic Cavitation and Cold Plasma for the degradation of Emerging Organic Contaminants in water

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Water pollution is increasingly recognized as one of the major problems associated with industrial activities. The continuous rise in the variety and concentration of pollutants in aquatic environments requires the development of sustainable and economically viable treatment technologies. The hybridization of hydrodynamic cavitation (HC) and electrical discharge plasma (ED) represents a promising green alternative to traditional advanced oxidation processes (AOPs) as it ensures high contaminant removal efficiency, reduced energy consumption, and it is well-suited for continuous flow applications. Moreover, it enables rapid degradation of organic pollutants without the addition of external oxidants due to the *in situ* generation of shock waves, UV radiation and highly reactive species, such as hydroxyl radicals, hydrogen peroxide and ozone[1]. A pilot-scale HC-ED hybrid reactor was employed to evaluate the degradation of various emerging organic contaminants, including dyes and active pharmaceutical ingredients (APIs)[2]. The degradation was analyzed under both flow-through and recirculating conditions (up to 300 L/h) starting from an initial volume of 5 L and a starting concentration of organic pollutants ranging from 5 to 80 ppm. Anti-inflammatory drugs and dyes, such as Rhodamine B (RhB) and Salicylic Acid (SA) among others (figure 1), were tested and more than 98% degradation was achieved for all compounds within 15 minutes of recirculation in the HC-ED reactor[3]. Additionally, dosimetry tests were performed to quantify the hydroxyl radicals generated by the hybrid system and the results were compared with acoustic cavitation alone. Furthermore, key operational metrics such as Electric Energy per Order (EEO) and Technology Readiness Level (TRL) were determined for the HC-ED system and compared with conventional AOP technologies to assess its development stage and industrial applicability.

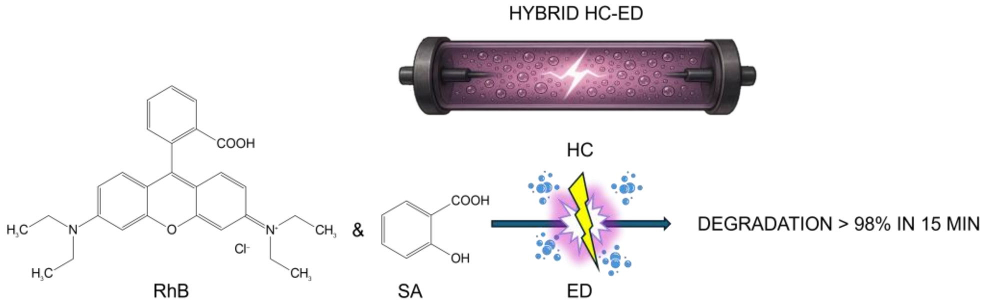

Figure 1. RhB and SA degradation through HC-ED hybrid system

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Pilot scale PHA production, polymer extraction and drop-in chemical production by depolymerization

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Among all the bioplastics, polyhydroxyalkanoates (PHA) are bio-based and biodegradable polymers with properties close to petrochemical ones. Commercial production of PHA was generally made by pure bacterial culture, leading to high operational and capital costs due to the sterile conditions needed and the expensive carbon feedstock used to feed bacteria. Mixed Microbial Cultures (MMC) are an interesting alternative to limit these costs since they do not need sterile growth conditions and can be fed with cheap substrates. Extracting PHA from microbial cells is economically feasible when the PHA content is above 30%, otherwise, solvent costs overcome potential polymer value[1]. Herein, a pilot-scale bioreactor operating in a continuous mode was set up and run for 4 months to produce microbial biomass enriched in PHA starting from MMC. When PHA content was >30%, extraction was performed with novel and green solvents, such as dimethylcarbonate[2] and ethanol in mild conditions (110°C, 1h). High polymer recovery was achieved (>90%) in both cases. Ethanol as a solvent has never been reported before for PHA extraction since its high polarity suggests its use as an antisolvent for PHA; however, at high temperature and under pressure, it becomes a good solvent for extraction, while at room temperature its behaviour as antisolvent makes the separation of the polymer and recovery of the solvent easy. When PHA content was below 30%, an affordable PHA depolymerization into crotonic acid was achieved via thermolitic distillation[3] at 270°C, 150mbar, and without the need for any catalyst. These conditions ensure low protein and lipid degradation. This approach allows the production of crotonic acid by a more direct and greener pathway than the fossil-based approach.

Acknowledgements

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TOWARDS A MORE SUSTAINABLE PHOTOCATALYZED α-ARYLATION OF AMINES

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Nowadays, one of the greatest challenges in the field of chemistry concerns the reduction of the environmental impact of chemical transformations and the limitation in the use of scarcely available metal-based catalysts in order to make processes more suitable for large-scale applications. With this in mind, we selected an α-arylation of amines, previously reported by MacMillan and coworkers,[1] and we envisioned the possibility to increase the efficiency and the sustainability of a photoredox reaction by performing it in green solvent and recycling the metal-based photocatalyst. As first step, we efficiently replaced the toxic medium dimethylacetamide (DMA) with the greener solvents 1-butyl-2-pyrrolidone (NBP) and 2-pyrrolidone (NHP), and we further improved the process efficiency by lowering both the amine and the base amount. Then, we moved to the evaluation of a recycling protocol and we were pleased to observe that when the reaction is carried out in NHP, both the photocatayst *fac*-Ir(ppy)$_3$ in its commercially available form and the solvent can be recycled up to 19 times. Finally, we scaled up the reaction in both the green solvents NHP and NBP up to 10 mmol of the limiting reagent, maintaining excellent performances also lowering the photocatalyst loading down to 0.05 mol%.[2] To the best of our knowledge, this is the first example of photocatalytic α-arylation of amines promoted by such a low amount of catalyst.

Acknowledgements.

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Use of Polyols for the Eco-Friendly Leather Tanning: A Sustainable Choice

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Leather tanning is a chemical process of fundamental importance for the national territory, requiring the use of chemical agents to establish stable bonds with the collagen matrix of animal hides. This sequence of treatments prevents the putrefaction of the animal's skin, converting it into stable leather and improving the chemical-mechanical properties of the final product. Alkaline chromium salts are still the main tanning agents used for this chemical treatment[1], but their use poses considerable environmental drawbacks, primarily due to environmental and toxicological concerns.[1] In this context, the INCANTO project ("INnovative Tanning Through New Types of Optimized Polyol-Based Tanning Agents") explores the synthesis and use of polyglycerols as a sustainable and metal-free alternative to chromium salts for leather tanning. Polyglycerols have been produced from glycerol feedstock, the main by-product of biodiesel production, thus improving the development of a circular economy approach in the biodiesel production chain. The hydroxyl groups in polyglycerol would facilitate the establishment of hydrogen bonds with collagen, stabilizing the protein macrostructure.[2] Its properties vary depending on the structure (linear or branched) and the degree of functionalization.[2] Up to now, branched polymers have been proposed in the literature as pre-tanning agents and/or for improving wet-blue leather[3], but the use of the linear forms has not been explored so far. Our study started from available polyglycerols, which have been characterized for their degree of functionalization, in terms of OH groups, as mg KOH/g and molecular weight distribution, in terms of weight-average molecular weight (Mw), number-average molecular weight (Mn) and polydispersity index (PDI = Mw/Mn), to assess structural uniformity and processability.[4] Tanning tests have shown promising results for short linear polyglycerins, and our attention is now focused on further increasing their molecular weight to evaluate possible correlations with tanning performances. For this purpose, preliminary polymerization reactions, catalyzed by either *p*-toluenesulfonic acid or sulfuric acid, are in progress to modulate the degree of functionalization, molecular structure and chemical reactivity, to enhance collagen interaction and optimize the mechanical, thermal and chemical properties of the tanned leather.

Acknowledgements
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A multi-stage biorefinery process for the valorization of green seaweed biomass

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Rapid green seaweed proliferation in eutrophic coastal waters, known as "green tides", causes severe hypoxia, harming marine ecosystems and coastal economies. This necessitates valorizing this underutilized marine biomass for novel materials within a sustainable biorefinery framework[1]. This investigation explored a multi-stage process designed for the comprehensive utilization of the entire seaweed biomass. The process facilitated the recovery of three distinct fractions with potential industrial applications:
i) a liquid fraction, rich in minerals, was obtained from initial biomass washes. This fraction exhibits potential for application in the agricultural sector as a biostimulant.
ii) an anionic sulfated polysaccharide, ulvan. This polysaccharide constitutes 9–36% of the seaweed's dry weight and is recognized for its potential utility across diverse sectors, from food to medicine[2]. Depolymerization of ulvan with acidic heterogeneous catalysts is under investigation to expand the field of application of small oligomers.
iii) the residual biomass fraction, obtained after polysaccharide extraction, was subsequently utilized as a feedstock for the preparation of biomaterials. These materials were prepared via extrusion and compression molding techniques, incorporating various plasticizing agents.

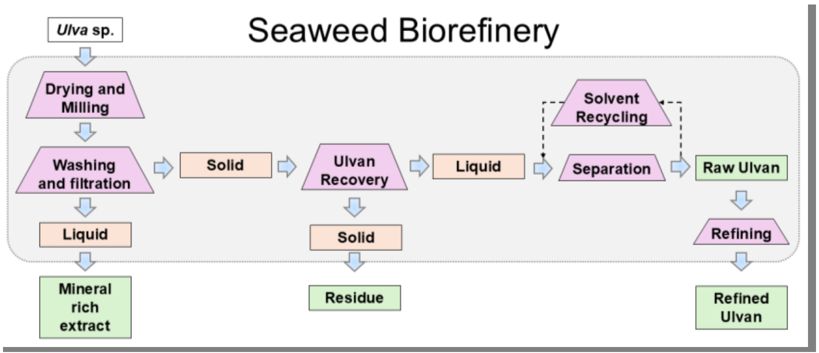

Figure 1. Seaweed biorefining flowchart

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Selective C–C Bond Cleavage of α-Hydroxy Acids by V^v-aminotriphenolate complexes

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Abstract.

Photocatalytic transformation of lignocellulosic biomass components (polysaccharides, lignin) and some of their key platform molecules via the photocatalytic cleavage of C–O and C–C bonds is an extremely important process for their valorisation.[1]

In the recent years our group have developed a catalytic system based on homogeneous vanadium(V) aminotriphenolate complex **V1**, capable to catalyse, under aerobic conditions, the C–C bond cleavage 1,2-diols and lignin models.[2] More recently the **V1** photocatalytic process with blue light has been also explored, affording C-C cleavages with increased selectivity's and operating at room temperature.

In this communication we will report preliminary results on the reactivity of **V1** photocatalytic system for the aerobic oxidative cleavage of α-hydroxy acids (Figure 1). Using mandelic acid as model substrate, a clean and fast decarboxylation can be obtained, to the corresponding benzaldehyde and benzoic acid in high yields. We will report on the optimization of the reaction, also using green solvents, as well as on the scope of the reaction using a series of substituted mandelic acids.

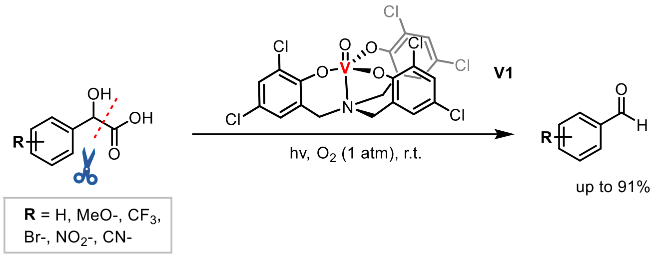

Figure 1. Aerobic oxidative C-C bond cleavage of substituted α-hydroxy acids by vanadium(V) aminotriphenolate complex **V1**.

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Eco-functional biocomposites: the utilization of chestnut shells in sustainable materials

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Plastics have played a crucial role in technological progress, thanks to their versatility. However, their fossil origin and non-biodegradable nature have led to severe environmental issues. This makes the shift toward bio-based and sustainable alternatives increasingly urgent. This work fits within this context by employing a bio-based, compostable polymer, the poly(butylene succinate *co*-adipate) (PBSA), further enhanced through the incorporation of an agro-industrial by-product with promising properties: the chestnut shells.

In 2023 the production of raw chestnut shells is mainly located in China, Spain, Bolivia, Türkiye and Italy, with a global production of 2,095 million tons[1]. Currently, the primary use of chestnut shells is for energy recovery through combustion[2]. However, they are also rich in polyphenols, tannins, and other bioactive compounds with high added value[2]. For this reason, directing them solely toward low-end energy applications represents a missed opportunity for more sustainable and value-driven valorization strategies, as their utilization in innovative sustainable materials.

The chestnut shells were microbiologically characterized and then incorporated as a biofiller into a PBSA matrix. The final material was analyzed for its thermal, mechanical, and surface properties. The study was further complemented by the evaluation of newly introduced functionalities, such as antioxidant activity.

The obtained results demonstrate the successful development of an innovative and functional bio-composite material, aligning with the principles of sustainability and circular economy.

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Harnessing Electron Donor − Acceptor Complexes in the Enantioselective β-Alkylation of Aromatic Enals: a Sustainable Strong Oxidant-Free Approach

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β-Alkyl-γ-azo-aldehydes are key intermediates in the synthesis of many important biologically active compounds that are traditionally synthesized using organocatalysis[1], rhodium-catalyzed hydroformylations[2], or radical addition methods[3]. All these methodologies display limitations regarding the overall catalytic sustainability. Herein, we propose a sustainable and straihtforward protocol for the β-alkylation of aromatic enals involving an Electron Donor-Acceptor (EDA) complex as the key photoactive catalytic intermediate. The peculiar mechanistic pathway enables the asymmetric synthesis of unprecented compounds with excellent yields and *ee*s. This strategy has the advantage to have an enhanced overall process sustainability deriving from the mechanism, the optimized reaction parameters and the readily avalailable, structurally simple organocatalyst. Mass-based metrics were employed to quantitatively confirm the enhanced sustainability of the developed method.

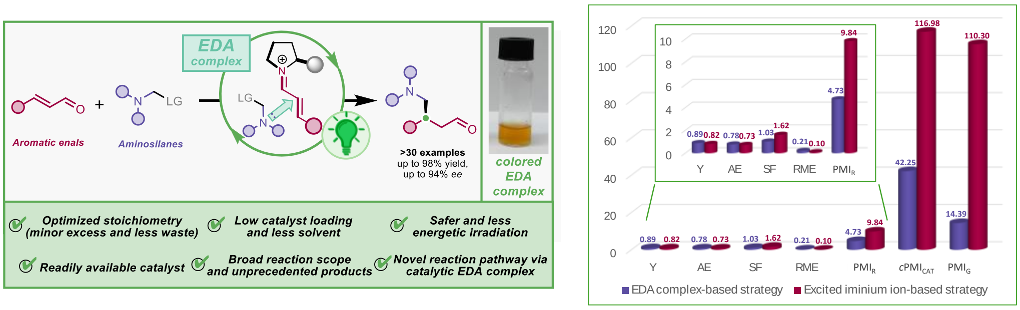

Figure 1. Advantages and mass-based metrics of EDA promoted β-alkylation of aromatic enals

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Innovative End-of-Life Strategies for Bioplastics: The Potential of Mechanical Recycling

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The significant environmental impact of conventional, petroleum-based plastics, which dominate global production, poses a considerable challenge due to issues like resource depletion and persistent waste.[1] Although traditional plastics offer numerous advantages in terms of durability, flexibility, and cost-effectiveness, their end-of-life management remains a major concern. In response, bioplastics have emerged as a more sustainable alternative offering potential benefits such as derivation from renewable resources and, in some cases, biodegradability or biocompostability. However, their widespread adoption is still hindered by factors such as high production costs and limited availability.

In this context, mechanical recycling of bioplastics can be a valuable strategy to improve their overall sustainability.[2] Indeed, mechanical recycling presents a compelling strategy to reduce the overall cost of bioplastic materials and extend their service life.

To assess the recycling potential of bioplastics, a study was conducted to investigate the mechanical recyclability of a biopolymer blend through repeated extrusion cycles employing a microcompounder. Five consecutive extrusion steps were performed to simulate industrial reprocessing. The evolution of material properties was monitored across cycles through rheological analysis and mechanical testing.

This work highlights the potential of mechanical recycling as a complementary end-of-life option for bioplastics, promoting a more circular use of these materials, aiming to support the development of more sustainable biopolymer-based packaging solutions.

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Urea hydrolysis in batch reactors: preliminary optimisation of reaction setup and process conditions

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Hydrogen is a clean and sustainable vector for energy generation[1]. A variety of hydrogen carriers have been proposed; among them urea, a major component of human/animal urine, is a safe and sustainable chemical with a high hydrogen content[2]. Valorisation of urea-rich animal farm-waste, a non-critical feedstock detrimental for soil and water, to green hydrogen, will contribute to decarbonise energy sector while simultaneously mitigating environmental pollution.

Urea hydrolysis was carried out in liquid phase using two different magnetic stirred batch reactor setups: i) a basic reaction setup consisting of a three-necked flask heated with an oil bath and equipped with a thermometer, a gas inlet tube for flush the system with nitrogen and a reflux condenser connected to three traps in series for ammonia and isocyanic acid (the first filled with water and the other two with HCl 1M); ii) a stainless steel autoclave reactor pressurized with nitrogen and equipped with temperature and pressure indicators, as well as a valve for gas sampling and a heating jacket. Temperature and reaction time were the reaction parameters investigated. The concentrations of unreacted urea and heavy byproducts were determined by HPLC equipped with a DAD detector using a reversed-phase column, ammonia and isocyanic acid were quantified by UV-Vis analysis using the salicylate method.

Two different reaction setups were used for the preliminary tests of urea hydrolysis carried out with and without TiO_2 as catalyst. Both systems have their advantages and challenges, therefore the limitations and advantages of each system will be presented. The basic reaction setup is the simplest in operation and control but is not gas-tight and the reproducibility of the catalyst suspension preparation is low, therefore this system was not used for further investigations. The reactions carried out in the autoclave reactor have improved reproducibility, but lower conversions compared with the former setup were obtained at the same reaction conditions, because gaseous products were not continuously removed from the reaction environment.

Further studies varying catalyst loading will be conducted with this setup. Finally, this reaction setup will be used to investigate the catalytic steam reforming of urea using metal catalysts supported on TiO_2, with the reaction conditions previously optimized.

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Chemical technologies for increased sustainability in waste management

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The focus of sustainability in waste management is to reduce, reuse and recycle waste in order to conserve resources, reduce pollution and minimise the amount of waste sent to landfill sites. In this context, chemical technologies can be used to both valorise and inertise waste, as demonstrated by these two examples selected from the many activities of the Department of Engineering 'Enzo Ferrari' at UNIMORE.

Room temperature waste encapsulation: New synthesis pathways for inorganic solid materials have emerged, involving the addition of highly concentrated alkaline solutions to aluminosilicate powders at room temperature. This chemical approach to solid-state chemistry reduces waste and emissions compared to the traditional processes used in the manufacture of ceramics and cement. Once alkali-activated, aluminosilicate precursors lead to criptozeolitic cages capable of encapsulating cations, anions and organic macromolecules. Our work focuses on formulating and characterising original matrices that can stabilise various industrial liquid and solid waste containing different types of contaminants[1].

Low-impact and circular fertilization systems: While conventional fertilizers are effective in promoting rapid plant growth, they often lead to significant environmental degradation due to inefficient nutrient uptake and subsequent pollution. We are exploring alternative nitrogen, phosphorus and potassium sources by using animal and plant residues, combined with pumice scraps to develop slow-release nutrient formulations in both crystalline and glassy phases[2]. Two other approaches involve the incorporation of bacteria that solubilize the insoluble phosphate phases in soils and the bioremediation of nitrocellulose wastes to extract the nitrogen component. Overall, this integrated approach demonstrates a viable pathway for producing low-impact, circular fertilizers that reduce dependence on synthetic chemicals, improve nutrient use efficiency, and recover valuable elements from waste.

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Homogeneous Ruthenium Catalysts in the Production of 2,5-Diformylfuran and Polyimines from HMF

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Shifting towards renewable biomass is crucial for mitigating the environmental footprint of energy and fossil resources, positioning 5-hydroxymethylfurfural (HMF) as a pivotal building block.[1] Its oxidation product, 2,5-diformylfuran (DFF), is significant for furan-based chemistry and material science, and this study investigates its selective synthesis using ruthenium catalysts to minimize byproducts. Various catalytic pathways employing organometallic ruthenium species, including Shvo's catalyst, were explored, utilizing quinones as oxidants and Co-salen as a redox mediator. The investigation determined optimal reaction parameters by adjusting temperature, time, catalyst loading, and quinone identity. Subsequently, DFF served as a monomer in polycondensation reactions with ethylenediamine and p-phenylenediamine to yield polyimines (Figure 1).[2] FT-IR, TGA, and DSC analyses verified imine bond formation and oligomer generation, exhibiting reduced thermal stability relative to conventional polyimines. Future work will focus on refining these polymerizations to enhance material characteristics.

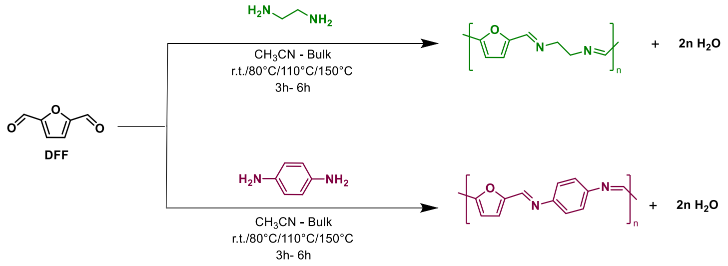

Figure 1. Synthesis of the polyimines obtained by reacting DFF with ethylenediamine (in green) and with p-phenylenediamine (in magenta)

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Deep Eutectic Solvents (DESs) as sustainable alternative electrolytes for Vanadium Redox Flow Batteries (VRFBs)

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VRFBs are large-scale energy storage systems that currently use a H_2SO_4-based aqueous electrolyte for vanadium redox couples, originating deep challenges related to waste management and recovery of the metal ions. Such setup also frequently leads to cross-contamination, poor thermal stability of the redox ions, a potential window limited by water electrolysis and an overall low concentration (≈1,5M) of the redox species.[1] The aim of the present work is to substitute H_2SO_4 with DESs, to both decrease the environmental impact of the systems and increase the concentration of the vanadium species, to improve the performances of VRFBs in a non-acidic, biodegradable, non-toxic, and non-inflammable medium. Different DESs formulations based on choline chloride (ChCl) as hydrogen bond acceptor (HBA) were tested; a variety of carboxylic acids, polyols or amides were used as hydrogen bond donors (HBD) with different ratios and variable water content; some ternary mixtures like ChCl:ethylene glycol:urea were also tested. VCl_3 was solubilized to reach concentrations of 2-3M. The best performing mixtures in terms of viscosity, the main limiting factor, were the ones with ethylene glycol, glycerol or propanediol as HBD, as well as the ternary mixtuers. The only two formulations that were able to dissolve VCl_3 at a concentration of 3M were ChCl:ethylene glycol = 1:2 and ChCl:propanediol = 1:6.

Preliminary evaluations with TGA validated the chance of working at temperatures up to 100°C without any significant degradation in the DES, confirming the good thermal stability of the compounds and the possibility of working at 60-70°C, to decrease the high viscosity of the electrolyte.

Cyclic voltammetry conducted with a three-electrode setup on ChCl:propanediol=1:6 with VCl_3 3M between -2V and +0,5V at 60°C showed visible peaks related to the vanadium redox ions. This analysis demonstrated the importance of decreasing the viscosity of the compound to allow the movement of the ions and proved the absence of any interference between the electrolyte and the working electrode in graphite.

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