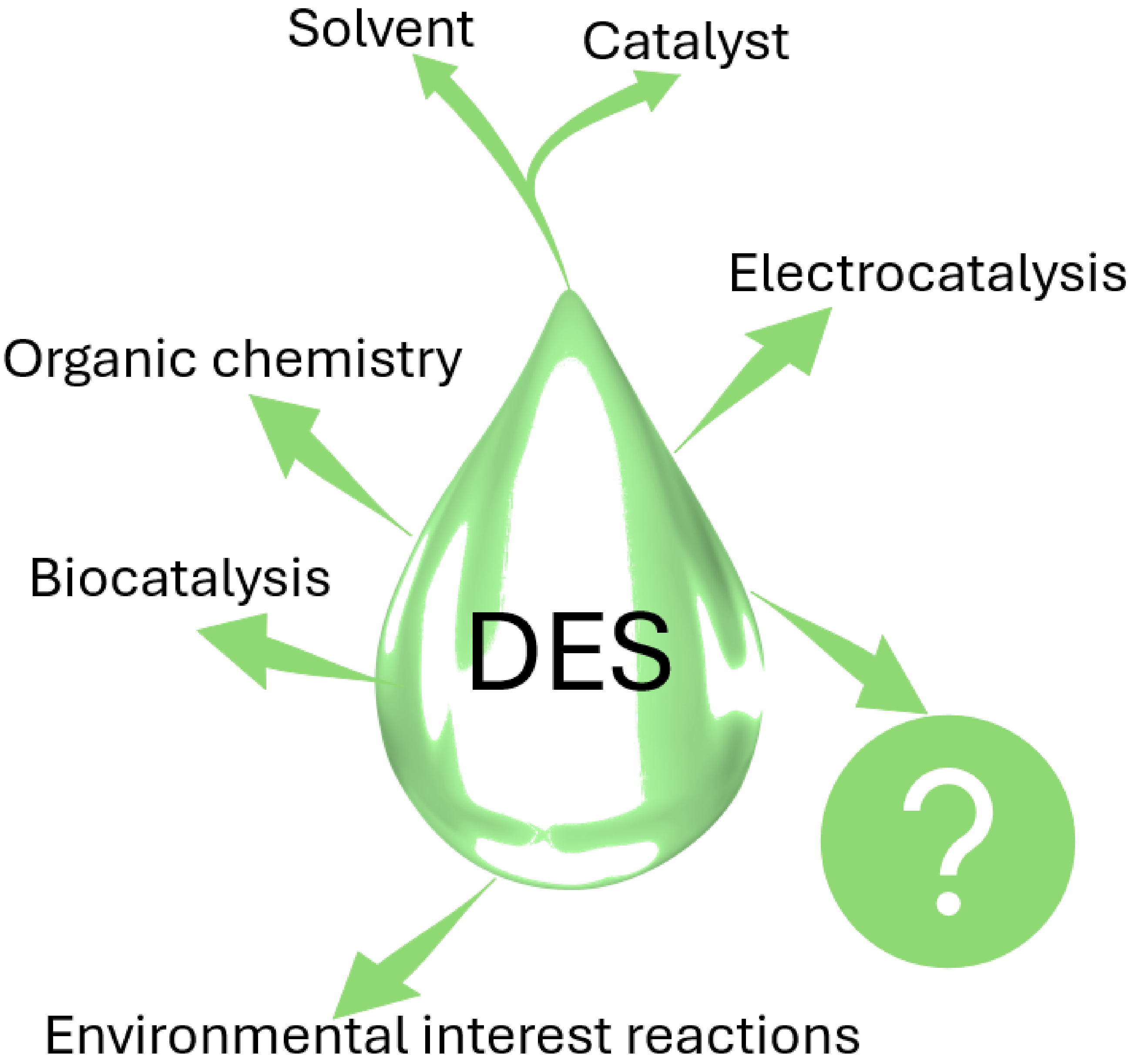
# Catalysis with Deep Eutectic Solvents: Challenges and Opportunities

Eduardo Guzmán*[a],[b]



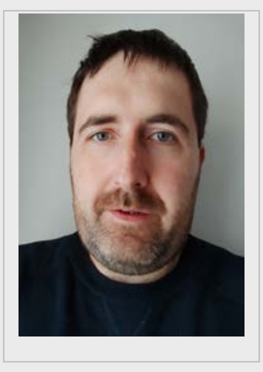
[a] E. Guzmán
Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Plaza de las Ciencias 2, Ciudad Universitaria, Madrid 28040, Spain
[b] E. Guzmán
Instituto Pluridisciplinar, Universidad Complutense de Madrid, Paseo Juan XXIII 1, Ciudad Universitaria, Madrid 28040, Spain
E-mail: eduardogs@quim.ucm.es

**Abstract:** Deep eutectic solvents (DESs) have emerged as a transformative class of green solvents, offering unique advantages in catalysis due to their tunable physico-chemical properties, low toxicity and biodegradability. This review explores the dual role of DESs as both solvents and catalytic media, highlighting their impact on diverse catalytic processes, including organic transformations, biomass valorization and environmental remediation. DESs exhibit remarkable solvation properties that enhance reaction selectivity, yield and efficiency, often surpassing traditional organic solvents. Their versatility extends to homogeneous and heterogeneous catalysis, where they not only facilitate reactions but also stabilize catalytic species, thereby prolonging catalyst life. In addition, task-specific DESs have demonstrated enhanced catalytic activity in key reactions such as esterification, condensation, oxidation and carbon-carbon bond formation. Despite these advantages, challenges such as high viscosity and water sensitivity remain areas of active research. Further exploration of deep eutectic solvent (DES) structural modifications and mechanistic insights will drive their wider adoption in sustainable chemistry. This review provides a comprehensive overview of recent advances in DES-based catalysis, highlighting their role in promoting greener and more efficient chemical processes.

## 1. Introduction

Catalysis is of fundamental importance to the achievement of main objectives in the field of sustainable (green) chemistry. However, the advancements in this field require of innovative strategies for the development of novel catalysts and catalytic technologies [1]. A key focus in this context is related to the progressive substitution of conventional solvents, mainly volatile organic compounds, by the utilization of greener alternatives that mitigate environmental and health risks associated with the toxicity and flammability of common organic solvents [2–5]. This is of paramount importance in synthetic chemistry, as solvents constitute approximately 80% of the total chemical volume used [6].

Eduardo Guzmán is currently Associate Professor in the Physico-Chemistry Department of the Complutense University of Madrid (Spain). His research interests include the physico-chemistry different colloidal and interfacial systems, including polyelectrolyte multilayers, polyelectrolyte–surfactant systems, particle-laden interfaces and emulsions, biophysics, encapsulation for drug delivery, pest control and cosmetics and catalysis. Furthermore, he is coauthor of more than 130 publications in JCR journals and 15 book chapters and member of the editorial boards of different journals.



Several alternative solvents have been explored in the last decades. Among them are included supercritical fluids, perfluorinated solvents, glycerol, bio-based solvents, water, and ionic liquids (ILs), all of which have demonstrated potential as reaction media in catalytic applications [3,7–14]. While these alternatives address some sustainability challenges, they also present many limitations such as high costs, complex synthesis, poor solubility of the substrates, or the need for specialized equipment. For instance, the use of supercritical fluids requires sophisticated equipment, while some ILs may exhibit high toxicity, particularly those based on imidazolium or pyridinium cations. This is largely due to the inherent properties of their lipophilic cations, which tend to bioaccumulate and adversely affect living organisms. In contrast, DESs are typically composed of benign, naturally derived components (e.g., choline chloride, urea, glycerol) that present a much lower toxicity profile and are more environmentally compatible [15,16]. Moreover, while there are some cost-effective ILs available on the market, DESs generally offer an even more economical alternative. DESs are typically synthesized from simple procedures using readily inexpensive available, such as choline chloride, urea, or glycerol, which reduces raw material and production costs. In contrast, many ILs, even the lower-cost variants, often involve more complex synthesis routes and expensive precursors, contributing to higher overall production expenses [17]. On the other hand, water poses challenges due to the instability or low solubility of many substrates in this medium. Consequently, there is a growing interest in exploring more suitable solvent alternatives, such as DESs. However, DESs often display inherent limitations such as high viscosity and water sensitivity, which can negatively impact mass transfer and reaction kinetics, particularly at larger scales. Addressing these challenges is crucial for their broader industrial adoption. It is worth noting that from a chemical perspective, DESs exhibit physicochemical properties similar to those of ILs, including negligible vapor pressure (reducing air pollution), non-flammability (enhancing process safety), and tunable thermophysical properties.

The above aspects make DESs ideal candidates for green chemistry applications, including organic synthesis, polymer chemistry, analytical chemistry, and biomass valorization. Furthermore, variants such as natural deep eutectic solvents

(NADESs), low-melting mixtures (LMM), and deep eutectic ionic liquids (DEILs) have further broadened their applicability [18–20]. One area where DESs have gained particular attention in recent years is synthetic chemistry. They can enhance reaction rates, selectivity, and yields in various transformations, such as cyclization, condensation, oxidation, and reduction reactions. This is largely due to their dual role as both reaction media and catalysts, enabling more efficient processes [5,21–25]. Despite the advances in this area, challenges remain in expanding the use of DESs in catalysis. Further research is needed to develop task-specific DESs tailored for particular reactions, deepen mechanistic understanding, and facilitate industrial-scale applications. This review provides an updated overview DESs in catalyzed reactions by examining their dual role as both solvents and catalysts in diverse chemical transformations. It opens with an outline of the fundamental properties, classifications, and families of DESs, establishing a solid foundation for understanding their significance in sustainable chemistry. The discussion then transitions to the unique dual functionality of DESs, with dedicated sections on both homogeneous and heterogeneous catalytic applications. Subsequent sections delve into key organic transformations, including Knoevenagel condensations, Friedel–Crafts reactions, Michael additions, Diels–Alder cycloadditions, cross-coupling, and multicomponent reactions, highlighting mechanistic insights and performance advantages. Further sections broaden the scope by examining environmental applications, biocatalysis, electrocatalysis, and other emerging reaction types. Finally, the review assesses the overall sustainability of DESs and outlines future directions for their use in greener chemical processes, before concluding with final remarks.

## 2. Deep Eutectic Solvents: General Aspects

DESs, first introduced by Abbott et al. [16,26,27], are liquid mixtures resulting from the interaction between hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) at a specific molar ratio. Figure 1 shows examples of typical HBD and HBA species used to prepare DESs [28].

In general, the self-association process mediated by hydrogen bonds occurring is DESs lead to the formation of new liquid phase characterized for exhibiting a melting point ($T_m$) substantially lower than those corresponding to the individual components [17]. This can be better understood by considering the widely studied mixture of choline chloride (ChCl) and urea in a 1:2 molar ratio. This combination results in the formation of a eutectic mixture with a melting temperature of about 12°C, which is notably lower than the individual melting points of ChCl (302°C) and urea (133°C). The substantial reduction in melting point arises from the strong hydrogen bonding interaction occurring between the halide anion and the HBDs. This occurs through charge-assisted hydrogen bonding interactions, where the negative charge on halide anion enhances its ability to attract the partially positive hydrogen atoms of the HBD groups. This strong interaction helps to disrupt the individual crystalline lattices, leading to a liquid state at room temperature. It may be possible that urea carbonyl group can also participate in hydrogen bonding with hydroxyl groups present (from choline or water), reinforcing the hydrogen bond network. While not as dominant as the $Cl^-$ interaction, it may play an important secondary role in stabilizing the DES structure [29].

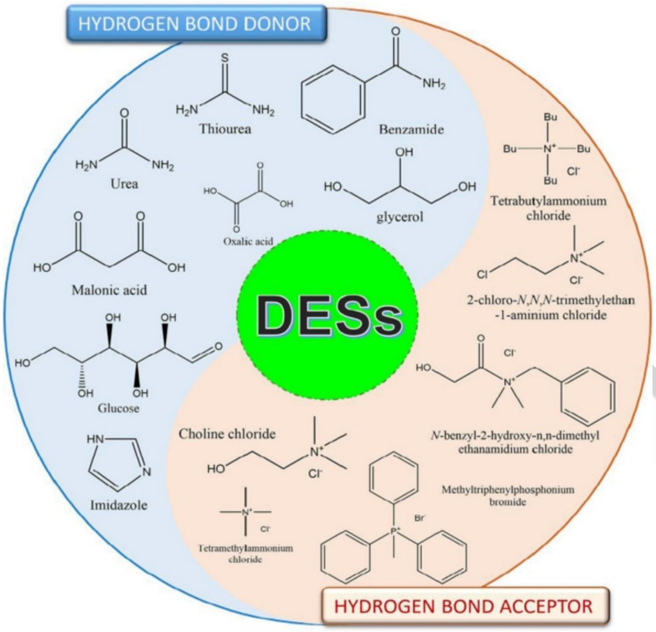


**Figure 1.** Examples of some HBD and HBA species used in the production of DESs. Adapted from Shafique et al. [28] , Copyright (2025), with permission from Elsevier.

It is worth noting that most common DESs exhibit freezing points below 150°C, with those having freezing points under 50°C being particularly attractive for practical applications [17]. In general, the proportion of salt (or HBA) to HBD plays a critical role in influencing the melting point of DESs. However, The melting point of DESs is not directly correlated with the melting temperatures of the pure components. In general, the melting point is determined by a combination of factors, including the lattice energy of the DESs, the specific interactions between the anion (or HBA) and the HBD, and the entropy changes associated with the transition to the liquid state [30]. In this context, the eutectic point of DESs plays a very important role. However, to date many binary phase diagrams of DES forming mixtures remain poorly explored. Figure 2 illustrates an idealized solid–liquid phase diagram for a binary eutectic system that exhibits a pronounced melting point depression.

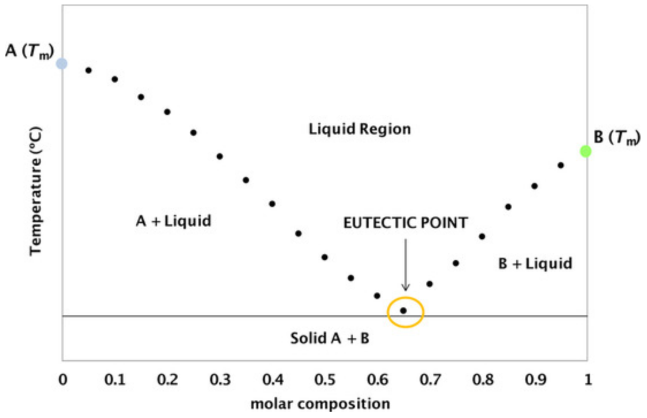


**Figure 2.** Idealized solid-liquid phase diagram for a binary eutectic mixture. Reproduced from Florindo et al. [31], Copyright (2019), with permission from John Wiley and Sons.

In some cases, DESs may exist as cloudy, opaque solids when cooled below their eutectic temperature ($T_{eut}$). However, their solid-state appearance can be misleading, as DESs often exhibit complex thermal transition behaviors distinct from conventional materials. Unlike standard crystalline solids, many DESs can undergo both crystallization and glass transitions, largely influenced by their composition and cooling rates. Notably, vitrification is a prevalent phenomenon among DESs, occurring even at moderate cooling rates. The frequent occurrence of vitrification in DESs suggests a strong correlation between their physicochemical properties, molecular dynamics, and the intermolecular interactions responsible for their characteristic "deepness" compared to conventional eutectic mixtures. These interactions primarily involve entropy of mixing, van der Waals forces, hydrogen bonding, and ionic interactions. However, the precise mechanisms governing their formation and stabilization remain an area of ongoing research, as the interplay between these forces is not yet fully understood [15,27,32–34].

DESs can be categorized into five main types based on their composition and structure. Most types (I-IV) follow the general formula $Cat^{+}X^{-}$ zY, where $Cat^{+}$ represents ammonium cations, $X^{-}$ is a halide anion, and Y (with stoichiometry indicated by z) is a Lewis or Brønsted acid [22]. In addition, it has been recently introduced a new category (Type V), comprising non-ionic DESs, that rely on the interaction between asymmetric HBDs (e.g., thymol, phenolic compounds) and “lone” HBAs (e.g., ethers, ketones, esters, or aldehydes) [5,35]. Table 1 summarizes the composition and general formula for these DES families.

**Table 1.** Composition and general formula of the different families of DES. Adapted from Álvarez et al. [5] , Copyright (2024), with permission from Elsevier.

| Type | Composition | General formula |
|---|---|---|
| I | QAS[a]+metal chloride | $Cat^{+}X^{-}+zYCl_x$ (Y=Zn, Sn, Al, Ga) |
| II | QAS[a]+metal chloride hydrate | $Cat^{+}X^{-}+zYCl_x{\cdot}wH_2O$ (Y=Cr, Co, Fe) |
| III | QAS[a]+HBD | $Cat^{+}X^{-}+zRY$ (Y=$CONH_2$, COOH, OH) |
| IV | Metal chloride hydrate+HBD | $MCl_x+RY$ (M=Al, Zn; Y=$CONH_2$, OH) |
| V | Non-ionic compounds of HBA and HBD | L+A (L=lone HBA, A=asymmetric HBD) |

[a] QAS: quaternary ammonium salt.

The properties of DESs can be finely tuned by selecting different HBD and HBA species or by altering their molar ratios, leading to two types of DESs, hydrophilic or hydrophobic systems, with distinct density, viscosity, conductivity, and acid–base characteristics [31]. Moreover, incorporating water into DESs enables a precise tuning of some of the above-mentioned properties, broadening the utility of DESs as solvents [30]. The posibility to tune the physicochemical properties of DESs is important because they play a crucial role in determining the suitability of the DESs for various catalytic applications.

DESs generally appear as highly viscous liquids with color variations from transparent to amber. Their high viscosity, which typically stands much higher than that of conventional solvents, is attributed to the extensive intermolecular forces, including hydrogen bonding and van der Waals interactions, occurring within the mixture. For instance, ethaline, a mixture of ethylene glycol and ChCl, exhibits a viscosity of 52 cP at 20°C. This contrasts with the viscosity of water, 1 cP, or organic solvent under similar conditions [36]. In fact, most of the DESs present density values well-above 100 cP [17]. It is worth noting that the addition of small amounts of water has been shown to reduce the viscosity of DESs [32,37]. An important effect of the high viscosity of DESs is that it tends to reduce the diffusion rates of reactants and products, but simultaneously contributes to increase the contact time, which have in turn a important influence in the reaction rates [28].

Density also provides insight into the extent of intermolecular interactions; typical DES densities are higher than water (e.g., ethaline has a density of ~1.14 g/cm³ at 20°C) [36]. Modifying the HBA-to-HBD ratio and selecting different components can be tuned the density and free volume in these systems. For instance, Basaiahgari et al. [38] showed that DES-based on ethylene glycol have lower densities compared to those formulated with glycerol (Gly). This trend is attributed to the greater number of hydroxyl groups in Gly, which promotes enhanced hydrogen bonding and reduces free volume. Shafie et al. [39] reported that an increase in the amount of ChCl relative to citric acid leads to a decrease in the density of the mixture, whereas a higher proportion of citric acid results in an increased density, again pointing out the critical role of hydrogen bonding [15]. Generally, hydrophobic DESs present lower densities than hydrophilic one, and longer alkyl chains in HBD and HBA species tend to decrease density [31].

The pH of DESs, linked to the acid–base properties of their constituents, is important both for defining their behavior and for compatibility in various applications. For example, ChCl/D-glucose mixtures maintain nearly neutral pH values (around 7) within a moderate temperature range (25–45°C) [40], though pH typically increases with temperature in a HBD-dependent manner [41,42].

Ionic conductivity in DESs is particularly important in the context of electrochemical and energy storage applications. In general, DES conductivity falls between 0.1 and 10 mS cm⁻¹, which is lower than that of high-temperature molten salts. For example, ethaline shows a conductivity of around 6.17 mS cm⁻¹ at 20°C, which contrasts with values as high as 350 mS cm⁻¹ observed for molten salts like $BiCl_3$ at elevated temperatures [36,43]. This poor conductivity is commonly ascribed to the high viscosity of these type of liquid mixtures [30].

The molecular interactions within DESs also influence surface tension, which represents the energy required to expand a liquid’s surface area, a parameter that reflects. This physicochemical property is affected as result of the formation of DESs. For instance, the surface tension of ethylene glycol decreases from 48.90 to 45.66 mN·m⁻¹ upon formation of ethaline, and the eutectic composition generally corresponds to the lowest surface tension in the system [44]. Furthermore, the surface tension of DESs is sensitive to the molar ratios of their components, highlighting the subtle balance between cohesive forces and molecular interactions [40,44–49].

Although DESs are often considered to have negligible vapor pressures as occurs in most ILs, direct measurements show that their vapor pressures, while low, are higher than those of many aprotic ILs. For example, a DES based on N-methylacetamide and lithium bis(trifluoromethylsulfonyl)imide exhibits a vapor pressure of 20 Pa at 313 K, significantly lower than water’s (~7400

Pa), but higher than typical ILs [50]. Shahbaz et al. [51,52] reported similar low vapor pressure values for a broad range of DESs.

The refractive index of DESs, although less frequently reported, provides valuable insights into molecular interactions and polarizability. For instance, DESs such as ChCl/gly mixtures achieve their highest refractive indices at the eutectic composition over a temperature range of 15–55°C [53,54]. Studies involving tetrabutylammonium chloride (TBAC) with different HBDs, such as phenylacetic acid and propionic acid, indicate that bulkier HBDs enhance molecular association, thereby increasing this parameter. Moreover, calculations of molar refractivity based on refractive index data have revealed that while temperature has a minimal effect, the composition and mole fraction of the HBDs are critical determinants of this property [54–56].

Overall, the complex interplay between composition, temperature, and intermolecular forces in DESs governs a wide range of properties, which in turn dictate their performance in catalytic applications. Table 2 summarized the physico-chemical properties of some common DESs.

**Table 2.** Physicochemical properties of some common DESs. Adapted from Khandelwal et al. [30] , Copyright (2016), with permission from Elsevier.

| **Salt (HBA)** | **HBD** | **Salt (HBA): HBD molar ratio** | **$T_m$ (ºC)** | **Densities (at 25ºC) (g/cm$^3$)** | **Viscosity($\eta$) (cP)** |
|---|---|---|---|---|---|
| ChCl | urea | 1:2 | 12 | 1.25 | 750 (25ºC) |
| ChCl | gly | 1:2 | 40 | 1.18 | 259 (25ºC) |
| ChCl | gly | 1:3 | -* | 1.20 | 450 (20ºC) |
| ChCl | ethylene glycol | 1:2 | 66 | 1.12 | 37 (25ºC) |
| ChCl | malonic acid | 1:2 | -* | 1.25 | 1124 (25ºC) |
| ChCl | malonic acid | 1:1 | 10 | * | * |
| $EtNH_3Cl$ | $CF_3CONH_2$ | 1:1.5 | * | 1.273 | 256 (40ºC) |
| $EtNH_3Cl$ | acetamide | 1:1.5 | -* | 1.041 | 64 (40ºC) |
| $EtNH_3Cl$ | urea | 1:1.5 | 29 | 1.140 | 128 (40ºC) |
| $ZnCl_2$ | urea | 1:3.5 | -* | 1.63 | 11340 (25ºC) |
| $ZnCl_2$ | acetamide | 1:4 | 303.15 | 1.36 | * |

* Not data available

## 2.1. Common families of DESs

DESs have emerged as an innovative class of green solvents whose unique behavior emerges from the specific interactions between HBDs and HBAs. Their remarkable ability to dissolve both polar and nonpolar compounds, combined with their lower toxicity, biodegradability, and ease of recovery, has expanded their interest across multiple fields. Among the most studied DESs are included ammonium-based DESs are prepared by combining ammonium salts with HBDs. These solvents are characterized by their exceptional heat endurance, low viscosity, and high ionic conductivity, attributes that render them highly suitable for applications in electrochemical devices such as supercapacitors and batteries, as well as in various separation and extraction processes. Their unique properties open new avenues for development in both biotechnology and green chemistry [57]. ChCl-based DESs, which often use HBDs such as urea, glycerol, or ethylene glycol, are probably the most extended among the ammonium-based DESs. The properties of DESs make them attractive for organic synthesis, extraction, and electrochemical applications [58].

Another significant group consists of imidazole-based DESs. In these systems, imidazole, a heterocyclic compound characterized by a five-membered ring containing two nitrogen atoms, plays a central role in establishing a robust hydrogen bonding network. The resulting DESs are not only thermally stable and less toxic but also capable of dissolving a wide spectrum of compounds, which is essential for selective separation processes. Despite their advantages, issues such as high viscosity and the possibility of certain components exerting adverse effects have led researchers to explore ways to mitigate these challenges and broaden their application potential in chemical and pharmaceutical processes [59].

Betaine-based DESs represent another promising category, wherein a betaine component is combined with a HBD. These solvents have been noted for their high-temperature resilience, which make them useful in industries as diverse as food, cosmetics, and medicine. They are particularly promising for the extraction and separation of natural products, such as alkaloids, flavonoids, and phenolic compounds, and even in the formation of metal ion complexes, which can be leveraged for metal recovery and recycling. Furthermore, the potential of betaine-based DESs to improve the solubility and bioavailability of poorly soluble drugs makes them an attractive candidate for advancing drug delivery systems, although their relatively high viscosity can limit some applications [60].

Urea-based DESs, produced by blending urea with compounds such as ChCl, have also attracted considerable attention. Their combination of low toxicity, high thermal stability, and biodegradability make them an effective media for biomass conversion, extraction of natural products, and the synthesis of fine chemicals and pharmaceuticals. However, the corrosive effects on certain metals and the higher production costs compared to traditional solvents remain challenges that are driving ongoing research to refine their properties [61].

Innovative approaches have also led to the development of lignin-based DES, which utilize lignin-based compounds (e.g., vanillin, catechol or p-coumaric acid) in conjunction with HBAs such as ChCl or urea [62]. These solvents facilitate the breakdown of lignocellulosic biomass into valuable chemicals and fuels. The environmentally friendly nature of lignin-based compounds, coupled with the low toxicity of its common co-solvents, underscores the potential of lignin-based DESs in sustainable biomass processing [63].

Acid-based DESs are generated by mixing carboxylic acids, such as acetic acid, with HBAs like Gly or ethylene glycol. Their capability to solubilize a diverse range of organic substances makes them valuable in processes such as organic synthesis, biofuel production, and the recovery of metals and dyes. However, the corrosive nature of these solvents toward certain metals and the potential toxicity of some acid constituents require further refinement to fully realize their industrial applications [64].

Polyol-based DESs, which involve the use of polyols, including ethylene glycol or Gly, with HBAs, have gained recognition in recent years. The flexibility in tailoring their viscosity, density, and solvation capabilities makes these solvents highly promising for use in extraction processes, carbon-based synthesis, and electrochemical applications. Their straightforward synthesis and inherent biodegradability further reinforce their appeal in the development of sustainable chemical processes [65].

Lastly, sugar-based DESs are formulated by merging sugar syrups, such as maltose or sucrose, with HBAs like betaine or thiourea. These solvents exhibit significant dissolving power for various natural compounds, which can be harnessed in both electrochemical applications and biomass transformation processes [66].

## 3. DESs in Catalysis

DESs have attracted considerable interest as media for catalytic processes due to their unique properties. Recent investigations have shown that DESs can achieve remarkable catalytic performance, positioning them as promising, environmentally benign alternatives to conventional solvents and catalysts in a wide range of chemical reactions [30,67]. DESs have been used effectively as both reaction media and active catalysts in numerous homogeneous and heterogeneous catalytic systems. Moreover, their ability to be efficiently recycled and reused over multiple reaction cycles further enhances their sustainable profile [68]. In practice, the efficient recycling may achieved through the exploitation of the low volatility of DESs, which limits solvent loss during processing and recycling. Moreover, the high viscosity of DESs may facilitate recycling by promoting the detachment of the activator from the reaction mixture, thus simplifying its recovery and reuse However, the high viscosity can hinder mass transfer and limit the diffusion of reactants and products, potentially impacting the kinetics of the reaction. This drawback can be overcome by carefully selecting the HBD/HBA composition and molar ratios, thereby tuning the viscosity into an ideal range that balances efficient catalytic performance with ease of recycling. This adjustment is critical because it prevents the viscosity from reaching levels that impede the mobility of reactants and products Moreover, DESs tend to be highly sensitive to water and other impurities, which may affect their stability and catalytic activity. Therefore, the addition of water for lowering viscosity must guarantee a negligible distortion of the hydrogen bond network that maintains the DES stability. Additionally, maintaining a controlled, inert environment during reactions can minimize moisture uptake and preserve DES performance over successive cycles [28]. The above aspects makes can hinder the effective scaling up of the catalytic process at industrial level. In this context, the lower viscosity and superior electrochemical properties of Ils may bring certain advantages. However, they suffer from other drawbacks. Therefore, a critical assessment of the physicochemical properties of ILs and DESs is essential to guide further optimization of catalytic processes.

### 3.1. Homogeneous catalysis

Homogeneous catalysis plays a crucial role in organic synthesis, where the catalyst and reactants exist in the same phase, typically as a liquid. This mode of catalysis enables precise control over reaction parameters such as temperature, pressure, and catalyst concentration, leading to enhanced selectivity and efficiency compared to heterogeneous systems [69]. However, a significant drawback of homogeneous catalysis is the challenge of catalyst separation and recovery, which increases process costs and limits sustainability. Moreover, traditional homogeneous catalytic processes often suffer from long reaction times, harsh reaction conditions, and the requirement for an excess of catalysts, including acids, bases, or metal complexes, which may pose environmental and economic concerns [70,71]. Thus, developing efficient, cost-effective, and environmentally benign catalytic systems remains an ongoing challenge in modern organic synthesis.

Conventional organic solvents have been widely employed as reaction media in homogeneous catalysis. However, growing environmental awareness and the need for green chemistry approaches have driven the search for more sustainable alternatives. In this context, DESs can replace traditional solvents while also offering unique interactions that influence catalytic performance.

One of the most intriguing aspects of DESs in catalysis is their dual functionality. In addition to serving as reaction media, DESs can actively participate in catalytic processes by stabilizing intermediates, modulating reaction pathways, and even acting as catalysts themselves. The physicochemical properties of DESs, such as viscosity, density, and conductivity, directly impact catalytic efficiency and selectivity. For instance, ChCl-based DESs, such as ChCl/urea or ChCl/ethylene glycol, have been extensively studied for their ability to enhance reaction rates and selectivity, while also providing a sustainable alternative to conventional solvents [72].

Several studies have demonstrated the advantages of using DESs in homogeneous catalysis. Their ability to dissolve a wide range of substrates, including metal salts and organic molecules, makes them ideal for metal-catalyzed transformations such as hydrogenation, oxidation, and C–C coupling reactions. Additionally, DESs can stabilize catalytic species, preventing deactivation and prolonging catalyst lifetimes. Notably, certain DESs have shown catalytic activity themselves, eliminating the need for additional catalysts and simplifying reaction procedures. Several DESs have been shown to act not only as environmentally friendly reaction media but also as active catalysts in various organic transformations. For instance, L-proline-based DESs have been utilized to catalyze Knoevenagel condensations [73,74]. In Friedel–Crafts processes, a DES-based on ChCl/ZnCl$_2$ catalyzed the acylation of 1,2,4-trimethoxybenzene with benzoyl chloride [75], while a ZnCl$_2$-based DESs with acetic acid has been used in the acetylation of phenols [76]. In heterogeneous catalytic applications, an Fe(III)-based DES, formed by combining hydrated FeCl$_3$ with glycerol, has been used to catalyze the benzylation of arenes [77]. Furthermore, betaine-based DESs have been applied in Michael additions [78]

Recent developments have also explored the potential of task-specific DESs, where the components of the DESs are designed to actively participate in the catalytic cycle. For example, the incorporation of Lewis or Brønsted acidic components into DESs has led to improved catalytic efficiency in acid-catalyzed reactions, including esterifications, condensations, and polymerizations. Furthermore, metal-containing DESs, where transition metals are integrated into the DES structure, have opened new avenues for catalysis by providing recyclable and highly efficient catalytic systems [79].

Overall, the integration of DESs into homogeneous catalysis represents a promising approach to achieving greener and more sustainable chemical transformations. Their multifunctionality, tunability, and environmental compatibility make them valuable alternatives to traditional solvents and catalysts.

### 3.2. Heterogeneous catalysis

Heterogeneous catalysis remains a cornerstone in both bulk and fine chemical synthesis, playing a vital role in numerous industrial applications ranging from oil refining and wastewater treatment to polymer production, biomass conversion, and the automotive industry [80]. In these processes, the catalyst is typically present in a phase distinct from the reactants, most often as a solid, allowing reactant molecules to adsorb onto its surface and undergo chemical transformations with lower energy requirements. Although homogeneous catalysts often offer superior activity and selectivity, the ease of separation, recovery, and reuse associated with heterogeneous systems makes them more attractive for industrial-scale operations [81]. Moreover, the possibilities of recycling the heterogeneous catalysts may contribute to enhance the sustainability of the process by extending catalyst lifetimes and reducing waste and costs [82].

ChCl-based DESs are among the most extensively studied in heterogeneous catalysis. For instance, Shaabani and Afshari [83] compared different ChCl-based DESs for the synthesis of carboxamide-functionalized graphene oxide as a nanocatalyst. They found that the eutectic mixture ChCl/Gly (1:2 molar ratio) outperformed ChCl/urea (1:2 molar ratio), achieving conversion yields of 97% versus 70%, respectively. This work highlighted not only the improved reaction conditions, such as lower temperatures and reduced reaction times, but also the benefits of catalyst and solvent recyclability, with only a minor decline in activity after multiple cycles. Similarly, Messa et al. [84] demonstrated that the ChCl/Gly DESs could significantly enhance the Sonogashira cross-coupling reaction. This is possible because conventional protocols often require ligands, co-catalysts, or tailored palladium complexes to achieve efficiency and suppress unwanted side reactions such as Glaser-type homocoupling. In contrast, DESs not only provide a benign and biodegradable medium, but also enable ligand-free, heterogeneous catalysis using inexpensive Pd/C under mild conditions (60 °C), achieving yields up to 99% across a broad substrate scope. In another innovative study, Zhang et al. [85] utilized ChCl/urea (1:2 molar ratio) as a co-solvent in the microwave-assisted synthesis of spirooxindole dihydropyridines via multicomponent reactions. Using a graphene oxide-supported molybdenum magnetic catalyst, they optimized reaction conditions to obtain nearly quantitative conversion, although similar results were not replicated with other ChCl-based DESs such as ChCl/Gly, ChCl/citric acid, or ChCl/glucose. These findings underscore the importance of DES composition in dictating catalytic performance and the potential for recycling both the catalyst and the DES without significant loss of activity.

The versatility of DESs is further exemplified in the synthesis of bioactive molecules. For instance, ChCl/urea (1:2 molar ratio) has been employed as an environmentally friendly reaction medium for synthesizing tetrazolic acids, compounds with significant pharmacological potential, using copper acetate as the catalyst. This approach results in an isolated yield of 90% within 12 hours of reaction at 100°C [86]. DESs have also been applied in other areas, such as the modification of activated carbon electrodes to enhance ion adsorption via complex charge restructuring [87] and the conversion of sugars like fructose and sucrose into 5-hydroxymethylfurfural (5-HMF) with the help of ChCl/Glutaric acid (1:1 molar ratio) and Amberlyst-15 resin. This methodology allows for achieving yields of up to 78% and successful catalyst recycling over multiple cycles [88].

In addition to ChCl-based systems, DESs formulated with natural compounds such as caffeic acid have shown promising results. Sun and Hou [89] prepared a DES using solid caffeic acid, as the HBD, with ChCl. In this case, the caffeic acid was effectively used as a donor of caffeoyl residues in the synthesis of glycerol caffeates. This approach significantly improved the solubility of caffeic acid and enhanced reaction rates at lower temperatures (70°C). In other study, Wang et al. [90] reported even higher caffeic acid conversions (95%) using a similar DES system. Furthermore, the development of magnetic DESs, such as those synthesized by Bakhtiarian and Khodaei [91], which combines ChCl with metformin immobilized on pectin, has opened new possibilities for catalyst recovery and reuse in the synthesis of medicinally relevant quinazolinone derivatives.

Recent advances in the field also include the use of DESs in coupling reactions. Niakan et al. [92] employed a magnetic catalyst for the Suzuki–Miyaura cross-coupling reaction in both hydrophilic and hydrophobic DESs. The results showed that the improved catalyst dispersion in hydrophilic media led to superior activity and higher yields (around 90%) even after multiple reuse cycles. Moreover, DESs have been utilized as precursors in the fabrication of heterogeneous catalysts for cycloaddition reactions, such as the conversion of $CO_2$ and epoxides into cyclic carbonates. Gu et al. [93] reported that incorporating a DESs, specifically a mixture o f urea, melamine, and $ZnCl_2$ (24:1:2 molar ratio), into the design of nanocomposites based on graphitic carbon nitride resulted in catalysts with dual Lewis acid–base functionalities and enhanced activity under mild conditions (90°C, 3 hours).

The role of DESs in catalyst design extends to photocatalytic applications as well. Mou et al. [94] demonstrated that DESs could be used to improve the coupling between precursors in the synthesis of g-$C_3N_4$ (graphitic carbon nitride)/metal oxide nanocomposites for nitrogen fixation, leading to catalysts with increased surface areas and more active sites. In a similar way, Iqual et al. [95] synthesized nitrogen-doped ceria nanomaterials via a hydrothermal treatment in the presence of a eutectic solvent composed of acetic acid and Cetyltrimethylammonium bromide (1:1 molar ratio), achieving nearly complete photocatalytic degradation of sulfamethoxazole.

Despite these promising advances, developing heterogeneous catalysts, that combine the high selectivity of homogeneous systems with the practical advantages of heterogeneous catalysts, remains a challenge.

## 4. Catalyzed organic reactions in DESs

DESs have attracted significant interest as alternative media for organic reactions because of their unique environmental and practical advantages, which give them an edge over traditional solvents. Furthermore, DESs are not merely inert reaction media; they often actively participate in reactions, with their components participating as catalyst [21].

DESs have been applied in various condensation and multicomponent reactions. For instance, they facilitate the Knoevenagel condensation for synthesizing coumarin derivatives and dyes, and serve as reaction media in processes like the Biginelli and Ugi reactions, where their unique polar environment enhances reaction rates and selectivities. This fine-tuning of the solvent environment improves reaction efficiency, atom economy, and overall sustainability. Despite challenges such as high viscosity and density that can limit mass transfer, strategies such as water addition or the formulation of ternary mixtures have been developed to mitigate these issues [21]. In the following, we discuss selected examples of catalyzed organic reactions using DESs, focusing on a limited number of reaction families [2,5,17,21,30].

### 4.1. Knoevenagel condensation

The Knoevenagel condensation is a widely utilized carbon-carbon bond-forming reaction involving an aldehyde or ketone and a methylene-active compound, such as malononitrile or cyanoacetamide, in the presence of a base [96]. This reaction is pivotal for synthesizing *α,β*-unsaturated carbonyl compounds, which are key intermediates in the production of fine chemicals, pharmaceuticals, and agrochemicals. Traditionally, this reaction requires organic solvents and bases, leading to the generation of waste and necessitating purification steps. Recent advances employ DESs for Knoevenagel reactions as green, sustainable alternatives, offering high efficiency, selectivity, and recyclability while minimizing environmental impact [97].

Karadendrou et al. [73] showed that L-proline-based DESs (e.g., L-proline and glycine at a 1:2 molar ratio) can serve as both reaction medium and catalysts in the synthesis of flavonoids, specifically aurones, with high purity and relative high yields (up to 76%). The yield is reduced when the pH is lowered, which highlights the critical role of pH as controlling parameter of the reaction efficiency. On the other hand, the substitution of L-proline by other components hinders the reaction. This result together with the importance of the pH of the medium may be a result of the hydrogen bonding interactions within the system. Similarly, Hesse et al. [74] showed that L-proline based DESs (e.g. L-proline and Gly at a 1:2 molar ratio) can be used for catalyzyng Knoevenagel condensations with various substrates, including rhodanine derivatives and thiazolidine-2,4-dione (TZD). In addition, the works by Karadendrou et al. [73] and Hesse et al. [74] pointed out that the reaction velocity and yield can be significantly increased by ultrasound and microwave irradiation. A notable advantage of using L-proline-based DESs as a reaction medium in the Knoevenagel condensation is their ability to facilitate the reaction without requiring protection or deprotection of highly reactive functional groups, such as free hydroxyl groups, thereby aligning well with Green Chemistry principles. Moreover, these DESs exhibit excellent recyclability, maintaining catalytic efficiency over at least seven consecutive cycles without any loss in performance.

Wang et al. [98] studied the condensation between benzaldehyde and acetylacetone catalyzed by L-proline in nine different DESs. Among these, ChCl/Gly (1:1 molar ratio) and ChCl/ethylene glycol (1:3 molar ratio) were identified as optimal, leading to yields of 96.6% and 95.6%, respectively. Deviations from these compositions or the addition of water significantly reduced yields, highlighting the critical role of both DES composition and molar ratio in influencing catalytic efficiency through specific molecular interactions. Under solvent-free and aqueous conditions, yields dropped markedly to 67.5% and 17.9%, respectively, underscoring the necessity of a well-structured solvent environment. Further analysis revealed that increasing water content in the DESs (20%, 50%, and 80%) led to a progressive decline in yield, while simultaneously increasing the Z/E stereoisomer ratio [99]. This suggests that while DESs facilitate intermediate formation, excessive water disrupts catalytic activity and solvent structuring. On the other hand, compared to ILs, DESs promote the formation of reaction intermediates and stabilize transition states. Temperature optimization experiments identified 50°C as ideal for performing the reaction, with yields decreasing at higher temperatures, likely due to the instability of reactive intermediates. Moreover, the presence of electron-withdrawing substituents on benzaldehyde enhanced reactivity through intramolecular hydrogen bonding but reduce the reaction yield, while electron-donating groups increased reaction yields [99]. Combined experimental and computational tools revealed that DESs stabilize key imine intermediates, thereby accelerating the reaction. Finally, recyclability tests demonstrated that DESs could be reused for at least four catalytic cycles without significant loss of activity [99].

The effect of the reaction medium in the catalytic performance of enzymes in the Knoevenagel condensation was also explored by Wang et al. [100]. They showed that both DESs and ILs enhance enzymatic activity compared to conventional solvent-free conditions. In particular, ChCl/Gly (1:2 molar ratio) emerged as the most effective DES, yielding up to 92.7% when porcine pancreas lipase is used as biocatalyst, outperforming ILs, which reached a maximum yield of 73.3%. The superior performance of DESs is attributed to their biocompatibility, hydrogen bonding network, and tunable polarity, which together create a favorable environment for enzyme stability and reactivity. It should be noted that as occurred in the above discussed study, the addition of water to DESs lowered the catalytic efficiency, reinforcing the importance of optimizing DES composition for ensuring enzyme stability and reactivity. This is also important for controlling the chemoselectivity, diastereoselectivity, and enantioselectivity in the competitive condensation of aldehyde with aldol and Knoevenagel nucleophiles catalyzed by aminoacids [101]. Interestingly, the increase in water solubility of the Knoevenagel nucleophile did not notably affect selectivity, suggesting that the water phase itself played a key role in modulating reactivity. Building on these findings, Al Beiruty et al. [101] evaluated ChCl/urea mixtures with and without water as medium of reaction. In an anhydrous ChCl/urea mixture (2:1 molar ratio), the aldol/Knoevenagel ratio was 8:1, while the enantioselectivity of the aldol product remained low (32%). However, adding water to create a ternary DES (ChCl/urea/water, 1:2:5.7) significantly enhanced both chemoselectivity (15:1) and diastereoselectivity (anti/syn = 8:1), while also improving the enantioselectivity to 96%. This mirrors the earlier observation that water suppresses the Knoevenagel pathway, reinforcing the importance of aqueous environments in controlling selectivity. A comparison with other DES formulations revealed that reducing the water content

(ChCl/urea/water, 1:2:1.4) lowered diastereoselectivity (from 9:1 to 4.5:1), while using alternative hydrogen bond donors, e.g., Gly, also resulted in diminished selectivity. Notably, reaction efficiency was improved when using ball-mill stirring, reducing reaction time from 36 h to just 7 h while maintaining high selectivity.

Further studies by Molnar et al. [102] and Jeeta Devi et al. [103] reported that DESs ChCl/urea can catalyze Knoevenagel condensations without additional catalysts, simplifying product isolation and enabling recyclability over multiple cycles. In fact, the reaction mixture can be directly treated with water to precipitate the product, eliminating the need for extensive purification steps. Following product isolation, the DES can be recovered by evaporating water and subsequently reused for multiple cycles. Dong et al. [104] demonstrated that integrating DESs into polymeric materials enhances the catalytic activity for the Knoevenagel condensation of benzaldehyde and malononitrile in relation to their non-polymeric counterparts, achieving excellent yields (95–98%) for benzaldehydes with both electron-donating and electron-withdrawing groups. This superior performance was attributed to the synergistic effect between the polymeric framework and the basic catalytic sites provided by the DESs and imine bonds, which enhance catalytic activity and stability. Compared to traditional IL-based catalytic systems, DES-containing polymeric materials offer distinct benefits, including lower toxicity, enhanced stability, and structural versatility. Unlike ILs, which require careful selection of cation-anion pairs to optimize enzyme or catalyst compatibility, DES-based polymeric catalysts provide a confined, tunable microenvironment that enhances reactivity while maintaining recyclability.

### 4.2. Friedel-Crafts reaction

In Friedel–Crafts processes, DESs offer a dual functionality by acting both as solvents and as catalysts through their intrinsic Lewis or Brønsted acidic properties. This unique combination not only enhances the efficiency of alkylation and acylation reactions, achieving high conversion rates and selectivities, but also facilitates catalyst recycling [5,21].

Jin et al. [75] evaluated a series of DESs for synthesizing aromatic ketones, finding that a mixture of ChCl and $ZnCl_2$ was the most efficient catalytic system when using 1,2,4-trimethoxybenzene and benzoyl chloride as model substrates. Under optimized conditions (70 °C with one equivalent of the DES), the reaction yielded 83%, a significant improvement over traditional $ZnCl_2$ catalysis in organic solvents, which only achieved 27%. Reaction parameters, including catalyst loading, temperature, and time, were crucial, with higher DES amounts enhancing yield, while excessive temperatures led to side reactions. Acyl halides outperformed anhydrides, and the electron-donating strength of the aromatic substrates influenced efficiency. Recycling studies showed that the DES remained stable and reusable for at least five cycles, with yields between 80–85% [75]. Similarly, Wang et al. [105] explored DESs in Friedel–Crafts alkylations of electron-rich arenes with aldehydes, producing triarylmethanes and diarylalkanes. The ChCl/$ZnCl_2$-based DES exhibited superior performance, achieving up to 94% yield with reduced reaction times compared to traditional methods. The dual role of the DES as both solvent and catalyst, its Lewis acidity, and hydrophilicity facilitated the reaction by promoting electrophilic substitution and removing water by-products. Optimization experiments showed that increasing the DES-to-benzaldehyde ratio improved conversion, and temperature adjustments balanced reaction rate and efficiency. FTIR analysis revealed rapid intermediate formation, suggesting high reactivity and efficiency. Recycling tests showed only a minor yield decrease (94% to 89%) after five cycles, further supporting its robustness and potential for sustainable industrial applications. Tran et al. [106] also exploited the strong Lewis acidity of ChCl/$ZnCl_2$ DESs to efficiently form acylium intermediates under microwave irradiation. This approach overcame limitations of traditional catalysts, such as moisture sensitivity and the inability to recycle stoichiometric quantities of conventional Lewis acids. The DES system showed broad substrate scope, enabling acylation of electron-rich arenes and heterocycles like indole and pyrrole with high regio- and chemoselectivity. Indoles, in particular, were acylated at position 3 without the need for N-protection. The method also accommodated various acid anhydrides, including sterically demanding ones like pivalic anhydride, demonstrating the flexibility and robustness of the DES-mediated process. The DESs not only provides an ideal polar medium that stabilizes reactive intermediates but also actively participates in the catalytic cycle, facilitating the generation of electrophilic species required for Friedel–Crafts acylation. Microwave-assisted conditions accelerate the process, reducing reaction times to minutes, enhancing sustainability by lowering energy consumption. Additionally, the DESs can be recovered and reused with minimal catalytic activity loss, offering industrial appeal. The simple workup, involving diethyl ether washing and vacuum drying, enables multiple recycling cycles, reducing waste and costs. Following with the use of DES eutectic solvent based in $ZnCl_2$, Tamaddon and Rashidi [76] used a $ZnCl_2$-based DES wlth acetic acid (1:2 molar ratio) for the chemo-selective synthesis of long-chain esters and Friedel–Crafts acetylation of phenols. Acetylation of phloroglucinol at 60°C for 60 minutes yielded up to 98%. The DES facilitates the formation of an arenium ion intermediate, which quickly rearranges to form the desired product. Recycling studies showed that the DES maintained catalytic efficiency for at least four cycles with minimal activity loss DES can be recovered via water addition and acetone extraction, followed by a drying step.

Nguyen et al. [107] developed a novel Friedel–Crafts acylation approach using metal triflate catalysts in DESs to synthesize aromatic ketones. They screened various metal triflates under microwave irradiation and found praseodymium triflate to be the most effective, achieving high yields and excellent regioselectivity with electron-rich arenes and acid anhydrides. The DES, prepared from ChCl and appropriate hydrogen bond donors (HBDs), not only serves as a recyclable, benign medium but also enhances catalytic performance. Density functional theory (DFT) studies revealed that the catalytic cycle involves the formation of an active acylium intermediate via ligand exchange, followed by electrophilic aromatic substitution, where the triflate anion and acidic conditions play crucial roles. Figure 3 displays the proposed mechanism for the acylation reaction in DESs using rare-earth triflate catalysts.

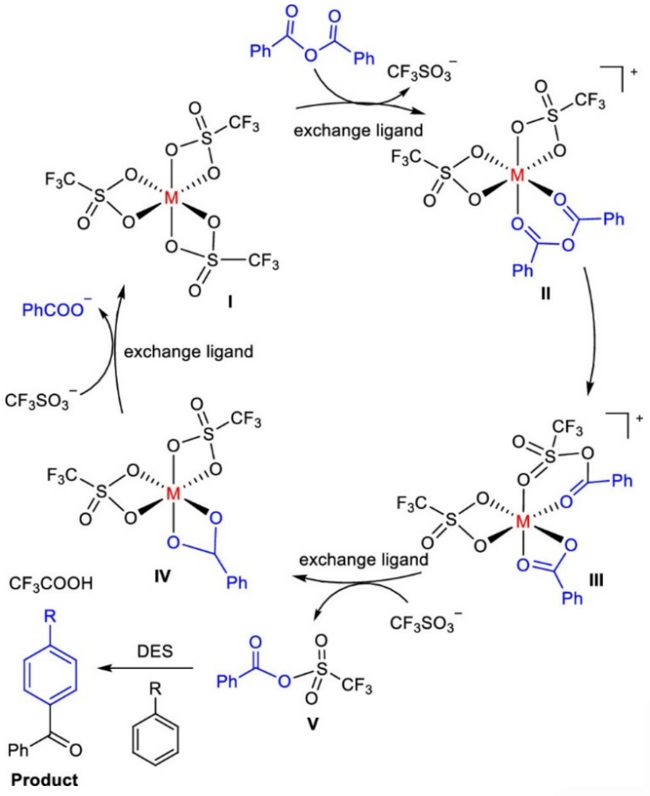


**Figure 3.** Scheme of the proposed mechanism for the acylation reaction in DES using rare-earth triflate catalysts. Reprinted from Nguyen et al. [107] with permission under Creative Commons Attribution (CC BY NC ND) license.

Ramos-Martín et al. [77] introduced an eco-friendly, sustainable approach for synthesizing 1,1-diarylalkanes through Friedel–Crafts benzylation mediated by an Fe(III)-based-DES. This DES is formed by combining hydrated $FeCl_3$ ($3FeCl_3{\cdot}6H_2O$) with Gly in a 3:1 molar ratio, creating a liquid medium with strong Lewis acidity that remains stable under ambient conditions. The system catalyzes the benzylation reaction of a wide range of arenes, including some with deactivating groups, with various benzylating reagents, yielding over 130 examples of substituted 1,1-diarylalkanes with high regioselectivity. Operating under mild conditions (typically 120 °C under air), the reaction benefits from a simple product isolation process due to natural phase separation and demonstrates robust recyclability, maintaining catalytic activity for up to 20 cycles.

### 4.3. Michael addition

The Michael addition, a widely utilized conjugate addition reaction, traditionally catalyzed by acidic or basic conditions, has been substantially advanced through the integration of DESs that offer greener reaction media and improved catalytic outcomes. ChCl-based systems, such as ChCl/Gly and ChCl/urea have been successfully employed in the Michael addition of *β*-nitrostyrene with various nucleophiles, yielding comparable results to conventional catalysts. In particular, ChCl/urea evidenced an enhanced catalytic performance in the reaction between cyclohexanone and trans-*β*-nitrostyrene, resulting in higher yields than when traditional catalysts are used [28]. In the realm of enantioselective transformations, Nígez et al. [108] demonstrated that incorporating chiral 2-aminobenzimidazole catalysts in DESs, especially ChCl/gly, at an optimal 10%mol/mol loading, not only achieves complete conversion in the Michael addition of 1,3-dicarbonyl compounds to *β*-nitroalkenes but also secures enantiomeric excesses as high as 80%. This is a result attributed to enhanced hydrogen bonding interactions confirmed by NOESY NMR studies, particularly when the catalyst bears strong electron-withdrawing substituents.,is an effective route for enantioselective Michael additions of 1,3-dicarbonyl compounds to *β*-nitroalkenes. Platten et al. [109] further expanded the utility of DESs by revealing that ChCl-based DESs paired with either urea or gly can modulate interfacial interactions and influence reagent aggregation in organometallic additions of both Grignard and organolithium reagents to chalcone. This is a result of the ability of DESs to direct exclusive regioselectivity towards 1,4- or 1,2-addition products by controlling the DES composition, DES-to-substrate ratio, and the incorporation of donor additives. The methodology was extended to double-addition and one-pot sequential reactions, illustrating the versatility and tunability of DESs in mediating complex synthetic transformations.

Complementing the above findings, Gutiérrez-Hernández et al. [110] optimized a DES system composed of ChCl and pTSA for the aza-Michael addition of maleimide to aniline, finding that the judicious addition of small amounts of water significantly improves yields up to 93% by enhancing reactant solvation and stabilizing key intermediates. This is an improvement compared to traditional organic solvents, such as methanol or toluene. The presence of water in the DES system likely facilitates the dissolution of reactants and stabilizes key intermediates, reducing the occurrence of side reactions and ensuring a more selective pathway. The solvation effect of water is thought to lower the energy of activation required for the aza-Michael addition. This is because water and DESs act synergistically to stabilize the transition states and intermediates, thus optimizing the reaction pathway. This supports the idea that DESs, in combination with water, can modify the energetics of a reaction, leading to improved selectivity and higher product yields.

Gutiérrez-Hernández et al. [111] explored the catalytic efficiency of DESs in the Michael addition of pyrrole to maleimides, demonstrating that the ChCl/$ZnCl_2$ formulation outperforms other DESs at room temperature. By combining experimental data with theoretical calculations, they showed that although the direct reaction between pyrrole and maleimide is initially unfavorable, the DES system lowers activation barriers by enhancing nucleophilicity via ChCl and increasing electrophilicity through Lewis-acidic $ZnCl_2$. Adding a small amount of water further promotes zinc-zincate species formation, which stabilizes intermediates and optimizes molecular orientation, thereby enhancing both kinetic and thermodynamic parameters. Rizzo et al. [112] introduced 1,3 : 2,4-dibenzylidene-D-sorbitol (DBS)-based eutectogels formed in various ChCl-DESs for a L-proline catalyzed Michael addition reaction. Their study determined the critical gelation concentration and gel-sol transition temperature, revealing that DESs with strong hydrogen bond donors such as ChCl/Gly yield lower gelation temperatures and enhanced thermal stability, while glycol-based DESs with ether-like oxygens demand higher temperatures. Rheological analysis confirmed the gels' solid-like behavior, and circular dichroism spectra indicated significant changes in molecular organization upon gelation. When applied to the Michael addition of malononitrile to trans-chalcone, these eutectogels delivered higher conversions and yields than DES solutions, likely due to the confined environment that increases local catalyst concentration, although no enantioselectivity was observed. Variations in reaction conditions, gelator concentration, and reactant structure suggested that flexible nucleophiles and dienones with extended π-surfaces favor a stabilized transition state, ultimately boosting catalytic performance.

Most of the above studies dealt with the use of ChCl-based DESs. Alternatively, Fonseca et al. [78] employed betaine-based DESs for the Michael addition of acetylacetone to trans-β-nitrostyrene using an immobilized cinchonidine–squaramide catalyst. Tested in betaine/D-sorbitol/water and betaine/D-xylitol/water systems, the catalyst in betaine/D-sorbitol/water exhibited excellent stability and recyclability at 5% mol/mol loading with quantitative yields (≥99%) over nine cycles, though enantioselectivity varied between 62% and 97% ee. Reducing the catalyst loading to 1% mol/mol led to a slight drop in yield (above 80%) and a pronounced decline in enantioselectivity, reaching 17% ee by the ninth cycle; at 0.5% mol/mol, enantioselectivity further diminished to 43% ee after five cycles. A similar trend was observed in the betaine/D-xylitol/water system, with performance differences attributed to hydrogen bonding interactions and solvent microenvironments. Kinetic studies confirmed that while the catalyst maintained its activity over multiple cycles, enantioselectivity was highly sensitive to catalyst loading and reuse.

### 4.4. Diels-Alder reaction

Despite the limited exploitation of DESs in Diels–Alder reactions, they have demonstrated a strong potential for improving reaction kinetics and substrate dispersion, thereby potentially enhancing cycloaddition outcomes [5,21].

Marullo et al. [113] demonstrated that DESs act as both sustainable media and active participants when combined with ultrasound irradiation. Their systematic study showed that optimizing reaction parameters such as temperature and diene/dienophile ratio significantly boosts yields, for instance, raising the temperature from 20 °C to 40 °C improved yield from 53% to 69% in one DES system, while 1:1.2 diene/dienophile ratio provided optimal conversion. Among DESs evaluated, ChCl/ethylene glycol delivered the best performance with a yield as high as 96%. This was attributed to its balanced of viscosity, polarity, and hydrogen bond network as confirmed by resonance light scattering and $^1$H NMR studies. Furthermore, the strength and compactness of the DES hydrogen bond network directly influenced reaction efficiency, and the use of ultrasound irradiation reduces the reaction time from 24 hours to 70 minutes, while maintains the high yields. This results in energy saving of over 99% compared to conventional heating. Additionally, the DESs demonstrated excellent recyclability over eight cycles without significant yield loss.

Grosso et al. [114] showed that natural DESs can enhance the synthesis of complex bis(indolyl)methanes (BIMs) through a one-pot hetero-Diels–Alder strategy. The ternary mixture of water, ChCl and glycerol provides an optimal medium that not only help to overcome the inherent viscosity issues associated with the use of glycerol but also improves reaction efficiency and product isolation; under these conditions, reactions between alkyl or aryl hydrazones and indoles yielded BIMs in high yields and steroselectivity within minutes. Additionally, this methodology enabled a cascade reaction converting hydrazone intermediates into carbonyl-functionalized BIMs, offering a versatile route for further synthetic modifications. Following with the use of natural DESs, Torres et al. [115] investigated the influence of the use of different HBAs and HBDs in natural DESs on the stereoselectivity and efficiency of Diels–Alder reactions They found that a eutectic mixture of 2,3-dihydroxypropyl-1-triethylammonium chloride (DPTAC) and lactic acid (1:2 molar ratio) delivered the highest yields (78–89%) and improved endo selectivity (endo/exo ratios of 2.7–2.9) compared to DESs based on Gly or ethylene glycol. This was attributed to the strong hydrogen bond network in the lactic acid-based DES, which provided a highly organized and polar microenvironment that facilitates the reaction. Functional modifications, such as acetylation of HBAs, further increased endo selectivity by altering hydrogen bonding and solvent polarity. Interestingly, while chiral DESs were also tested, the anticipated enhancement in stereoselectivity was not consistently observed, indicating that factors like hydrogen bonding and polarity more dominantly influence reaction outcomes.

Le et al. [116] utilized the Diels–Alder reaction in DESs for the covalent functionalization of multi-walled carbon nanotubes (MWNTs). In this study, a poly(ionic liquid), synthesized via RAFT polymerization of poly(chloromethylstyrene-alt-maleic anhydride) and then post-functionalized to incorporate furfuryl pendants and imidazolium groups, was grafted onto MWNTs under ultrasonic irradiation in ChCl/ethylene glycol, achieving significantly higher grafting ratio compared to reactions in water or conventional traditional solvents, while preserving the structure of the nanotrubes.

### 4.5. Cross-coupling reactions

Cross-coupling reactions are essential in modern organic synthesis for forming carbon–carbon and carbon–heteroatom bonds, typically using palladium-based catalysts. However, traditional methods still rely on hazardous solvents such as toluene and benzene, which conflict with green chemistry principles [5].

Marset et al. [117] explored DESs as alternatives to volatile organic solvents in palladium-catalyzed cross-coupling reactions, including Suzuki–Miyaura, Sonogashira, and Heck couplings. They synthesized a new cationic pyridiniophosphine ligand with higher effectiveness in DES-mediated Suzuki–Miyaura coupling than conventional phosphine ligands. When the ligand was combined with $PdCl_2$ (1.0%mol/mol) in a ChCl/Gly (1:2 molar raio), a 88% yield was achieved under mild conditions. On the other hand, modified Sonogashira couplings even reached excellent yields without needing a copper co-catalyst, and Heck reactions generally produced moderate to high yields. The study also highlighted the recyclability of the DES, which allowed the recovery and reuse of the catalyst without significant activity loss. Complementary DFT and spectroscopic studies confirmed that the cationic ligand favored a trans-coordination mode, mimicking classical phosphine ligands, and demonstrated the compatibility of these complexes with DES media. In a subsequent work, Marset et al. [118] employed a mesoionic carbene-palladium complex as a pre-catalyst in DESs in cross-coupling reactions, finding that the compatibility of DES-specific ligands enhanced catalyst stability and efficiency, enabling room-temperature

Suzuki reactions and underscoring the role of palladium nanoparticles as active catalysts. Saavedra et al. [119] also highlighted the benefits of DESs in palladium-catalyzed cross-coupling reactions using a bipyridine-palladium complex as a pre-catalyst. Their work demonstrated high efficiency, excellent recyclability, and the importance of cooperative interactions, especially hydrogen bonding by a free amino group in the ligand, with the hydrophilic ChCl/gly DES facilitating the reaction and the formation of Pd(0) species as the active catalyst.

Monteiro et al. [109] investigated glycerol as a sustainable medium for Suzuki–Miyaura cross-coupling reactions of aryl bromides with phenylboronic acid as model substrates at 80 °C. Although the ligand-free Pd catalyst initially provided moderate yields (46–54%), yields improved to 70% with extended reaction times and KOH, while phosphine-based Pd catalysts reached nearly quantitative yields (up to 99%). The study also showed that chlorodiphenylphosphine served as an excellent pre-ligand with yields of 98%. Despite glycerol's ease of product isolation via hexane extraction, its recyclability was limited by Pd black formation and catalyst leaching. To address these issues, a triethanolamine/glycerol DES was introduced, enhancing reaction efficiency under base-assisted conditions and enabling effective base-free coupling with moderate to high yields and excellent selectivity. The in situ formation of triethanolamine phenylboronate, confirmed by $^{11}$B NMR, underscored the pivotal role of the DES in facilitating the cross-coupling process.

It is worth noting that in the case of metal-catalysed cross-couplings reactions, ILs have also demonstrated promising potential. ILs have been widely used due to their tunable polarity, thermal stability, and capacity to stabilize catalytic species. However, concerns over their synthesis complexity, high cost, and ecological impact have led to increased interest in DESs as a more sustainable alternative [120,121]. Moreover, DESs display a similarly favorable solvent environment for catalytic reactions, particularly in Pd-catalysed C–C couplings such as Heck, Suzuki, and Sonogashira reactions [68,122,123]. Notably, recent studies show that certain DESs can outperform ILs in terms of reaction selectivity, catalyst recoverability, and recyclability. For instance, glycerol-based DESs have enabled higher yields and improved catalyst reusability in Heck reactions compared to Ils highlighting their capability to fine-tune both solvent–catalyst interactions and product profiles [122,124].

### 4.5. Multicomponent reactions

Multicomponent reactions (MCRs) allow the construction of complex molecular architectures from three or more starting materials in a single-step process. This approach offers a high atom economy, reduced reaction times, and the ability to generate diverse molecular scaffolds. Kumar et al. [125] demonstrated the dual role of a ternary DES as both solvent and catalyst in the synthesis of pyrano[2,3-d]pyrimidines, achieving high yields and shortened reaction times under ambient conditions, alongside excellent recyclability, thereby addressing many of the drawbacks of traditional synthetic methods, such as the need for high temperatures, lengthy procedures, and the use of hazardous reagents.

Lokesh Kumar et al. [126] synthetized multisubstituted pyrrole derivatives by integrating MCRs with a novel three-component DES (ChCl combined with two HBDs), addressing challenges such as poor regioselectivity and lengthy procedures. Their optimal system, comprising ChCl, ethylene glycol, and adipic acid, reached yields as high as 96% at ambient conditions within 60 minutes, with mechanistic studies suggesting that specific amine substrates are crucial for key intermediate formation and cyclization, while the DES retained its structural integrity through multiple cycles. Azizi and Shahiri Haghayegh [127] further demonstrated that three-component ChCl-based DESs provide an effective catalytic medium for synthesizing highly substituted pyridines from benzaldehyde, malononitrile, and thiophenol. Optimization studies revealed that increasing the reaction temperature from room temperature to 60 °C improved yields from 12% to 82%, whereas other DES formulations and conventional solvents lower conversions or sluggish reactions. The reaction scope was further expanded to include various aromatic aldehydes, substituted thiophenols, aliphatic, and heteroaromatic substrates, affording the desired pyridine derivatives in good to excellent yields (60–82%), and the DES medium demonstrated excellent recyclability over multiple cycles with only a marginal decrease in efficiency. Mechanistic investigations suggest that the DESs promote the Knoevenagel condensation between the aldehyde and malononitrile, followed by a Michael addition and cyclization process that culminates in oxidative aromatization to form the pyridine scaffold. In another study, Azizi et al. [128] developed a catalyst-free method for synthesizing benzopyran and pyran derivatives using ChCl-based DESs. High yields were achieved under mild conditions, with ChCl/urea proving the most efficient and demonstrating multiple-cycle recyclability, thereby underlining the green, sustainable advantages of using DESs as both reaction media and promoters.

As summary of the discussion included in this Section, Table 3 presents some examples of catalyzed organiz reactions carried out in DESs.

## 5. Catalyzed reactions of environmental interest in DES

DESs have emerged as versatile catalysts for environmental processes, offering eco-friendly routes to produce biofuels and value-added chemicals while reducing reliance on fossil fuels. Their ability to efficiently dissolve substrates of varied chemical nature enables highly selective transformations. For example, DESs not only serve as solvents but also promote catalytic activity by incorporating acid functionalities that enhance reaction selectivity, thus underpinning greener processes overall [28].

### 5.1. Biomass valorization

In biomass valorization, DESs are ideal for converting biomass into valuable intermediates, aligning with the principles of green chemistry. In these processes, DESs often facilitate the efficient breakdown and transformation of biomass components into valuable chemicals such as biofuels, organic acids, furans 5-HMF and furfural, and fermentable sugars. By incorporating Lewis or Brønsted acid functionalities, catalytic DES enhance reaction selectivity and efficiency, reducing the need for harsh conditions or additional reagents [129]. Figure 4 presents a schematic representation of the process by which biomass is converted into value-added chemicals through catalytic methods using DES.

**Table 3.** Example of catalyzed reactions carried out in DESs.

| DES System | Reaction Type | Reported Yield (%) | Recyclability (Retention Cycles/Yield) | Comments | Reference(s) |
|---|---|---|---|---|---|
| ChCl/Urea | Knoevenagel condensation | 95–96 | Up to 4–7 cycles; yield loss <5% | Provides high yields in reactions where the DES plays a dual role as solvent and catalyst. However, the high viscosity of the system can limit mass transfer, necessitating formulation adjustments (e.g., HBD/HBA ratio tuning) to optimize catalytic performance. | [73] |
| $ZnCl_2$-based DESs | Friedel–Crafts Benzylation | 88–93 | 5–6 cycles; yield drop <10% | Leverages the strong Lewis acidity provided by $ZnCl_2$, promoting efficient benzylation under mild conditions. This system competes effectively with traditional catalysts, although the inclusion of metal salts requires careful control to balance viscosity and catalyst recovery. | [75,76] |
| Betaine-based DESs | Michael addition | 90–99 | 8–9 cycles; consistent high yields | Inexpensive and readily tunable through manipulation of hydrogen bonding networks. Yields are excellent in enantioselective additions, although moderate viscosity can still impact diffusion in large-scale processes. | [78] |
| ChCl/Gly | Knoevenagel condensation | 83–94 | 4–5 cycles; yield decrease ca. 5–10% | Enhances catalyst stabilization while offering lower toxicity than many ILs. The relatively high viscosity, however, remains a concern when compared to ILs that benefit from lower viscosity. | [100] |
| Natural DES (DPTAC/Lactic Acid) | Diels-Alder | 78–89 | 4–5 cycles; good yield retention | Utilizes natural components to achieve lower toxicity and enhanced selectivity (e.g., improved endo/exo ratios) due to a well-organized hydrogen-bond network. Functional modifications (e.g., acetylation of HBAs) can further fine-tune reactivity, though intrinsic viscosity challenges persist. | [115] |
| ChCl/Ethylene Glycol | Diels-Alder | Up to 96 | 6–8 cycles; good stability | Exhibits an optimal balance of viscosity and polarity, promoting favorable reaction kinetics. Performance is competitive with traditional solvents and some ILs, especially when reaction conditions are enhanced through techniques such as ultrasound irradiation. | [116] |
| Ternary DES (ChCl+Ethylene Glycol + Adipic Acid) | Multicomponent reactions | Up to 96 | ≥4 cycles; minor yield decline | Facilitates rapid one-pot syntheses (e.g., multisubstituted pyrrole derivatives) with high atom economy. The system provides fast reaction kinetics under ambient conditions; however, consistent regioselectivity and recyclability require careful optimization of the ternary composition. | [126] |

Wang et al. [130] converted biomass feedstock into 5-HMF using a DES based on fructose corn syrup and ChCl with aluminum-based catalysts. They compared a homogeneous catalyst ($AlCl_3 \cdot 6H_2O$) with a heterogeneous one ($\gamma$-$Al_2O_3$) and found that the heterogeneous system produced a higher yield (60.9% vs. 55.3%) and improved efficiency upon recycling (up to 63.9%). The superior performance of $\gamma$-$Al_2O_3$ was attributed to the *in situ* formation of Lewis acid sites at very low acid concentrations, which are crucial role for glucose isomerization, a key step in 5-

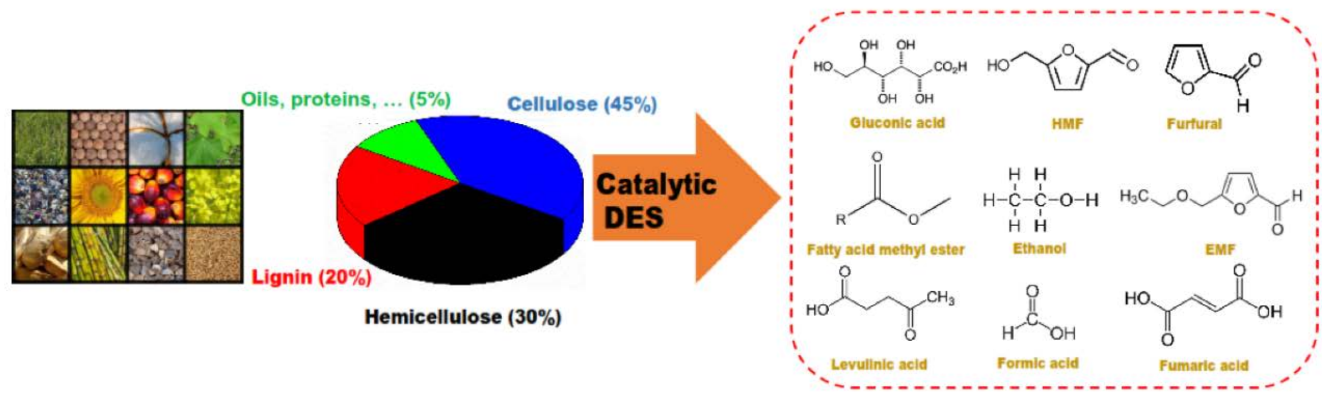


**Figure 4.** General scheme of the conversion of biomass into value-added chemicals through catalytic methods using DES. Reprinted with permission from Kahlor and Ghandi [129] with permission under Creative Commons Attribution (CC BY) license

HMF synthesis. Notably, adding extra water did not significantly hinder 5-HMF formation, enabling the effective degradation of other carbohydrates such as glucose. Guo al. [131] further compared acidic ChCl-based DESs with a ChCl/fructose DES in the presence of various acid (boric, oxalic (OxAc), citric, and p-toluensulfonic) and also tested ChCl/fructose and ChCl/glucose DESs with boric acid for 5-HMF synthesis. They found that the ChCl/fructose DES outperformed the other acidic DESs for fructose conversion. Optimized conditions (6:4 weight ratio, 20%water, 80 mg boric acid, 120°C for 120 minutes) yielded 65.2% 5-HMF from fructose, while a ChCl/glucose system reached 33.7% yield under similar conditions, highlighting that moderate water addition reduced viscosity and enhanced mass transfer despite both DESs exhibiting high viscosities.

Aslanli and Sert [132] explored the transformation of fructose into alkyl levulinates using DESs as both catalysts and reaction media. They compared ChCl/pTSA with ChCl/OxAc and showed that the stronger Brønsted acidity of pTSA led to nearly complete fructose conversion (99.8%) within 10 minutes under microwave-assisted conditions, producing higher yields of methyl (51.0%) and ethyl levulinate (41.6%). In contrast, ChCl/OxAc yielded significantly lower amounts (24.5% methyl and 21.3% ethyl levulinate). The study also noted that microwave irradiation shortened reaction times and improved selectivity, with an optimal temperature of 140°C and a 20-minute reaction time before side reactions reduced the yields. Additionally, reaction temperature was identified as a critical parameter, with maximum levulinate yields observed at 140°C. Beyond this temperature, side reactions such as humin formation became more pronounced, reducing product yields.

Mamilla et al. [133] investigated DES-based on ChCl for lignocellulosic biomass fractionation. They found that ChCl/OxAc and ChCl/KOH were most effective for dissolving beech wood polymers, with ChCl/OxAc selectively isolating phenols, suggesting its potential in lignin-first biorefineries. Process parameters such as reaction time (2–24 h), temperature (60–100 °C), and biomass loading were systematically examined, revealing that dissolution peaked between 4 and 6 hours, with acidic DESs favoring lignin solubilization and alkaline DESs primarily fractionating cellulose. ChCl/KOH extracts showed negligible polyphenol content, indicating minimal lignin dissolution, whereas ChCl/OxAc resulted in polyphenol concentrations exceeding 15 g/L. DES recovery was examined via centrifugation, phase separation, and vacuum distillation, although further improvements in recyclability, stability, and cost-effectiveness are needed.

Wu et al. [134] designed a strategy for the conversion of chitin biomass into high-value chemicals using ChCl-based DESs. In particular, ChCl/urea DES (in a 1:2 molar ratio) effectively catalyzes the conversion of D-glucosamine (see Figure 5 for a scheme of the reaction), a building block derived from chitin, nto deoxyfructosazine at 100°C in 150 minutes. Complete conversion was achieved with a 13.5% yield of deoxyfructosazine and only trace amounts of of fructosazine. On the other hand, the addition of arginine as a cocatalyst further boosted the yield to 26.5–30.1% by enhancing hydrogen bonding and facilitating the formation of key intermediates, such as dihydrofructosazine, underscoring the synergistic role of DESs and arginine in enhancing reaction efficiency.

Morais et al. [135] developed an efficient process for furfural production from xylan using acidic DESs based on ChCl with malic acid or glycolic acid. Optimizing variables such as water contend, *γ*-valerolactone addition, solid/liquid (S/L) ratio, and microwave heating, resulted in furfural yields 75%, with recovery up to 89.5% via back-extraction using 2-methyltetrahydrofuran. Their DES/γ-valerolactone system was recyclable for at least three cycles, maintaining yields above 69%.

Very recently, Zhou et al. [136] developed a ternary DES ($ZnCl_2$/phosphoric acid/$H_2O$) for the efficient dissolution and acetylation of bamboo pulp cellulose at room temperature. The process involved wetting, swelling, and subsequent solubilization, leading to the synthesis of cellulose acetate (degree of substitution 0.42–1.81) without additional catalysts. The substituent followed a C6>C2>C-3 distribution , and the resulting cellulose acetate was soluble in dimethyl sulfoxide, facilitating further applications and symplifying solvent recovery. Figure 6 displays the acetylation process of cellulose using a DES system, along with the subsequent solvent recovery steps. Additionally, the visual comparison showcases cellulose acetate samples with varying degrees of substitution, highlighting differences in their physical properties as a result of controlled reaction conditions.

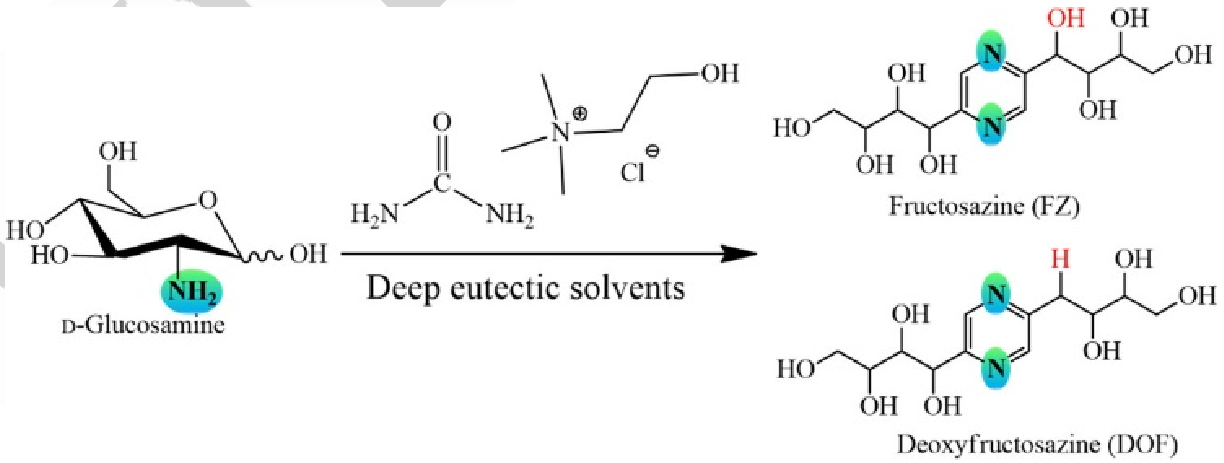


**Figure 5.** Schematic representation of the catalytic self-condensation of D-glucosamine in DES. Reprinted with permission from Wu et al. [134] Copyright (2018) American Chemical Society.

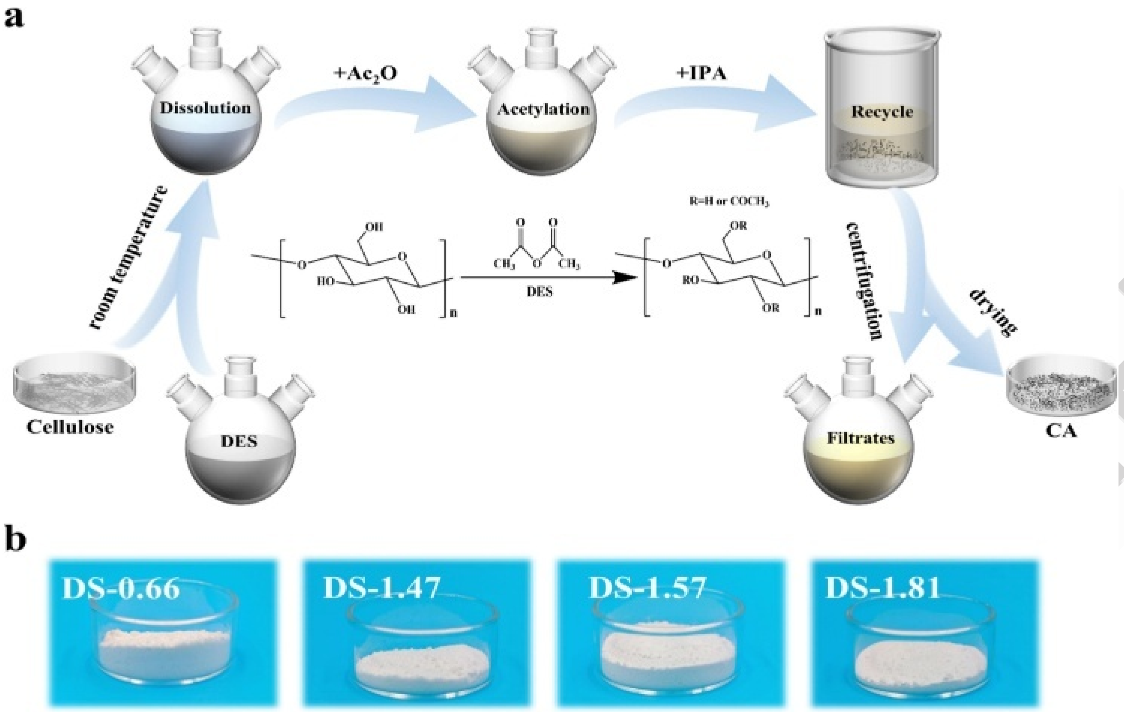


**Figure 6.** (a) Schematic representation of the acetylation process of cellulose using a DES system, along with the subsequent solvent recovery steps. (b) Visual comparison of cellulose acetate samples with varying degrees of substitution. Adapted from Zhou et al. [136], Copyright (2025), with permission from Elsevier.

### 5.2. Biofuel production

DESs are increasingly recognized as promising tools in sustainable biofuel production due to their dual functionality as solvents and catalysts. They facilitate key catalytic transformations under milder conditions, reducing energy input, environmental burden and operational costs. On the other hand, by integrating DESs, the biofuel industry can move toward greener production methods that lessen dependency on non-renewable energy sources and minimize environmental impacts. For instance, Williamson et al. [137] developed a phosphonium-based DES for the esterification of oleic acid with glycerol. This DES not only accelerates the conversion of free fatty acids present in low-grade oils but also transforms them into valuable mono-, di-, and triglycerides, which serve as key intermediates for biodiesel synthesis. By systematically varying the reaction temperature and catalyst concentration, it was identified optimal conditions (5%w/w catalyst loading at 150 °C) that enabled to achieve 95% conversion in 30 minutes. Kinetic analyses revealed that increased catalyst loading lowers the activation energy, thus enhancing the reaction rate. Importantly, the system was reusable over several cycles, indicating its potential for industrial application.

Similarly, Gu et al. [138] addressed mass transfer and purification challenges in rapeseed oil transesterification by introducing a ChCl/Gly DES as co-solvent. The system improved catalyst solubility, reduced side reactions, and enabled a high fatty acid methyl ester (FAME) (98%). One of the key findings of this work was the role of DESs in enhancing the solubility of NaOH in the methanol phase, thereby increasing catalyst availability and reducing saponification side reactions. Notably, DESs provided a pseudo-homogeneous reaction medium and facilitated phase separation, streamlining downstream processing and making it easier to isolate the biodiesel product from glycerol and other reaction byproducts. Compared to traditional methods, the use of DESs led to a faster and more efficient separation process, eliminating the need for extensive purification steps. Moreover, the study also employed response surface methodology to optimize reaction parameters such as methanol-to-oil molar ratio, catalyst concentration, and DES concentration, ensuring maximum biodiesel yield with minimal side reactions. Furthermore, kinetic studies confirmed that the transesterification reaction followed a second-order model, with DESs playing a crucial role in stabilizing intermediates and enhancing reaction kinetics.

Alhassan et al. [139] extended this approach to the supercritical esterification, i.e., above the critical temperature and pressure of the used DESs. of waste tire pyrolysis oil, aiming to improve its fuel quality, including calorific power, density, and viscosity. Their study addressed the inherent challenges of pyrolysis oil, such as high total acid number (TAN) and suboptimal fuel properties, by converting the fatty acids into their corresponding methyl esters. Among several tested systems, ChCl/pTSA (1:4 molar ratio) proved most effective, reducing TAN by 86.6%, he DES's strong acidity promoted oxonium ion formation, accelerating esterification and minimizing undesirable side reactions. However, excessive DES concentrations were found to trigger secondary pathways, highlighting the need for precise process control.

Collectively, the above studies underscore the versatility and effectiveness of DESs in various biofuel applications, though careful design and optimization remain essential to avoid performance trade-offs.

## 5.3. Polymer degradation

In the realm of polymer recycling, both ILs and DESs have been applied as catalysts and reaction media, facilitating the breakdown of large polymer structures into smaller, more manageable molecules [140]. This is particularly relevant in the context of plastic production and recycling, where reducing waste and enhancing material recovery have become critical priorities. However, they exhibit distinct advantages and limitations. ILs are known for their high thermal stability and effective catalytic performance in depolymerization reactions, which often leads to high conversion rates under harsh reaction conditions [141–144]. However, their drawbacks include complex synthetic procedures, elevated production costs, and potential environmental hazards. In contrast, DESs enable polymer degradation at milder temperatures with lower energy input. Recent studies comparing the two have shown that DES-assisted processes yield a more favorable energy economy and reduced environmental impact based on key green metrics [141]. This improved overall profile positions DESs as a more sustainable and economically attractive alternative for the chemical recycling of polymer. In particular, one notable application of DESs is in the hydrolysis of polyethylene terephthalate (PET), where DESs promote its conversion into different types of monomers, enhancing reaction rates and selectivity. However, further research is needed to fully understand the mechanisms behind their catalytic activity and to optimize their application in various depolymerization systems [28].
Urea-based DESs have shown remarkable promise in PET glycolysis under relatively mild conditions. For example, urea–metal salt combinations, optimized at molar ratios between 6:1 and 4:1, achieve complete PET degradation within 30 minutes at 170 °C, substantially reducing reaction times compared to conventional metal salts, solid acids, or even ILs, which require longer reaction times or harsher conditions [145]. This enhanced catalytic efficiency is attributed to a synergistic effect wherein robust hydrogen bonding and coordination interactions, validated through Infrared spectroscopy and DFT calculations, accelerate the formation of bis(hydroxyalkyl) terephthalate (BHET) with selectivities as high as 83%. Liu et al. [146] further demonstrated that DESs based on a urea derivative (1,3-dimethylurea) and metal salts exhibit a dual catalytic effect from both Lewis acid sites from metal salts and basic sites urea derivatives, enhancing PET depolymerization. The molar ratio of DES components significantly influences catalytic efficiency, with optimal performance observed at a specific 1,3-dimethylurea to the metal salt ratio. The study reports a high PET conversion rate and a notable yield of BHET under optimized reaction conditions. Compared to traditional catalysts, DES provide a more sustainable alternative, requiring lower catalyst loading while maintaining high efficiency. The glycolysis reaction proceeds efficiently at moderate temperatures, around 180°C, avoiding excessive energy consumption. Likewise, Zhou et al. [147] achieved complete PET conversion and 84.7% yield of dioctyl terephthalate via alcoholysis using a ChCl-based DES, emphasizing the crucial role of hydrogen bonding in the mechanism. Additionally, kinetic analysis demonstrated that the alcoholysis reaction follows first-order kinetics. Moreover, Li et al. [148]reported that a nonmetallic DES system composed of 1,5-diazabicyclo [4.3.0]-5-nonene (DBN) and phenol can drive PET methanolysis to produce dimethyl terephthalate in 95.3% yield at just 130 °C in one hour, owing to a synergistic N–H–O hydrogen bonding network that lowers the activation energy. By avoiding metal-containing catalysts, the system eliminates residual metal contamination, reduces the necessary reaction temperature, and minimizes side reactions, thereby simplifying downstream purification. Kinetic studies indicate that the methanolysis follows a first-order model with a comparatively low activation energy of 103.3 kJ/mol, a result attributed to the simultaneous dissolution and degradation of PET which enhances mass transfer. Figure 7 shows a scheme of the reaction mechanism corresponding to the methanolysis of PET in DESs without metal salt.
Complementary, Wei et al. [149] demonstrated that a DBN/urea DES shifts PET glycolysis from heterogeneous to homogeneous catalysis, achieving complete conversion and a BHET yield of approximately 79%. Kinetic investigations reveal a first-order reaction mechanism with an activation energy near 155.65 kJ/mol. Moreover, the enhanced surface roughness and swelling of PET, together with favorable hydrogen bonding between the catalyst, ethylene glycol, and PET, amplify the nucleophilic attack on ester bonds, thereby accelerating the depolymerization.

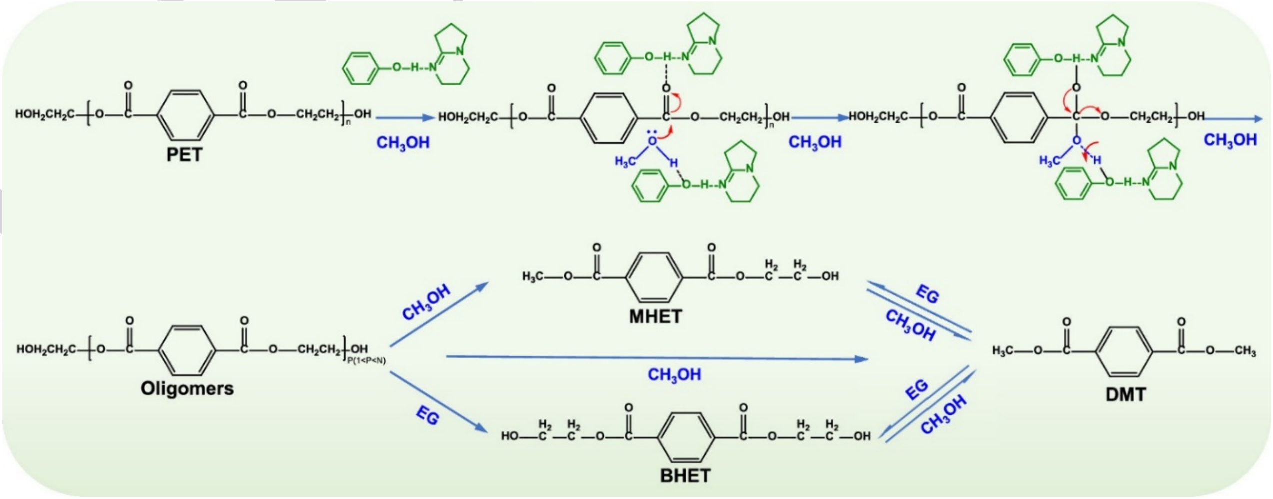


**Figure 7.** Schematic representation of the proposed mechanism for the methanolysis of PET in DES without metal salts. Reprinted with permission from Li et al. [150] Copyright (2021) American Chemical Society.

### 5.4. $CO_2$ fixation

Excessive fossil fuel consumption has led to a dramatic rise in atmospheric $CO_2$, intensifying the greenhouse effect and prompting the development of innovative $CO_2$ utilization strategies to produce high value-added chemicals such as cyclic carbonates, which have applications ranging from battery electrolytes to synthetic intermediates [151–153]. In this context, DESs have emerged as highly effective catalysts for $CO_2$ fixation via the cycloaddition of $CO_2$ to epoxides, enabling the production of cyclic carbonates under mild conditions.

Yang et al. [150] demonstrated that by combining protic ionic liquids and amines in a DES system, styrene carbonate could be obtained in yields up to 97% at room temperature and 1 bar $CO_2$ pressure due to enhanced hydrogen bonding that activates the styrene oxide under mild conditions, significantly outperforming its individual components and several other DES variants. Spectroscopic analysis confirmed the formation of hydrogen bonding interactions, as evidenced by shifts in the –OH stretching vibrations and downfield shifts in NMR signals, which are indicative of enhanced activation of the epoxide ring. Additionaty, a strong synergistic effect between the protic ILs and the amine in promoting the reaction was observed (see Figure 8). Building on this, Yang et al. [154] reported that a biobased DES catalyst, composed of acetylcholine bromide and L-malic acid in a 2:1 molar ratio, further improved the process, achieving yields up to 98% at 80 °C under 0.1 MPa. Moreover, the results evidenced a synergistic interaction between the HBA (acetylcholine bromide) and HBD (L-malic acid), which effectively activates the epoxide through hydrogen bonding. This cooperative effect facilitates the nucleophilic attack of bromide ions, leading to the rapid formation of cyclic carbonates. In both studies, kinetic studies further reveal that the reaction follows first-order kinetics with respect to both the catalyst and the epoxide, confirming that the rate-determining step is intimately linked to the effective formation of the DES. Additionally, the DES catalyst exhibits excellent thermal stability and maintains its performance over multiple recycling cycles, even in the presence of moisture.

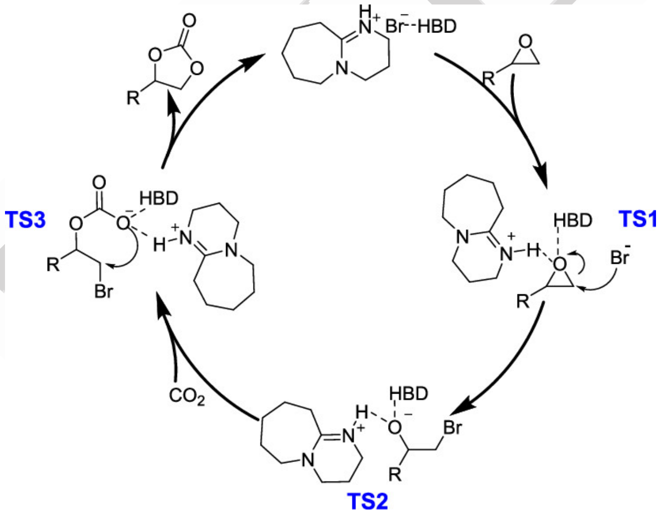


**Figure 8.** Schematic representation of the synergistic reaction mechanism of $CO_2$ fixation in DES based on a protic ionic liquid and amines. Reprinted with permission from Yang et al. [150] Copyright (2021) American Chemical Society.

DESs formed from strong organic bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), combined with various HBDs, such as ethylene glycol, benzyl alcohol, and methyldiethanolamine, were critically evaluated for $CO_2$ fixation by García-Argüelles et al. [155].They demonstrated that such DESs facilitate nucleophilic $CO_2$ fixation, with systems containing excess alcohol (1:4 molar ratio) reducing viscosity to improve $CO_2$ absorption due to reduced mass transfer limitations. However, excessive viscosity can hinder complete $CO_2$ conversion, leading to a mixture of hydroxyl and carbonate species. Comparative studies show that when paired with suitable HBDs, these DES systems offer a slight boost in catalytic activity compared to bare DBU/TBD. Moreover, the study emphasized that lower pressure conditions (1.2 bar vs. 6 bar) unexpectedly enhanced catalytic efficiency, a phenomenon attributed to altered $CO_2$ solubility and DES interactions. Mechanistic studies suggested that in contrast to prior reports, the zwitterionic DBU-$CO_2$ adduct was not the dominant pathway in these reactions. Instead, DBU itself appeared to act as the primary nucleophile, promoting epoxide activation and subsequent $CO_2$ incorporation. This deviation from the classical mechanism has implications for the design of next generation organocatalysts using DESs, particularly in tailoring bifunctional catalytic systems where both $CO_2$ activation and substrate interaction are optimized. Qian et al. [156] reported that a DBU-based DES using iodized DBU and 4-methoxyphenol enabled cycloaddition at ambient temperature and pressure with excellent yields, highlighting a synergistic effect between the HBA and HBD that promotes epoxide activation, with iodide ions enhancing nucleophilic ring-opening activity and hydrogen bonding interactions promoting $CO_2$ activation. Similarly, imidazole-derived DESs developed by Sheng et al. [157] allow achieving nearly quantitative yields in the formation of cyclic carbonates as a result of the cycloaddition of $CO_2$ to epoxides under mild conditions, with performance critically dependent on the HBA’s functional groups, with hydroxyl groups outperforming carboxyl and ester functionalities, This is likely due to its stronger hydrogen bonding capability that enhances epoxide activation and $CO_2$ fixation. Moreover, the DES-based catalyst demonstrated excellent stability and recyclability, maintaining high yields over several cycles. Norouzi and Abdolmaleki [158] further advanced the field by designing a pyridinium-based DES by combining 1-(carboxymethyl)pyridinium bromide ([CMPy]Br) with various HBDs, such as maleic acid, pentaerythritol, and urea, to enhance $CO_2$ absorption and effectively activate epoxides. Among the prepared systems, the [CMPy]Br/maleic acid (1:1 molar ratio) mixture demonstrated superior catalytic activity, achieving complete conversion of styrene oxide to styrene carbonate within one hour at 90°C under atmospheric $CO_2$ pressure. This high efficiency is attributed to strong hydrogen bond interactions, where maleic acid effectively activates the epoxide by polarizing its oxygen–carbon bond and the pyridinium moiety stabilizes the reaction intermediates. The DES not only functions as a catalyst but also serves as a solvent, eliminating the need for additional organic solvents and metal catalysts, which are often associated with high energy demands and environmental concerns. Moreover, the catalyst system exhibits excellent recyclability, maintaining high activity over several cycles, which is crucial for practical applications. selectivity. Table 4 provides an overview of representative reactions with environmental interest that employ DESs.

´**Table 4.** Representative DES-catalyzed reactions with environmental interest.

| DES System | Reaction Type | Reported Yield (%) | Recyclability (Retention Cycles/Yield) | Comments | Reference |
|---|---|---|---|---|---|
| ChCl/Fructose+ Boric Acid | Biomass conversion to 5-HMF | 65.2 (fructose),<br>33.7 (glucose) | Not specified | Optimal conditions: 120°C, 120 min, 20% water. Higher fructose conversion due to lower activation energy. | [131] |
| ChCl/pTSA | Fructose conversion to alkyl levulinates | 99.8 (conversion), | Not specified | Microwave-assisted, strong Brønsted acidity of PTSA enhances reaction efficiency. | [132] |
| ChCl/OxAc | Lignocellulosic biomass fractionation | Polyphenols >15 g/L | Not specified | Selective lignin solubilization, acidic DESs favor lignin dissolution. | [133] |
| ChCl/Urea+ Arginine | Chitin conversion to deoxyfructosazine | 30.1 (with arginine) | Not specified | Arginine enhances hydrogen bonding and intermediate formation. | [134] |
| ChCl/Malic Acid | Xylan conversion to furfural | 75 (yield) | 3 cycles (yield >69%) | Microwave-assisted, γ-valerolactone improves furfural recovery. | [135] |
| $ZnCl_2$/Phosphoric Acid/$H_2O$ | Cellulose acetylation | DS 0.42–1.81 | Not specified | Room-temperature process, no additional catalysts required. | [136] |
| ChCl/Gly+NaOH | Rapeseed oil transesterification | 98 (FAME) | Not specified | DES enhances NaOH solubility, reduces saponification. | 139] |
| ChCl/pTSA | Waste tire pyrolysis oil esterification | TAN reduction: 86.6% | Not specified | Supercritical conditions, strong acidity promotes oxonium ion formation. | [139] |
| Urea/$ZnCl_2$ | PET glycolysis | 83 (BHET selectivity) | 5 cycles (yield drop <10%) | Synergistic Lewis acid-base catalysis. | [145]. |
| DBN/Phenol | PET methanolysis | 95.3 (DMT yield) | Not specified | Nonmetallic DES avoids metal contamination, mild conditions. | [149] |
| Acetyl Choine/Malic Acid | $CO_2$ to cyclic carbonates | 98 | Multiple cycles (stable) | Biobased DES, synergistic HBA-HBD interaction. | [154] |
| DBU/Iodide+4-Methoxyphenol | $CO_2$ cycloaddition | >90 | Not specified | Ambient conditions, iodide enhances nucleophilic ring-opening. | [156] |

## 6. Biocatalysis in DES

DESs have emerged as versatile media for biocatalysis when compared to conventional organic solvents and Ils [159]. From the seminal work by Gorke et al. [160], DESs have been widely investigatigated as reaction media or co-solvents for various enzyme-catalyzed reactions [161,162]. While organic solvents are often limited by issues such as high volatility, toxicity, and poor substrate solubility, ILs, despite their favorable thermal stability and tunable properties suffer from high synthesis costs, potential toxicity, and intricate purification steps [26,163]. In contrast, DESs offer, in general, low vapor pressure, excellent substrate solubility, and enhanced thermal stability, all of which contribute to improved enzyme activity and stability [16,160]. Moreover, DESs can maintain the native structure of enzymes, mitigating deactivation that sometimes occurs in harsh organic media, and they facilitate easier catalyst recovery due to their low volatility, thereby promoting both sustainability and process efficiency in biocatalytic applications [161,164].

A broad range of enzymes, including lipases, lactate dehydrogenase, succinate dehydrogenase, cytochrome oxidase, catalase, and sugar hydrolases, have been employed in DES-based systems. However, most studies have primarily focused on degradation reactions, while relatively few have explored their potential in synthetic transformations. The design of reactions catalyzed by enzymes in DESs requires the evaluation of how DES properties, influence enzyme performance. Additionally, a thorough understanding of the individual contributions of DES components, as well as their collective effects on enzyme stability, activity, and selectivity, is crucial. These aspects are of a paramount importance for the rational optimization of DES formulations to enhance enzymatic efficiency and expand their applicability in biocatalysis [159]. In this context, Bittner et al. [165] provided a detailed evaluation of the stability and activity of horse liver alcohol dehydrogenase (HLADH) in various DESs (ChCl/Gly, ChCl/ethylene glycol and ethylammoniun chloride (EACl)/Gly) and their mixtures with water, using both experimental and computational approaches. A key takeaway was the observation that glycerol, when predominant in the solvation shell, stabilizes HLADH, yet this effect is attenuated in EACl/Gly due to competing interactions with chloride ions. Importantly, the optimal hydration level was critical but not sufficient to ensure enzyme stability across all systems, emphasizing that water content alone does not predict biocatalytic performance. Notably, a discrepancy emerged between simulation predictions and experimental outcomes, pointing to limitations in current modeling approaches, especially regarding the spatial organization and dynamics of

DES–protein interfaces. By systematically varying the DES composition and hydration levels, it was possible to dissect the individual contributions of each component, shedding light on the molecular mechanisms by which DESs influence enzyme function. On the other hand, the optimization of the solvent composition showed that ChCl/Gly in a molar ratio 1:9 provides an efficient media for the enzymatic reduction of cinnamaldehyde to cinnamyl alcohol. Figure 9 shows the scheme of the reduction of the cinnamaldehyde to cinnamyl alcohol as well as the reaction yield for this process when the enzymatic reduction is performed in ChCl/Gly mixtures with different molar ratio and a fixed amount of water. Building upon the above findings, Harifi-Mood et al. [166] examined bovine liver catalase activity in ChCl-based DESs, highlighting that not all DESs exert similar effects. The work showed that ChCl/Gly enhanced substrate binding, while ChCl/ethylene glycol showed no such benefit, likely due to solvent-induced perturbation of protein secondary structure. Although both systems retained moderate activity (~70–80%) at concentration of 100 mM, higher DES concentrations led to pronounced enzyme inactivation. Interestingly, in a highly concentrated aqueous ChCl solution, the enzyme remained nearly 40% active. This suggests that the chaotropic nature of the choline cation may counteract the decline in enzymatic activity in concentrated ChCl solutions, an effect that appears to be diminished in aqueous DESs. These results underscore the dualistic nature of DESs: while some components can stabilize enzyme conformation, others, depending on structure and concentration, can act as denaturants under different physiological conditions.

Zhang et al. [167] advanced the field by exploring hydrophobic DESs based on lidocaine and organic acids, which present thermo-switchable properties and phase separation behavior that can be leveraged for selective biocatalysis, for HLADH-catalyzed redox reactions, demostrating that hydrophibic DESs may perform as an alternative reaction media for enzymatic catalysis. The hydrophobic nature of the DESs enables enzyme hydration while minimizing water stripping, making them suitable for reactions with low water content. Under optimized conditions with controlled water content (≤20%w/w), the enzyme maintained its activity and stability in reduction reactions over extended periods. Notably, while the enzyme performed comparably to aqueous buffers in cyclohexanone reduction, the DESs significantly enhanced reaction efficiency for hydrophobic substrates like cinnamaldehyde, supporting higher substrate loadings (up to 800 mM). In addition, the increased solubility of nonpolar reactants in DESs alleviated mass transfer limitations and prevented enzyme deactivation, leading to high conversion rates. This is a promising result, yet their broader applicability remains uncertain due to their unique composition and limited compatibility with more polar enzymes. However, not all results support the widespread adoption of DESs for synthetic biocatalysis. Silvianti et al. [168] reported that while ChCl/urea DESs preserved enzyme activity in polyester synthesis, ChCl/Gly adversely affected *Candida antarctica* lipase B (CALB) stability, likely due to the interaction of glycerol with the enzyme's active site. Interestingly, ILs outperformed DESs in this reaction, highlighting their greater compatibility with CALB-catalyzed reactions. The variations in solvent performance can be attributed to differences in their hydrogen bond networks, which significantly influence enzyme activity and reaction kinetics, which emphasize the need to critically evaluate when DESs genuinely offer advantages over existing solvents. Further highlighting this complexity, Cao et al. [169]. demonstrated that CALB-catalyzed transesterifications could proceed in pure DESs, but efficiencies varied significantly with DES composition. Hydrophobic terpene-based DESs caused less CALB inactivation compared to hydrophilic ones. On the other hand, the catalytic efficiency in hydrophilic DESs increased with the hydroxyl group content, while the presence of carboxyl groups and quaternary ammonium salts led to CALB inhibition or inactivation. In hydrophobic DESs, carboxyl groups had a positive effect on maintaining the structure and activity of CALB. Additionally, increasing the carbon chain length of DES components improved CALB activity. A negative correlation was found between the basicity of DESs and CALB's transesterification efficiency. These findings reveal that even minor structural differences in DESs can drastically shift enzyme behavior, demanding careful consideration in solvent selection.

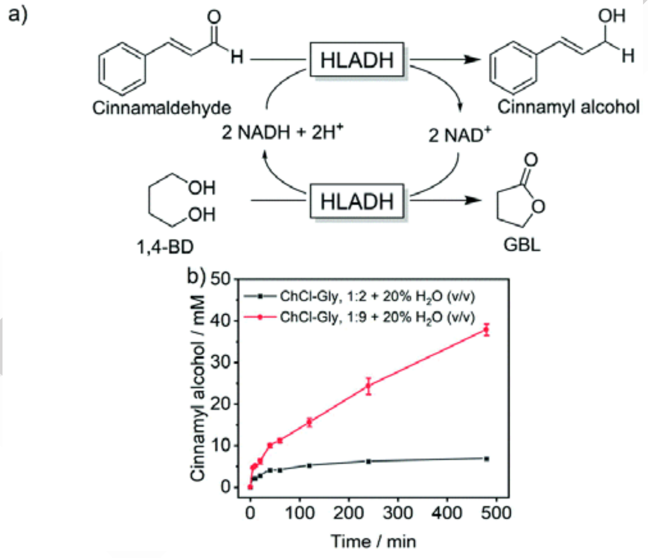


**Figure 9.** (a) Enzymatic reduction of cinnamaldehyde to cinnamyl alcohol catalyzed by HLADH. (b) Time-dependent formation of cinnamyl alcohol. for HLADH-catalyzed cinnamaldehyde reduction in ChCl–Gly with different molar ration and a fixed water content of 20%vol/vol at 25°C. Error bars represent data from duplicate experiments. Adapted from Bittner et al. [165] with permission from the Royal Society of Chemistry.

Zhou et al. [170] explored the impact of the composition and concentration of six DESs on the activity and structure of carbonic anhydrase (CA), revealing profound dependence on both HBA and HBD types.. Urea-based DESs caused $Zn^{2+}$ displacement and enzyme inactivation, whereas betaine-based DESs enhanced CA activity. However, high concentrations of DESs (92%) hindered enzyme activity due to their high viscosity, which affected mass transfer process. On the other hand, the addition of water to the DESs results in a reduction in the viscosity, increasing the CA activity. Structural investigations showed that high DES concentrations altered enzyme secondary structure, resulting in a more compact enzyme conformation within the DES network associated with a decrease in *α*-helical content and an increase in *β*-sheet formation. This suggests structural reorganization due to DES interactions. In addition, the influence of metal ions and anions on CA activity was also studied. While certain metal ions, particularly $Cu^{2+}$ and $Co^{2+}$, inhibited CA activity, the addition of Betaine/Gly DES in a molar ratio 1:2 alleviated this inhibition, especially for $Co^{2+}$. The effect of anions on CA activity was minimal, with DESs slightly enhancing activity in the

**Table 5.** Examples of biocatalytic reactions in DESs

| DES System | Enzyme/Reaction | Performance | Comments | Reference(s) |
|---|---|---|---|---|
| ChCl/Gly+water | HLADH (Cinnamaldehyde reduction) | 80% conversion in 24 h. | Gly stabilizes enzyme; water content critical for activity. | [165] |
| ChCl/Gly<br>ChCl/Ethylene Glycol | Bovine liver catalase | 70–80% retained activity at moderate DES concentrations. | ChCl/Gly enhances substrate binding; high DES concentrations inhibit activity. | [166] |
| Lidocaine/Organic Acid DES | HLADH (Cyclohexanone/cinnamaldehyde reduction) | 800 mM substrate loading, high conversion rates. | Hydrophobic DES improves solubility of nonpolar substrates. | [167] |
| ChCl/Urea<br>ChCl/Gly | CALB (Polyester synthesis) | Varies by DES; solvent-free conditions preferred. | ChCl/Urea maintains enzyme stability; ChCl/Gly deactivates CALB. | [168] |
| Betaine/Gly | Carbonic anhydrase | Optimal at 60°C, retains activity in DES. | Betaine/Gly enhances CA activity; urea-based DESs deactivate CA. | [170] |
| Hydrophobic DES | Lipase-catalyzed aldol reaction | Higher selectivity vs. hydrophilic DES. | Hydrophobic DES improves selectivity for aldol over dehydrated byproduct. | [171] |
| ChCl/Gly | Potato epoxide hydrolase | Improved substrate solubility without efficiency loss. | Minimal enzyme destabilization; enhances regioselectivity. | [172] |

presence of certain anions like $S_2O_3^{2-}$ and $I^-$. Thermal stability experiments revealed that CA retained a significant portion of its activity when incubated in Betaine/Gly DESs up to 60°C, whereas activity dropped sharply above this temperature due to the weakening of hydrogen bonds in DESs. The enzyme also demonstrated better stability at low temperatures in Betaine/Gly compared to other solvents.

Milker et al. [171] explored selectivity and efficiency in aldol reactions catalyzed by porcine pancreas lipase in various DESs. They found that hydrophobic DESs promoted aldol selectivity, while hydrophilic DESs enabled faster initial reaction rates despite lower substrate solubility. This suggests that substrate solubility alone does not dictate reaction performance, and DES properties must be carefully tailored to balance solubility, reaction rate, and selectivity. A key aspect of the study was the development of a novel DES incorporating the substrate 4-nitrobenzaldehyde as a component. This approach significantly enhanced substrate solubility, yet did not surpass the efficiency of a reaction conducted in pure acetone. The researchers found that high concentrations of acetone, which served as both a reactant and co-solvent, were the primary drivers of reaction efficiency rather than the DES itself. Consequently, the aldol reaction in acetone alone achieved the highest conversion and product yield. This open the question about the use of DESs when simpler, more effective solvent exists.

Lastly, Lindberg et al. [172] investigated DESs as co-solvents in epoxide hydrolysis by potato epoxide hydrolase. They demonstrated that the regioselectivity and stability of the enzyme were highly sensitive to DES type. Glyceline emerged as a promising co-solvent, whereas reline was detrimental. The ability of DESs to modulate regioselectivity is noteworthy; however, their benefit must be weighed against the risk of enzyme inactivation and reaction slowdown due to increased viscosity or unfavorable solute–solvent interactions.

Overall, while DESs represent a versatile and tunable class of solvents with substantial promise in biocatalysis, their benefits are highly context-dependent. The field would benefit from a shift toward mechanistic investigations that link solvent structure with enzyme function, as well as from more rigorous benchmarking against established solvent systems. Without this, DESs risk being employed more as a novelty than as a truly enabling technology in enzyme-catalyzed synthesis. Table 5 provides an overview of representative biocatalytic reactions that employ DES

## 7. Electrocatalysis in DES

Electrocatalysis, the acceleration of electrochemical reactions via catalytically active electrodes, is central to energy conversion technologies such as water electrolysis, fuel cells, $CO_2$ reduction, and next-generation batteries. In these systems, the electrode not only provides structural support for the catalyst but also mediates charge transfer between reactants and products. The quest for high-performance electrocatalysts has led to the design of novel nanostructured materials, in-depth mechanistic studies, and increasing reliance on computational approaches to guide synthesis and optimization [173–175]. In this context, deep eutectic solvents (DESs) have recently garnered attention as alternative reaction media for electrocatalysis. Despite being relatively underexplored, DESs offer unique physicochemical properties—such as high viscosity, ionic conductivity, wide electrochemical windows, and tunable polarity—that position them as versatile solvents for catalyst synthesis and electrochemical applications. Importantly, their complex hydrogen bonding networks and capacity to stabilize reactive intermediates offer opportunities to control nucleation and growth mechanisms in electrocatalytic systems. [176,177].

Elsharkawya et al. [178] demonstrated the electrodeposition of Nickel nanostructures in ethaline (a ChCl:ethylene glycol DES), revealing superior morphological and electrochemical characteristics compared to aqueous acetate buffers. Their study underscores the solvent's influence on nucleation kinetics, where the shift in $Ni^{2+}$ reduction potential from –0.9/–1.1 V (acetate) to –0.98 V (ethaline) reflects complexation effects that promote finer, nanostructures uniformly with a needle-flower morphology. The resulting needle-flower morphology, confirmed by electronic microscopy and X ray diffraction, exhibited smaller crystallite sizes (20 nm in ethaline vs. 28 nm in acetate) and enhanced catalytic surface areas.The obtained nanostructures showed enhancements in hydrogen evolution reaction (HER) performance, lower overpotentials, improved Tafel slopes, and higher exchange current densities. The interpretation of kinetics via the Randles–Sevcik equation should be approached cautiously due to the non-ideal diffusion behavior in viscous DESs. Additionally, electrochemical impedance and double-layer capacitance studies confirm that the ethaline-derived deposits possess a higher electrochemically active surface area, directly correlating with improved hydrogen evolution reaction kinetics. Similar trends were observed for the oxygen evolution reaction, where the ethaline deposit shows the lowest overpotential and fastest charge transfer kinetics.

Protsenko et al. [179] expanded on this by electrodepositing Ni/$TiO_2$ composites in ethaline. Notably, the inclusion of water in the DES decreased viscosity and increased electrolyte conductivity, facilitating $TiO_2$ incorporation. The resulting deposits displayed refined nanocrystalline features (6–10 nm), demonstrating that even subtle tuning of the DES environment—via water content, stirring rate, or current density—profoundly affects morphology and catalytic function. However, the underlying mechanisms governing particle incorporation remain insufficiently elucidated, especially in terms of the interplay between hydrodynamic conditions and DES structuring.

The work by Juárez-Marmolejo et al. [180] highlights the electrochemical deposition of Pd nanoparticles in reline (ChCl:urea) containin Pd(II) ions, which enabled control over the nucleation and growth process via an E1E2C mechanism mechanism, where initial three-dimensional nucleation and diffusion-controlled growth (E1) of palladium, along with the reduction of residual water on the growing nanoparticles (E2), lead to the formation of a $Pd(OH)_2$ layer that partially dehydrates in air to form a PdO shell. The PdNPs exhibit a core-shell morphology with average particle sizes that decrease with increasingly negative deposition potentials. In acidic media, cyclic voltammetry reveals distinct features corresponding to double-layer charging, oxide formation and reduction, and hydrogen adsorption/desorption, underscoring the stability of the PdNP-modified electrode. Notably, the highest mass activity toward formic acid oxidation was achieved with electrodes deposited at −700 mV versus an quasi reference electrode of Ag in perchloric acid, where the interplay between the catalyst's surface structure and the electrolyte's properties enhances reaction kinetics.

Li et al. [181] showcased the synthesis of Co-doped nitrogen porous carbon (Co@NPC) catalysts using DESs as both nitrogen donors and structure-directing agents. enabling the homogeneous dispersion of cobalt species within the carbon framework while preventing metal aggregation. Moreover, DESs facilitate nitrogen doping, which significantly improves electronic conductivity and catalytic activity by modulating charge transfer kinetics and increasing the density of active sites. Li et al. [181] also observed that DES-assisted synthesis leads to a well-developed porous structure, optimizing surface area and mass transport properties, which are critical for electrochemical reactions. Their findings further confirm that the use of DESs in Co@NPC preparation enhances performance in applications such as the oxygen reduction reaction, hydrogen evolution reaction, and carbon dioxide reduction reaction, attributing the improved catalytic efficiency to the synergistic effects of controlled nitrogen doping, optimized porosity, and uniform metal dispersion. The study also that DES composition allows tailoring tailor the catalyst's electronic properties and reactivity. Figure 10 shows a schematic representation of the fabrication of Co@NPC.

Recent studies have also extended DES applications to the deposition of ruthenium-based electrocatalysts. For instance, Ru nanoparticles synthesized onto stainless steel mesh (RuNPs@CSS) via DES-assisted electrochemical deposition demonstrated promising HER activity in acidic media [182]. The chronopotentiometric analysis confirmed the successful formation of ruthenium nanoparticles on the current collector substrate, indicated by a color change from colorless to brownish black. By the mean of X ray diffraction, it was observed that while the major austenite phases of the substrate remained, their peak intensities shifted slightly due to deposition of the nanoparticles. On the other hand, X ray photoelectron spectroscopy experiments revealed that the predominant phase of the nanoparticles was of metallic character, with minor contributions from DES-derived functional groups. Surface morphology studies via electronic microscopy confirmed the formation of a thin film of nanoparticles with a porous, rough structure, and the elemental composition of ruthenium, along with its integration into thestainless steel. Electrochemical performance evaluations established that RuNPs@CSS may operate as a promising hydrogen evolution reaction electrocatalyst, achieving low onset and overpotentials, a Tafel slope of –97 mV/dec, and modest Ru leaching (~21.5%) after extended operation., closely approaching the performance of Pt-based catalysts. While the performance approaches that of Pt-based catalysts, the study lacks a comparative framework to evaluate cost–performance trade-offs and long-term stability metrics critical for practical applications. In a related effort, NiFe alloy nanoparticles embedded in stainless steel (NiFe@SS) exhibited bifunctional activity for both HER and OER, with low overpotentials and favorable Tafel slopes [183]. This system exhibited excellent bifunctional performance for water splitting reactions. The structural characterization of the obtained system showed the successful deposition of NiFe alloy nanoparticles on stainless steel, and revealed a distinct porous and spherical morphology, with uniform distribution of Ni and Fe, that enhances catalytic performance.

Xue et al. [184] synthesized a Ni–Fe–P catalyst on Fe foam via galvanic replacement in ethaline, producing a Ni–Fe–P alloy with small, uniform particles and improved HER/OER performance. This work is notable for integrating phosphorus doping via $NaH_2PO_2$, which acts as both reductant and dopant source. However, whether phosphorus remains stable under cycling or evolves into active oxyphosphate species is not thoroughly examined. Moreover, the catalyst demonstrates robust stability over prolonged electrolysis, maintaining its nanoparticle-packed structure and active phase even after extended operation, thereby offering a promising, cost-effective solution for efficient and durable water splitting applications.

Hong et al. [185] employed a ChCl/malonic acid DES to synthesize $LaCoO_3$ perovskites under mild conditions. This approach enabled homogeneous precursor mixing, reducing the synthesis temperature and promoting phase-pure crystallization. The electrocatalytic performance of these DES-synthesized perovskites was evaluated for oxygen evolution reactions in 1 M NaOH, where $LaCoO_3$ outperformed other equivalent systems, exhibiting superior oxygen evolution reaction activity, with low overpotentials and a fast charge transfer. This may be attributed to the formation of oxygen vacancies during synthesis, a feature that stabilizes the material and enhances catalytic efficiency. Notably, the study indicates that the oxygen vacancies are preserved even after extensive electrochemical cycling, contributing to the stability and sustained OER activity of the catalyst. Comparisons with conventional electrocatalysts such as $IrO_2$ further underscore the potential of these DES-synthesized materials for scalable and cost-effective electrolysis applications.

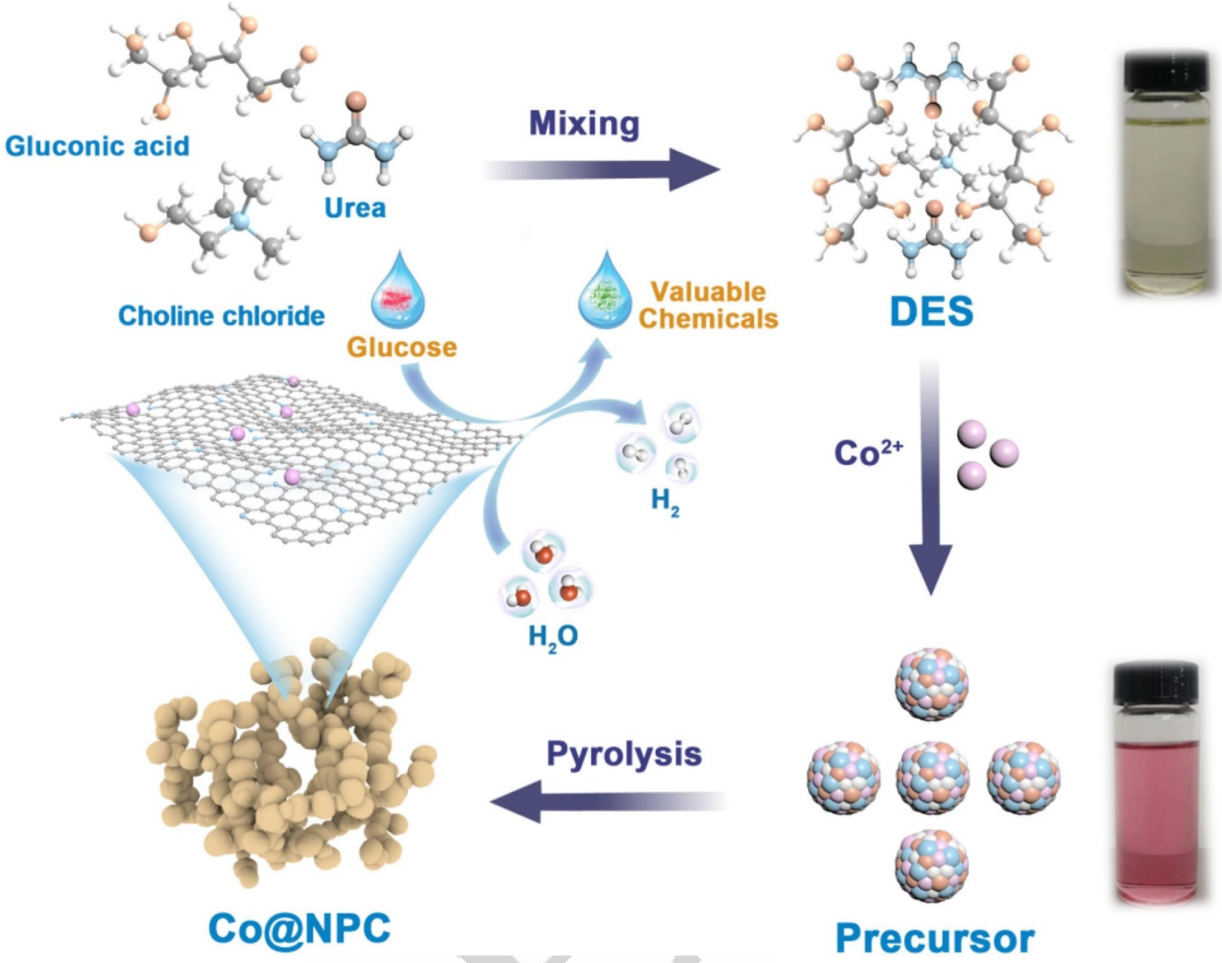


**Figure 10.** Schematic representation of the synthesis of Co@NPC using DESs. Adapted from Li et al. [181], Copyright (2022), with permission from Elsevier.

Collectively, the about studies highlight the vast but underutilized potential of DESs in electrocatalysis. Their tunable physicochemical properties and ability to direct catalyst morphology, composition, and surface chemistry present exciting avenues for sustainable materials design. owever, several challenges, including mechanistic understanding, scalability and recyclability, standardization and environmental impact, must be addressed to fully exploit their capabilities. Table 6 provides an overview of representative electrocatalytic reactions that employ DES.

**Table 6.** Examples of electrocatalytic reactions in DESs.

| DES System | Electrocatalytic Process | Performance | Comments | Reference |
|---|---|---|---|---|
| Ethaline (ChCl/Ethylene Glycol) | Ni electrodeposition | Overpotential: 154 mV (HER), Tafel slope: 130 mV/dec. | Needle-flower morphology; high active surface area. | [178] |
| Ethaline+Water | Ni/$TiO_2$ composite coating | 10% $TiO_2$ content; nanocrystalline Ni (6–10 nm). | Water reduces viscosity, improves $TiO_2$ incorporation. | [179] |
| Reline (ChCl/Urea) | Pd nanoparticle synthesis | High mass activity for formic acid oxidation. | Core-shell PdNPs (Pd(0) core, PdO shell). | [180] |
| ChCl/Urea/Gluconic Acid | Co@NPC synthesis (N-doped porous carbon) | Excellent ORR, HER, and $CO_2RR$ performance. | DES acts as N source and structure-director. | [181] |
| ChCl/Ethylene Glycol | RuNPs on stainless steel | Overpotential: -65.7 mV @ 10 mA/cm², Tafel slope: 97 mV/dec. | Porous Ru film; low overpotential for HER. | [182] |
| ChCl/Gly | NiFe alloy on stainless steel | Cell voltage: 1.56 V @ 10 mA/cm². | Bifunctional catalyst for water splitting. | [183] |
| Ethaline + $NaH_2PO_2$ | Ni-Fe-P on Fe foam | OER: 263 mV @ 10 mA/cm²; HER: 82 mV @ 10 mA/cm². | Solvothermal synthesis; smooth nanoparticle layer. | [184] |
| ChCl/Malonic Acid | $LaCoO_3$ perovskite synthesis | Low overpotential, comparable to $IrO_2$. | Oxygen vacancies enhance OER activity. | [185] |

## 8. Other catalyzed synthesis in DESs

The above discussion includes some of the most While these examples showcase the growing versatility of DESs, they also risk oversimplifying the complexities involved in their practical application. A more critical perspective reveals that, although DESs often fulfill multiple roles in catalysis, their mechanisms of action, long-term stability, and compatibility with diverse chemistries remain areas of ongoing investigation. For example, Li et al. [186] have recently advanced the field by employing betaine/hexafluoroisopropanol-based DESs in the synthesis of imine-linked covalent organic frameworks (COFs). These DESs reportedly enabled the formation of COFs with varied pore geometries, ranging from clover-like and quadrangular to hexagonal and trigonal hexagonal structures, under mild, room-temperature conditions (see Figure 11 for a representation of the steps of the reactive process and the idealized geometries of the different synthetized COFs). This is a significant improvement over traditional methods that often require elevated temperatures and corrosive acids. The dual role of the DES, as both an environmentally benign solvent and a catalyst,is facilitated by its capacity to establish a dense hydrogen-bonding network, which favors Schiff base formation while minimizing hydrolytic degradation. A significant advantage of this approach is the tunability offered by adjusting the molar ratios of betaine and hexafluoroisopropanol, which enables the tailoring of the crystallinities and morphologies of the obtained COFs. Notably, the synthesis conditions allowed the production of COFs with enhanced surface areas and thermal stability, further supporting their potential for practical applications. Beyond structural benefits, the obtained materials present a versatile functionality. For instance, one of the COFs exhibits pronounced fluorescence properties that vary with solvent polarity. This solvent-dependent fluorescence behavior not only provides insights into the material's photophysical characteristics but also paves the way for its application as a sensitive ratiometric fluorescence sensor. Such sensors can reliably quantify trace amounts of water in organic solvents (or vice versa), a feature that has been successfully integrated into a deep learning-based WeChat app for rapid, on-site analysis. Furthermore, the reusability of the used DESs, demonstrated over several recycling cycles with minimal loss in catalytic activity, underscores the sustainability of the methodology. This reusability, combined with the elimination of harsh conditions and toxic solvents, aligns well with the principles of green chemistry and positions DESs as promising candidates for scalable industrial applications. However, while these findings highlight the potential of DESs for mild and efficient COF synthesis, the study does not fully address the reproducibility of these morphologies across broader substrate scopes or over extended reaction times.

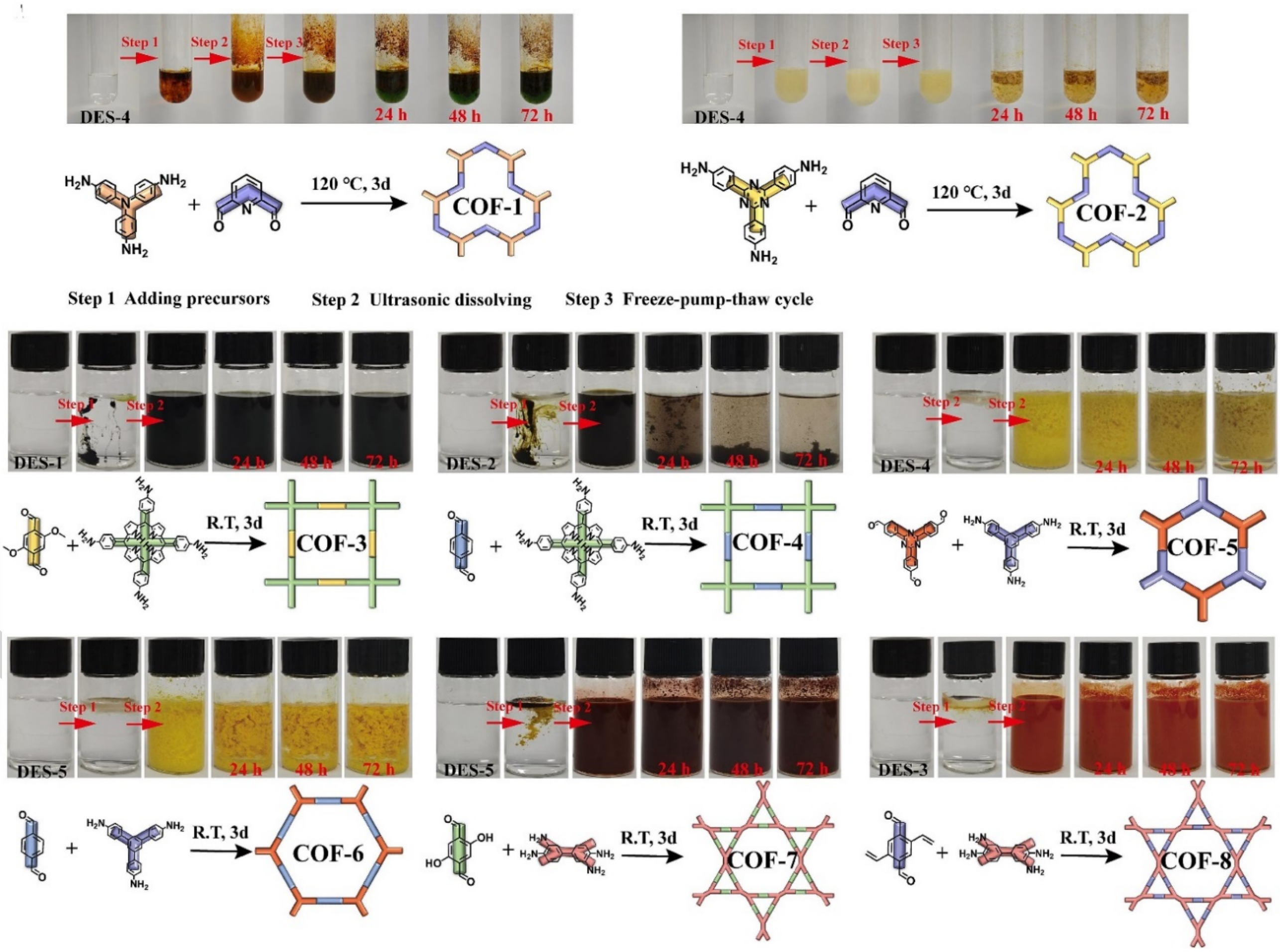


**Figure 11.** Representation of the steps of the reactive process together with the idealized geometries of the different synthetized COFs using DESs. Adapted from Li et al.[186], Copyright (2025), with permission from Elsevier.

Food technology is other domain where catalytic processes in DESs is gaining interest, as explored by Chen et al.[187]. Their study demonstrates the catalytic conversion of soybean isoflavone glycosides into more bioactive aglycones using DESs formed from choline chloride and organic acids. While the DESs effectively function as both extractive and catalytic agents, promoting glycosidic bond hydrolysis, this dual functionality is highly sensitive to water content and temperature. In fact, DESs effectively dissolved the isoflavones while providing a proton-rich environment that promoted deglycosylation. The results indicated that heating the DES–isoflavone mixture above 60 °C is critical for initiating the reaction, with temperatures up to 100 °C markedly increasing the aglycone yield. Kinetic analysis revealed that the conversion followed first-order behavior, and the rate of reaction was found to be dependent on the water content within the DESs. Though low water levels enhance hydrogen bonding networks and, consequently, catalytic efficiency, they may also pose practical challenges in maintaining solvent homogeneity and heat transfer in scaled systems. Moreover, the acidity-driven catalysis, while effective for isoflavone conversion, may limit DES reusability for substrates sensitive to acidic environments—an issue that could constrain broader applicability. When applied to soybean isoflavone extracts, the method allowed for a controlled adjustment of the glycoside-to-aglycone ratio simply by varying the reaction conditions, suggesting a promising route for producing “ready-to-use” extracts with enhanced bioavailability.

In the context of environmental catalysis, the work by Chu et al. [188] introduces a biomimetic oxidative desulfurization system that couples a DES (polyethylene glycol and sulfosalicylic acid) with an Anderson-type polyoxometalate (POM). This system achieves high efficiency under mild conditions, leveraging a synergistic extraction-oxidation mechanism. Although the sulfonic acid moiety in the DES plays a crucial role in sulfide removal, the catalytic cycle's dependence on the structural integrity of the POM remains a vulnerability. After four cycles, the catalytic performance declines, attributed to POM degradation, underscoring a persistent limitation in DES-POM systems: their finite operational lifetimes. While the authors rightly emphasize the system's potential for commercial diesel treatment, scalability remains an open question. The interplay between DES viscosity, sulfur compound diffusion, and POM redox stability under continuous flow conditions needs further exploration. Moreover, the environmental implications of widespread DES deployment, particularly in petroleum processing, must be carefully evaluated, including issues such as regeneration, contamination, and downstream separations.

## 9. Sustainability of the use of DESs in catalytic applications

The integration of DESs into catalytic processes represents a significant advancement toward more sustainable chemical manufacturing and aligns closely with the principles of green chemistry. These solvents, typically composed of naturally derived, biodegradable, and low-toxicity components such as ChCl, Gly, sugars, organic acids, or amino acids, provide a more environmentally friendly alternative to conventional organic solvents and ionic liquids [2–5][15][17]. heir synthesis is straightforward, often involving the simple heating and mixing of a HBA with a HBD, avoiding the use of hazardous reagents, multistep processes, and energy-intensive purification steps. As such, DESs offer a highly atom-economical and energy-efficient solvent platform.

In catalytic systems, DESs have demonstrated not only their utility as green solvents but also their potential to act as co-catalysts or reaction media that actively participate in facilitating reaction mechanisms [5,21]. Their ability to influence catalytic behavior arises from their highly tunable structure, which allows precise control over solvent polarity, acidity, viscosity, and solvation properties by varying the HBD/HBA components. This tunability enables the design of task-specific DESs that can enhance catalytic activity, selectivity, and substrate solubility, making them particularly valuable in biomass valorization, fine chemical synthesis, and environmental remediation.

A growing body of literature confirms the effectiveness of DESs in both chemical and enzymatic catalysis, particularly in the biorefinery sector. DESs have been used to depolymerize lignin and solubilize cellulose under relatively mild conditions, enabling more accessible catalytic conversion of lignocellulosic feedstocks into value-added products. Their compatibility with enzymes further supports integrated one-pot systems where DESs serve as reaction and extraction media, reducing the need for intermediate purification steps and minimizing waste generation. For example, DESs composed of lactic acid and ChCl or betaine have shown excellent performance in dissolving lignin while preserving the cellulose structure, thereby enhancing subsequent catalytic transformations [189]. In addition to their traditional catalytic roles, DESs have recently emerged as effective media for greener processing of biopolymers. For example, DESs have been successfully applied to promote the deacetylation of chitin, a process traditionally requiring harsh alkaline conditions, to produce chitosan from marine biowaste. Quantum chemical calculations and experimental screenings have identified promising DESs that achieve significant degrees of deacetylation under milder conditions, with optimized processes attaining up to approximately 40% deacetylation at moderate temperatures (80–120 °C). This not only lowers energy consumption but also minimizes the generation of toxic waste typically associated with conventional NaOH treatments. Furthermore, certain DES formulations exhibit hydrotropic behavior, enhancing chitin solubility and facilitating more efficient deacetylation. These findings broaden the scope of DES applications, expanding their utility to sustainable biopolymer conversion and valorization, while supporting circular economy principles by enabling the recovery and reuse of DES components [190,191]. Moreover, in enzymatic catalysis, DESs based on ChCl and HBDs such as Gly or urea have been shown to preserve enzyme activity and stability. This has been demonstrated in lipase-catalyzed alcoholysis, aminolysis, and transesterification reactions, where DESs maintained comparable or even superior catalytic performance compared to traditional solvents, including toluene and certain ionic liquids. In addition to enabling efficient reactions, these DESs showed minimal enzyme deactivation over time, particularly with CALB, further supporting their sustainable reuse in multi-cycle processes [192].

A key sustainability advantage of DESs lies in their reusability. Numerous studies report successful recycling of DESs over multiple reaction cycles with minimal loss in performance, reinforcing their potential to reduce chemical waste and promote process circularity [68,75]. Furthermore, DESs often enable catalytic processes at lower temperatures and in aqueous-compatible environments, resulting in reduced energy consumption and lower emissions compared to traditional systems [30,67]. In several instances, the tunability of DESs has been exploited to lower viscosity at elevated temperatures, thereby enhancing mass transfer and shortening reaction times without compromising system stability, which is critical for scale-up and industrial applications [192]. T

Despite their advantages, DESs are not without limitations. High viscosity and occasional sensitivity to moisture can present challenges in process scalability, particularly for continuous-flow or industrial-scale applications. However, these issues are addressable through rational DES design, such as incorporating low-viscosity components or water-tolerant systems tailored to specific reaction conditions [28,32]. M Moreover, careful selection of DES components is vital to prevent side reactions; for example, formulations employing ethylene glycol or highly acidic hydrogen bond donors may participate in undesired reactions with substrates, thereby altering the solvent's properties and affecting catalytic outcomes. Tailoring the eutectic mixture composition can mitigate such effects and enhance solvent inertness [192].

Overall, the use of DESs in catalysis offers a promising and practical route to greener chemical transformations. Their customizable nature, low environmental footprint, and potential for integration into multi-step catalytic processes make them ideal candidates for advancing sustainable technologies. While further innovation is needed to overcome certain physicochemical barriers and expand their industrial applicability. Taken together, the use of DESs in catalysis represents a significant step toward more sustainable chemical manufacturing, although ongoing innovation is needed to overcome physicochemical barriers and fully unlock their industrial potential.

## 10. Concluding remarks and perspectives

With the increasing awareness of environmental concerns, researchers have dedicated significant efforts to replacing toxic components with safer, more sustainable alternatives. In this context, the specific attributes of DESs have facilitated their successful use in areas such as metal processing, extraction, organic synthesis, and biotransformations, primarily as solvents or co-solvents. Their high solubility, non-volatility, and ease of handling have further strengthened their role in various chemical processes. Beyond their function as solvents, DESs have emerged as a powerful and sustainable alternative to conventional solvents and catalysts, offering tunable properties that enhance their applicability across a broad spectrum of catalytic processes. Their ability to act as both solvents and catalysts provides an unprecedented opportunity for greener chemistry, reducing the environmental impact associated with traditional organic solvents while maintaining high catalytic efficiency. In many cases, DESs exhibit catalytic performance comparable to or even superior to traditional catalysts positioning them as viable alternatives to them. Moreover, the application of DESs as catalysts offers many other advantages, such as their non-toxic nature, stoichiometric efficiency, recyclability, and the potential for recovery without significant loss of catalytic activity.

One of the main advantages of DESs is their structural versatility, allowing for fine-tuning of their properties to achieve specific catalytic functions. This has allowed researchers to design DESs incorporating specific characteristics, enabling catalytic activity in diverse reactions. This adaptability has been demonstrated in numerous reactions, including $CO_2$ fixation, biomass valorization, and polymer degradation, where DESs not only provide a reaction medium but also actively participate in the catalytic process. For instance, DES-based catalysts have been successfully applied in $CO_2$ cycloaddition reactions, achieving high product selectivity and conversion under mild conditions. The integration of bio-based DESs further enhances the sustainability of these systems, reinforcing their potential for industrial applications. In recent years, DESs have been explored for use in condensation and esterification reactions, where they exhibit advantages such as environmental friendliness, high selectivity, and stability. Recent studies indicate that DES not only offer adaptability and low toxicity but also deliver, in some cases, excellent thermal stability. Yet, challenges persist, including limited mechanistic understanding, high viscosity, hygroscopicity, scalability, and cost-effective recycling, hurdles that need to be addressed to realize their full industrial potential. Moving forward, collaborative research efforts between academia and industry will be crucial in overcoming existing barriers and driving the commercialization of DES-based catalytic systems. Looking ahead, several exciting directions are poised to redefine the landscape of DES-based catalysis. A critical aspect that requires attention is the economic feasibility of DES-based processes. While DESs are generally composed of inexpensive and biodegradable components, the scalability of DES production and its integration into industrial settings remain underexplored. Techno-economic analyses will be essential in determining the viability of DESs as replacements for traditional solvents and catalysts. Additionally, efforts should be directed toward optimizing recycling and recovery processes to enhance their sustainability and cost-effectiveness. In addition, the integration of DESs with flow chemistry, which offers enhanced control over reaction parameters and superior mass and heat transfer, may issues related to viscosity and facilitate continuous processing, thereby making DESs more viable for industrial implementation. Moreover, continuous-flow setups align well with process intensification strategies, offering a path forward for the scale-up of DES-mediated reactions. Another promising direction lies in the application of DESs in electrocatalysis and energy-related transformations. Their high ionic conductivity, thermal stability, and ability to solubilize diverse substrates make them ideal candidates for electrochemical processes such as $CO_2$ reduction, water splitting, and battery chemistry. Recent studies have already demonstrated the potential of DESs in stabilizing electroactive species and improving redox kinetics. Future work should focus on optimizing DES formulations tailored for specific electrochemical reactions, potentially leading to breakthroughs in sustainable energy storage and conversion.

Further research into the fundamental interactions between DES components and reactants, combined with computational modeling, will be crucial in designing more efficient and robust DES-based catalytic systems. For instance, the use of artificial intelligence (AI) and machine learning in DES design is gaining traction. Given the vast combinatorial space of possible DES formulations, AI-driven approaches can accelerate the discovery of optimal solvent systems by predicting key properties such as viscosity, polarity, and catalytic activity based on training data. Coupled with high-throughput screening, such strategies could drastically reduce the time and resources needed to identify high-performance DESs, enabling rapid development of task-specific formulations for diverse catalytic reactions.

The fusion of DESs with biocatalysis also presents a significant frontier. DESs have demonstrated excellent biocompatibility and the ability to stabilize enzyme structures, which can enhance enzymatic activity and selectivity. This compatibility opens new opportunities in pharmaceutical synthesis, where mild, selective transformations are essential. Research into DES systems that support multienzyme cascades or facilitate cofactor regeneration could expand their utility in complex biosynthetic pathways.

Finally, the role of DESs in environmental catalysis and circular chemistry remains a rich area for exploration. Whether in biomass processing, polymer degradation, or pollutant remediation, DESs provide a green platform that aligns with global goals for sustainability and waste minimization. In this context, several studied have recently demonstrated the promising application of DESs in lignin degradation, offering an efficient and recyclable catalytic system for biomass processing. Temperature-responsive DESs (TRDESs) have shown particularly promise in this regard, allowing phase separation and catalyst recovery with minimal energy input. This innovation paves the way for more sustainable biorefinery strategies, reducing dependency on harsh chemical treatments while maximizing lignin utilization. Moreover, DESs have shown excellent performance in polymer degradation, particularly in the methanolysis of PET. Nonmetallic DESs, such as DBN/Phenol, have enabled efficient PET conversion under mild conditions, avoiding metal contamination in the final products. The combination of DESs with advanced analytical techniques has further enhanced the understanding of reaction mechanisms and catalytic efficiencies, facilitating the rational design of improved DES-based systems.

In conclusion, the field of DES-based catalysis stands at a pivotal juncture. Continued progress in tailoring DES properties, understanding reaction mechanisms, and integrating DESs with cutting-edge will shape the next generation of catalytic strategies, offering a transformative platform for catalysis, balancing environmental sustainability with high catalytic performance. However, their complete implementation suffers from a number of challenges, including high viscosity, water sensitivity, recyclability, and industrial scalability. Compared to ILs, which offer lower viscosities but higher production costs and potential toxicity, DESs provide a more sustainable alternative provided their formulation is optimized. As the challenges associated with their use are overcome, DESs are poised not merely to supplement but to revolutionize green chemical processes. Their future lies not just in substitution, but in enabling catalytic transformations that were previously inaccessible, marking a transformative shift in how sustainable chemistry is practiced and implemented.

## Acknowledgments

Author acknowledge the financial support by MCIN/AEI/10.13039/501100011033 (Spain) under the grant PID2023-147156NB-I00 and UCM under grant PR12/24-31566 (Ayudas para la Financiación de Proyectos de Investigación UCM 2023).

**Keywords:** Deep Eutectic Solvents • Green Chemistry • Industrial Catalysis • Renewable Solvents • Sustainability

## References

[1] G. Centi, S. Perathoner, *Catal. Today* **2003**, *77*, 287–297.
[2] Y. Gu, F. Jérôme, *Chem. Soci. Rev.* **2013**, *42*, 9550.
[3] Y. Gu, *Green Chem.* **2012**, *14*, 2091.
[4] M. Cvjetko Bubalo, S. Vidović, I. Radojčić Redovniković, S. Jokić, *J. Chem. Technol. Biotechnol.* **2015**, *90*, 1631–1639.
[5] M. S. Álvarez, M. A. Longo, A. Rodríguez, F. J. Deive, *J. Ind. Chem. Eng.* **2024**, *132*, 36–49.
[6] P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686–694.
[7] P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, *39*, 301–312.
[8] B. Wang, S. Yang, L. Min, Y. Gu, Y. Zhang, X. Wu, L. Zhang, E. H. M. Elageed, S. Wu, G. Gao, *Adv. Synth. Catal.* **2014**, *356*, 3125–3134.
[9] A. Taheri, X. Pan, C. Liu, Y. Gu, *ChemSusChem* **2014**, *7*, 2094–2098.
[10] F. He, P. Li, Y. Gu, G. Li, *Green Chem.* **2009**, *11*, 1767.
[11] W. Zhang, *Green Chem.* **2009**, *11*, 911.
[12] Y. Medina-Gonzalez, S. Camy, J.-S. Condoret, *Acs. Sustain. Chem. Technol.* **2014**, *2*, 2623–2636.
[13] A. K. Rathi, M. B. Gawande, R. Zboril, R. S. Varma, *Coord. Chem. Rev.* **2015**, *291*, 68–94.
[14] T. Cheng, D. Zhang, H. Li, G. Liu, *Green Chem.* **2014**, *16*, 3401–3427.
[15] B. B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell, J. R. Sangoro, *Chem. Rev.* **2021**, *121*, 1232–1285.
[16] E. L. Smith, A. P. Abbott, K. S. Ryder, *Chem. Rev.* **2014**, *114*, 11060–11082.
[17] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, *Chem. Soc. Rev.* **2012**, *41*, 7108.
[18] M. Francisco, A. van den Bruinhorst, M. C. Kroon, *Angew. Chem. Int. Ed.* **2013**, *52*, 3074–3085.
[19] M. A. Skopek, M. A. Mohamoud, K. S. Ryder, A. R. Hillman, *Chem. Comm.* **2009**, *45*, 935–937.
[20] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, Y. H. Choi, *Anal. Chim. Acta* **2013**, *766*, 61–68.
[21] D. A. Alonso, A. Baeza, R. Chinchilla, G. Guillena, I. M. Pastor, D. J. Ramón, *Eur. J. Org. Chem.* **2016**, *2016*, 612–632.
[22] G. Di Carmine, A. P. Abbott, C. D’Agostino, *React. Chem. Eng.* **2021**, *6*, 582–598.
[23] J. García-Álvarez, *Eur. J. Inorg. Chem.* **2015**, *2015*, 5147–5157.
[24] M. Shaibuna, K. Hiba, L. V. Theresa, K. Sreekumar, *New J. Chem.* **2020**, *44*, 14723–14732.
[25] P. Liu, J.-W. Hao, L.-P. Mo, Z.-H. Zhang, *RSC Adv.* **2015**, *5*, 48675–48704.
[26] A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. K. Rasheed, *J. Am. Chem. Soci.* **2004**, *126*, 9142–9147.
[27] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Chem. Comm.* **2003**, *39*, 70–71.
[28] S. Shafique, A. S. Belousov, R. Rashid, I. Shafiq, K. H. H. Aziz, N. Riaz, M. S. Khan, A. Shaheen, M. Ishaq, P. Akhter, M. Hussain, *J. Mol. Liquids* **2025**, *419*, 126769.
[29] Z. Naseem, R. A. Shehzad, A. Ihsan, J. Iqbal, M. Zahid, A. Pervaiz, G. Sarwari, *Chem. Phys. Lett.* **2021**, *769*, 138427.
[30] S. Khandelwal, Y. K. Tailor, M. Kumar, *J. Mol. Liquids* **2016**, *215*, 345–386.
[31] C. Florindo, L. C. Branco, I. M. Marrucho, *ChemSusChem* **2019**, *12*, 1549–1559.
[32] D. J. G. P. van Osch, C. H. J. T. Dietz, J. van Spronsen, M. C. Kroon, F. Gallucci, M. van Sint Annaland, R. Tuinier, *ACS Sustainable Chem. Eng.* **2019**, *7*, 2933–2942.
[33] Q. Abbas, L. Binder, *ECS Trans.* **2011**, *33*, 57–67.
[34] H. F. Mohd Zaid, F. K. Chong, M. I. Abdul Mutalib, *Fuel* **2017**, *192*, 10–17.
[35] D. O. Abranches, J. A. P. Coutinho, *Curr. Opin. Green Sustain. Chem.* **2022**, *35*, 100612.
[36] F. S. Mjalli, H. Mousa, *Chin. J. Chem. Eng.* **2017**, *25*, 1877–1883.
[37] F. S. Mjalli, J. Naser, *Asia-Pac. J. Chem. Eng.* **2015**, *10*, 273–281.
[38] A. Basaiahgari, S. Panda, R. L. Gardas, *J. Chem. Eng. Data* **2018**, *63*, 2613–2627.
[39] M. H. Shafie, R. Yusof, C.-Y. Gan, *J. Mol. Liquids* **2019**, *288*, 111081.
[40] A. Hayyan, F. S. Mjalli, I. M. AlNashef, Y. M. Al-Wahaibi, T. Al-Wahaibi, M. A. Hashim, *J. Mol. Liquids* **2013**, *178*, 137–141.
[41] A. Skulcova, A. Russ, M. Jablonsky, J. Sima, *Bioresources* **2018**, *13*, 5042–5051.
[42] H. Zhang, Y. Wang, K. Xu, N. Li, Q. Wen, Q. Yang, Y. Zhou, *Anal. Methods* **2016**, *8*, 8196–8207.
[43] L. F. Grantham, S. J. Yosim, *J. Phys. Chem.* **1963**, *67*, 2506–2507.
[44] N. F. Gajardo-Parra, M. J. Lubben, J. M. Winnert, Á. Leiva, J. F. Brennecke, R. I. Canales, *J. Chem. Thermodyn.* **2019**, *133*, 272–284.
[45] A. Hayyan, F. S. Mjalli, I. M. AlNashef, T. Al-Wahaibi, Y. M. Al-Wahaibi, M. A. Hashim, *Thermochim. Acta* **2012**, *541*, 70–75.
[46] R. K. Ibrahim, M. Hayyan, M. A. AlSaadi, S. Ibrahim, A. Hayyan, M. A. Hashim, *J.Mol. Liquids* **2019**, *276*, 794–800.
[47] A. A. Kityk, D. A. Shaiderov, E. A. Vasil’eva, V. S. Protsenko, F. I. Danilov, *Electrochim. Acta* **2017**, *245*, 133–145.
[48] F. S. Mjalli, G. Vakili-Nezhaad, K. Shahbaz, I. M. AlNashef, *Thermochim. Acta* **2014**, *575*, 40–44.

[49] K. Shahbaz, S. Baroutian, F. S. Mjalli, M. A. Hashim, I. M. AlNashef, *Thermochim. Acta* **2012**, *527*, 59–66.

[50] A. Boisset, J. Jacquemin, M. Anouti, *Electrochim. Acta* **2013**, *102*, 120–126.

[51] K. Shahbaz, F. S. Mjalli, M. A. Hashim, I. M. AlNashef, *Fluid Phase Equilib.* **2012**, *319*, 48–54.

[52] K. Shahbaz, F. S. Mjalli, G. Vakili-Nezhaad, I. M. AlNashef, A. Asadov, M. M. Farid, *J. Mol. Liquids* **2016**, *222*, 61–66.

[53] S. Seki, S. Tsuzuki, K. Hayamizu, Y. Umebayashi, N. Serizawa, K. Takei, H. Miyashiro, *J. Chem. Eng. Data* **2012**, *57*, 2211–2216.

[54] H.-Z. Su, J.-M. Yin, Q.-S. Liu, Ch.-P. Li, *Acta Phys. Chim. Sin.* **2015**, *31*, 1468–1473.

[55] R. B. Leron, A. N. Soriano, M.-H. Li, *J. Taiwan Inst. Chem. Eng.* **2012**, *43*, 551–557.

[56] P. B. Sánchez, B. González, J. Salgado, J. José Parajó, Á. Domínguez, *J. Chem. Thermodyn.* **2019**, *131*, 517–523.

[57] I. Wazeer, I. M. AlNashef, A. A. Al-Zahrani, M. K. Hadj-Kali, *J. Mol. Liquids* **2021**, *332*, 115838.

[58] R. Amoroso, F. Hollmann, C. Maccallini, *Molecules* **2021**, *26*, 6286.

[59] L. Zhang, X.-M. Peng, G. L. V. Damu, R.-X. Geng, C.-H. Zhou, *Med. Res, Rev.* **2014**, *34*, 340–437.

[60] M. Binazadeh, M. Kabiri, L. D. Unsworth, in *Proteins at Interfaces III State of the Art* (Eds.: T. Horbett, J.L. Brash, W. Norde), American Chemical Society, Washington DC, USA, **2012**, pp. 621–643.

[61] B. Atashkar, M. A. Zolfigol, S. Mallakpour, *Mol. Catal.* **2018**, *452*, 192–246.

[62] Y. Wang, X. Meng, K. Jeong, S. Li, G. Leem, K. H. Kim, Y. Pu, A. J. Ragauskas, C. G. Yoo, *ACS Sustainable Chem. Eng.* **2020**, *8*, 12542–12553.

[63] Y. Wang, K. H. Kim, K. Jeong, N.-K. Kim, C. G. Yoo, *Curr. Opin. Green Sustain. Chem.* **2021**, *27*, 100396.

[64] C. Florindo, F. Lima, B. D. Ribeiro, I. M. Marrucho, *Curr. Opin. Green Sustain. Chem.* **2019**, *18*, 31–36.

[65] M. A. Hossain, M. S. Rahaman, D. Yelle, H. Shang, Z. Sun, S. Renneckar, J. Dong, S. Tulaphol, N. Sathitsuksanoh, *Ind. Crops Prod.* **2021**, *167*, 113480.

[66] T. El Achkar, H. Greige-Gerges, S. Fourmentin, *Env. Chem. Lett.* **2021**, *19*, 3397–3408.

[67] M. Shaibuna, L. V. Theresa, K. Sreekumar, *Soft Matter* **2022**, *18*, 2695–2721.

[68] S. E. Hooshmand, R. Afshari, D. J. Ramón, R. S. Varma, *Green Chem.* **2020**, *22*, 3668–3692.

[69] R. Karan, R. Bhatia, R. K. Rawal, in *Green Sustainable Process for Chemical and Environmental Engineering and Science* (Ed.: K. Marinakis), Elsevier, Amsterdam, The Netherlands, **2021**, pp. 159–188.

[70] V. Pascanu, G. González Miera, A. K. Inge, B. Martín-Matute, *J. Am. Chem. Soci.* **2019**, *141*, 7223–7234.

[71] N. Mulakayala, G. Pavan Kumar, D. Rambabu, M. Aeluri, M. V. Basaveswara Rao, M. Pal, *Tetrahedron Lett.* **2012**, *53*, 6923–6926.

[72] B.-Y. Zhao, P. Xu, F.-X. Yang, H. Wu, M.-H. Zong, W.-Y. Lou, *ACS Sustainable Chem. Eng.* **2015**, *3*, 2746–2755.

[73] M.-A. Karadendrou, I. Kostopoulou, V. Kakokefalou, A. Tzani, A. Detsi, *Catalysts* **2022**, *12*, 249.

[74] S. Hesse, J. Hertzog, S. Rup-Jacques, *J. Heterocycl. Chem.* **2024**, *61*, 1015–1023.

[75] X. Jin, A. Wang, H. Cao, S. Zhang, L. Wang, X. Zheng, X. Zheng, *Res. Chem. Int.* **2018**, *44*, 5521–5530.

[76] F. Tamaddon, H. Rashidi, *Res. Chem. Int.* **2023**, *49*, 3589–3603.

[77] M. Ramos-Martín, J. García-Álvarez, A. P. Soto, *ChemSusChem* **2025**, *18*, DOI 10.1002/cssc.202400892.

[78] D. P. Fonseca, A. C. Amorim, E. P. Carreiro, J. P. P. Ramalho, G. J. Hermann, H.-J. Federsel, A. R. C. Duarte, A. J. Burke, *SynOpen* **2023**, *07*, 374–380.

[79] M. Shaibuna, L. V. Theresa, K. Sreekumar, *Cat. Lett.* **2018**, *148*, 2359–2372.

[80] R. Schlögl, *Ang. Chem. Int. Ed.* **2015**, *54*, 3465–3520.

[81] J. C. Védrine, *Chin. J. Cat.* **2019**, *40*, 1627–1636.

[82] C. M. Friend, B. Xu, *Acc. Chem. Res.* **2017**, *50*, 517–521.

[83] A. Shaabani, R. Afshari, *J. Colloid Interface Sci.* **2018**, *510*, 384–394.

[84] F. Messa, G. Dilauro, F. M. Perna, P. Vitale, V. Capriati, A. Salomone, *ChemCatChem* **2020**, *12*, 1979–1984.

[85] M. Zhang, Y.-H. Liu, Z.-R. Shang, H.-C. Hu, Z.-H. Zhang, *Cat.Comm.* **2017**, *88*, 39–44.

[86] X. Xiong, C. Yi, X. Liao, S. Lai, *Tetrahedron Lett.* **2019**, *60*, 402–406.

[87] A. F. Arangadi, J. K. Ali, M. Abi Jaoude, D. H. Anjum, A. AlKhoori, K. Polychronopoulou, E. Alhseinat, *Desalination* **2022**, *530*, 115674.

[88] S. Marullo, C. Rizzo, F. D'Anna, *ACS Sustainable Chem. Eng.* **2019**, *7*, 13359–13368.

[89] S. Sun, X. Hou, *J. Mol. Liquids* **2019**, *277*, 556–562.

[90] X. Wang, S. Sun, X. Hou, *ACS Omega* **2020**, *5*, 11131–11137.

[91] M. Bakhtiarian, M. M. Khodaei, *Colloids Surf. A* **2022**, *641*, 128569.

[92] M. Niakan, M. Masteri-Farahani, S. Karimi, H. Shekaari, *J. Mol. Liquids* **2021**, *324*, 115078.

[93] Y. Gu, R. Ping, F. Liu, G. Zhang, M. Liu, J. Sun, *Ind. Eng. Chem. Res.* **2021**, *60*, 5723–5732.

[94] H. Mou, J. Wang, D. Zhang, D. Yu, W. Chen, D. Wang, T. Mu, *J. Mat. Chem. A* **2019**, *7*, 5719–5725.

[95] J. Iqbal, N. S. Shah, M. Sayed, J. Ali Khan, N. Muhammad, Z. U. H. Khan, Saif-ur-Rehman, M. Naseem, F. M. Howari, Y. Nazzal, N. K. Niazi, A. Hussein, K. Polychronopoulou, *Chem. Eng. J.* **2020**, *394*, 124869.

[96] E. Knoevenagel, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 2596–2619.

[97] J. van Schijndel, L. A. Canalle, D. Molendijk, J. Meuldijk, *Green Chem. Lett. Rev.* **2017**, *10*, 404–411.

[98] Y. Wang, Q.-X. Yao, J.-R. He, Z.-H. Liang, X. Li, H. Cheng, L.-L. Li, *Biomass Conv. Bioref.* **2022**, *12*, 87–93.

[99] Y. Wang, K. Dong, M. Zhen, J.-R. He, Q. Yao, *Biomass Conv. Bioref.* **2024**, *14*, 11243–11249.

[100] Y. Wang, H. Cheng, J.-R. He, Q.-X. Yao, L.-L. Li, Z.-H. Liang, X. Li, *Catal. Lett.* **2022**, *152*, 1215–1223.

[101] H. Al Beiruty, S.-S. Zhylinska, N. Kutateladze, H. K. T. Cheong, J. A. Ñíguez, S. J. Burlingham, X. Marset, G. Guillena, R. Chinchilla, D. A. Alonso, T. C. Nugent, *Molecules* **2023**, *29*, 4.

[102] M. Molnar, H. Brahmbhatt, V. Rastija, V. Pavić, M. Komar, M. Karnaš, J. Babić, *Molecules* **2018**, *23*, 1897.

[103] T. J. Devi, T. P. Singh, R. R. Singh, E. H. Singh, O. M. Singh, *ChemistrySelect* **2020**, *5*, 13351–13357.

[104] B. Dong, W.-J. Wang, Y. Yang, R. Wang, S.-C. Xi, *ACS Appl. Polym. Mat.* **2022**, *4*, 8092–8097.

[105] A. Wang, P. Xing, X. Zheng, H. Cao, G. Yang, X. Zheng, *RSC Adv.* **2015**, *5*, 59022–59026.

[106] P. H. Tran, H. T. Nguyen, P. E. Hansen, T. N. Le, *RSC Adv.* **2016**, *6*, 37031–37038.

[107] M.-T. T. Nguyen, N. Le, H. T. Nguyen, T. D. V. Luong, V. K. T. Nguyen, Y. Kawazoe, P. H. Tran, N.-N. Pham-Tran, *ACS Omega* **2023**, *8*, 271–278.

[108] D. R. Ñíguez, G. Guillena, D. A. Alonso, *ACS Sustainable Chem. Eng.* **2017**, *5*, 10649–10656.

[109] A. W. J. Platten, I. Manasi, M. Campana, K. J. Edler, E. Hevia, *ChemSusChem* **2025**, *18*, e202402083.

[110] A. Gutiérrez-Hernández, A. Richaud, L. Chacón-García, C. J. Cortés-García, F. Méndez, C. A. Contreras-Celedón, *J. Org. Chem.* **2021**, *86*, 223–234.

[111] A. Gutiérrez-Hernández, F. M. Soto-Suárez, A. Richaud, F. Méndez, C. A. Contreras-Celedón, *Molecules* **2024**, *29*, 5381.

[112] C. Rizzo, S. Marullo, M. Benaglia, F. D'Anna, *Eur. J. Org. Chem.* **2023**, *26*, e202300263.

[113] S. Marullo, A. Meli, F. D'Anna, *ACS Sustainable Chem. Eng.* **2020**, *8*, 4889–4899.

[114] C. Grosso, A. Brigas, J. M. de los Santos, F. Palacios, A. Lemos, T. M. V. D. Pinho e Melo, *Monatsh. Chem. - Chem. Monthly* **2019**, *150*, 1275–1288.

[115] P. Torres, M. Balcells, R. Canela-Garayoa, *ACS Omega* **2021**, *6*, 19392–19399.

[116] C. M. Q. Le, X. T. Cao, T. T. K. Tu, W.-K. Lee, K. T. Lim, *App. Surf. Sci.* **2018**, *450*, 122–129.

[117] X. Marset, A. Khoshnood, L. Sotorríos, E. Gómez-Bengoa, D. A. Alonso, D. J. Ramón, *ChemCatChem* **2017**, *9*, 1269–1275.

[118] X. Marset, B. Saavedra, N. González-Gallardo, A. Beaton, M. M. León, R. Luna, D. J. Ramón, G. Guillena, *Front. Chem.* **2019**, *7*, 00700.

[119] B. Saavedra, N. González-Gallardo, A. Meli, D. J. Ramón, *Adv. Synt. Catal.* **2019**, *361*, 3868–3879.

[120] S. Gracia-Barberán, A. Leal-Duaso, E. Pires, *Curr. Opin. Green Sustainable Chem.* **2022**, *35*, 100610.

[121] D. Zhao, Y. Liao, Z. Zhang, *Clean* **2007**, *35*, 42–48.

[122] A. Leal-Duaso, J. A. Mayoral, E. Pires, *ACS Sustainable Chem. Eng.* **2020**, *8*, 13076–13084.

[123] F. M. Perna, P. Vitale, V. Capriati, *Curr. Opin. Green Sustainable Chem.* **2020**, *21*, 27–33.

[124] D. S. Gaikwad, K. A. Undale, D. B. Patil, D. M. Pore, *J. Iran. Chem. Soc.* **2019**, *16*, 253–261.

[125] S. L. Kumar, S. Tabassum, S. Govindaraju, *J. Mol. Liquids* **2025**, *417*, 126651.

[126] S. Lokesh Kumar, S. Tabassum, S. Govindaraju, *J. Mol. Liquids* **2024**, *401*, 124592.

[127] N. Azizi, M. S. Haghayegh, *ChemistrySelect* **2017**, *2*, 8870–8873.

[128] N. Azizi, S. Dezfooli, M. Khajeh, M. M. Hashemi, *J. Mol. Liquids* **2013**, *186*, 76–80.

[129] P. Kalhor, K. Ghandi, *Catalysts* **2021**, *11*, 178.

[130] K. Wang, W. Che, X. Zheng, Y. Chen, M. Zuo, *Fuel* **2025**, *388*, 134487.

[131] H. Guo, X. Ma, Z. Chen, J. Guo, J. Lu, *RSC Adv-* **2025**, *15*, 3664–3671.

[132] İ. Aslanlı, M. Sert, *Renew. Energy* **2025**, *244*, 122698.

[133] J. L. K. Mamilla, U. Novak, M. Grilc, B. Likozar, *Biomass Bioenergy* **2019**, *120*, 417–425.

[134] M. Wu, H. Ma, Z. Ma, Y. Jin, C. Chen, X. Guo, Y. Qiao, C. M. Pedersen, X. Hou, Y. Wang, *ACS Sustainable Chem. Eng.* **2018**, *6*, 9434–9441.

[135] E. S. Morais, M. G. Freire, C. S. R. Freire, J. A. P. Coutinho, A. J. D. Silvestre, *ChemSusChem* **2020**, *13*, 784–790.

[136] S. Zhou, J. Xu, Z. Zhang, S. Zhu, J. Li, W. Zhang, F. Zhang, K. Chen, *Carbohydrate Polym.* **2025**, *349*, 122964.

[137] S. T. Williamson, K. Shahbaz, F. S. Mjalli, I. M. AlNashef, M. M. Farid, *Renew Energy* **2017**, *114*, 480–488.

[138] L. Gu, W. Huang, S. Tang, S. Tian, X. Zhang, *Chem. Eng. J.* **2015**, *259*, 647–652.

[139] Y. Alhassan, N. Kumar, I. M. Bugaje, *J. Energy Inst.* **2016**, *89*, 683–693.

[140] G. Kumar, K. Kumar, A. Bharti, *Ind. Eng. Chem. Res.* **2024**, *63*, 6024–6046.

[141] A. Shishov, A. Bulatov, M. Locatelli, S. Carradori, V. Andruch, *Microchem. J.* **2017**, *135*, 33–38.

[142] X. Zhou, X. Lu, Q. Wang, M. Zhu, Z. Li, *Pure Appl. Chem.* **2012**, *84*, 789–801.

[143] Q. F. Yue, C. X. Wang, L. N. Zhang, Y. Ni, Y. X. Jin, *Polym. Degrad. Stab.* **2011**, *96*, 399–403.

[144] H. Wang, R. Yan, Z. Li, X. Zhang, S. Zhang, *Catal. Comm.* **2010**, *11*, 763–767.

[145] Q. Wang, X. Yao, Y. Geng, Q. Zhou, X. Lu, S. Zhang, *Green Chem.* **2015**, *17*, 2473–2479.

[146] B. Liu, W. Fu, X. Lu, Q. Zhou, S. Zhang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 3292–3300.

[147] L. Zhou, X. Lu, Z. Ju, B. Liu, H. Yao, J. Xu, Q. Zhou, Y. Hu, S. Zhang, *Green Chem.* **2019**, *21*, 897–906.

[148] J. Li, D. Yan, X. Cheng, C. Rong, J. Feng, X. Feng, J. Xin, Q. Zhou, Y. Li, J. Xu, X. Lu, *Ind. Eng. Chem. Res* **2024**, *63*, 12373–12384.

[149] X. Wei, J. Qiu, H. Wang, W. Zheng, W. Sun, L. Zhao, *Chem. Eng. J.* **2025**, *508*, 161115.

[150] X. Yang, Q. Zou, T. Zhao, P. Chen, Z. Liu, F. Liu, Q. Lin, *ACS Sustainable Chem. Eng.* **2021**, *9*, 10437–10443.

[151] W. Guo, J. E. Gómez, À. Cristòfol, J. Xie, A. W. Kleij, *Angew. Chem. Int.* **2018**, *57*, 13735–13747.

[152] N. Yadav, F. Seidi, D. Crespy, V. D'Elia, *ChemSusChem* **2019**, *12*, 724–754.

[153] Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.* **2017**, *19*, 3707–3728.

[154] X. Yang, Z. Liu, P. Chen, F. Liu, T. Zhao, *J. CO2 Utilization* **2022**, *58*, 101936.

[155] S. García-Argüelles, M. Ferrer, M. Iglesias, F. Del Monte, M. Gutiérrez, *Materials* **2017**, *10*, 759.

[156] Z. Qian, X. Shang, W. Wang, D. Zhang, S. Sun, *Catal. Lett.* **2024**, *154*, 1201–1208.

[157] T. Sheng, J. Ou, T. Zhao, X. Yang, Y.-X. Peng, *Mol. Catal.* **2023**, *536*, 112907.

[158] F. Norouzi, A. Abdolmaleki, *J. Env. Chem. Eng.* **2024**, *12*, 111984.

[159] B. Nian, X. Li, *Int. J. Biol. Macromol.* **2022**, *217*, 255–269.

[160] J. T. Gorke, F. Srienc, R. J. Kazlauskas, *Chem. Comm.* **2008**, *44*, 1235–1237.

[161] A. K. Schweiger, N. Ríos-Lombardía, C. K. Winkler, S. Schmidt, F. Morís, W. Kroutil, J. González-Sabín, R. Kourist, *ACS Sustain. Chem. Technol.* **2019**, *7*, 16364–16370.

[162] Z. Chen, W. A. Jacoby, C. Wan, *Bioresour. Technol.* **2019**, *279*, 281–286.

[163] N. Paul, P. K. Naik, B. D. Ribeiro, P. S. Gooh Pattader, I. M. Marrucho, T. Banerjee, *J. Phys. Chem. B* **2020**, *124*, 7405–7420.

[164] Y. Liang, W. Duan, X. An, Y. Qiao, Y. Tian, H. Zhou, *Biores. Technol.* **2020**, 123389.

[165] J. P. Bittner, N. Zhang, L. Huang, P. Domínguez de María, S. Jakobtorweihen, S. Kara, *Green Chem.* **2022**, *24*, 1120–1131.

[166] A. R. Harifi-Mood, R. Ghobadi, A. Divsalar, *Int. J. Biol. Macromol.* **2017**, *95*, 115–120.

[167] N. Zhang, V. Lahmann, J. P. Bittner, P. Domínguez de María, S. Jakobtorweihen, I. Smirnova, S. Kara, *ChemSusChem* **2025**, *18*, e202402075.

[168] F. Silvianti, D. Maniar, L. Boetje, A. J. J. Woortman, J. van Dijken, K. Loos, *ACS Polymers Au* **2023**, *3*, 82–95.

[169] J. Cao, R. Wu, F. Zhu, Q. Dong, E. Su, *Biochem. Eng. J.* **2022**, *179*, 108336.

[170] Y. Zhou, Y.-J. Wu, L. Wang, J. Han, J.-C. Wu, C.-M. Li, Y. Wang, *Int. J. Biol. Macromol.* **2021**, *190*, 206–213.

[171] S. Milker, M. Pätzold, J. Z. Bloh, D. Holtmann, *Mol. Catal.* **2019**, *466*, 70–74.

[172] D. Lindberg, M. de la Fuente Revenga, M. Widersten, *J. Biotechnol.* **2010**, *147*, 169–171.

[173] G. Papanikolaou, G. Centi, S. Perathoner, P. Lanzafame, *ACS Catal.* **2022**, *12*, 2861–2876.

[174] A. Yazdani, G. G. Botte, *Curr. Opin Chem. Eng.* **2020**, *29*, 89–95.

[175] C. Ling, Y. Cui, S. Lu, X. Bai, J. Wang, *Chem* **2022**, *8*, 1575–1610.

[176] M. Guo, Z. Wei, Q. Zhang, *Int. J. Hydrogen Energy* **2022**, *47*, 6029–6043.

[177] C. Zhang, Y. Fu, W. Gao, T. Bai, T. Cao, J. Jin, B. Xin, *Molecules* **2022**, *27*, 8098.

[178] S. Elsharkawya, S. Hammad, I. El-hallaga, *J. Solid State Electrochem.* **2022**, *26*, 1501–1517.

[179] V. S. Protsenko, D. A. Bogdanov, S. A. Korniy, A. A. Kityk, A. S. Baskevich, F. I. Danilov, *Int. J. Hydrogen Energy* **2019**, *44*, 24604–24616.

[180] L. Juárez-Marmolejo, B. Maldonado-Teodocio, M. G. M. de Oca-Yemha, M. Romero-Romo, E. M. Arce-Estrada, A. Ezeta-Mejía, M. T. Ramírez-Silva, J. Mostany, M. Palomar-Pardavé, *Catal. Today* **2022**, *394–396*, 190–197.

[181] D. Li, Y. Huang, Z. Li, L. Zhong, C. Liu, X. Peng, *Chem. Eng. J.* **2022**, *430*, 132783.

[182] T. N. J. I. Edison, R. Atchudan, N. Karthik, S. Chandrasekaran, S. Perumal, P. B. Raja, V. Perumal, Y. R. Lee, *Fuel* **2021**, *297*, 120786.

[183] P. Maria Viyanni, T. N. Jebakumar Immanuel Edison, M. G. Sethuraman, *Mat. Today Sustainability* **2023**, *24*, 100565.

[184] R. Xue, R. Deng, Y. Li, M. Gao, J. Wang, Q. Zhang, *Green Chem. Eng.* **2025**, *6*, 93–101.

[185] S. Hong, A. M. Díez, A. N. Adeyemi, J. P. S. Sousa, L. M. Salonen, O. I. Lebedev, Y. V. Kolen'ko, J. V. Zaikina, *ACS Appl. Mat. Interfaces* **2022**, *14*, 23277–23284.

[186] L. Li, Q. Liu, D. Wang, M. Wang, Y. Cai, Y. Xiao, Y. Lan, J. Hu, P. Cheng, J. Zeng, Z. Li, Y. Liu, J. Wu, D. Gao, *Chem. Eng. J.* **2025**, *507*, 160541.

[187] J. Chen, Y. Ni, P. Zhang, X. Liang, S. Fang, *Food Chemi.* **2023**, *406*, 134999.

[188] M. Chi, Z. Zhu, L. Sun, T. Su, W. Liao, C. Deng, Y. Zhao, W. Ren, H. Lü, *Appl. Catal. B: Env.* **2019**, *259*, 118089.

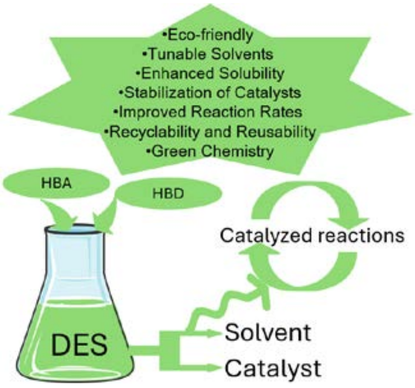
[189] A. Bjelić, B. Hočevar, M. Grilc, U. Novak, B. Likozar, *Rev. Chem. Eng.* **2022**, *38*, 243–272.

[190] F. A. Vicente, M. Huš, B. Likozar, U. Novak, *ACS Sustainable Chem. Eng.* **2021**, *9*, 3874–3886.

[191] F. A. Vicente, B. Bradić, U. Novak, B. Likozar, *Biopolymers* **2020**, *111*, e23351.

[192] E. Durand, J. Lecomte, P. Villeneuve, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 379–385.

## Entry for the Table of Contents



Deep eutectic solvents (DESs) are emerging as sustainable alternatives in catalysis, offering tunable properties for diverse chemical transformations. This review explores the dual role of DESs as solvents and catalysts, highlighting advancements in organic chemistry, materials science, $CO_2$ fixation, biomass valorization, polymer degradation, and oxidative desulfurization. The challenges, future directions, and industrial potential of DES-based catalytic systems are also discussed.