



ตัวทำละลายดีฟิวเทคติกในกระบวนการไบโอรีไฟเนอรี: ความก้าวหน้าด้านการปรับสภาพชีวมวล การเพิ่มมูลค่าลิกนิน และการผลิตสารเคมีสีเขียว

Deep Eutectic Solvents in Biorefineries: Advances in Biomass Pretreatment, Lignin Valorization, and Green Chemical Production

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Received 25 July 2026; Revised 26 August 2026; Accepted 16 September 2026; Published online: 23 September 2026

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Circular biorefineries have emerged as integrated platforms capable of converting renewable lignocellulosic biomass into a diverse range of biofuels, renewable chemicals, biomaterials, and bio-based products through comprehensive utilization of all biomass fractions [1]. Unlike conventional linear conversion processes, which primarily focus on cellulose utilization while treating hemicellulose and lignin as low-value residues,

Please cite this article as: K. Gopu, B. Dharmarlingam, S. S. Anandan, and J. Sundarababu, "Deep eutectic solvents in biorefineries: Advances in biomass pretreatment, lignin valorization, and green chemical production," *The Journal of KMUTNB*, vol. 37, no. 1, pp. 1–6, Jan.–Mar. 2027 (in Thai), Art. no. 271-008351, doi: 10.14416/j.kmutnb.2026.09.008.



circular biorefineries emphasize integrated biomass fractionation, recycling, and valorization to improve carbon efficiency and process sustainability [2].

Within this context, Deep Eutectic Solvents (DESs) have attracted considerable attention as environmentally friendly solvents because of their low toxicity, biodegradability, negligible vapor pressure, simple synthesis, and tunable physicochemical properties [3]. These unique characteristics enable selective fractionation of lignocellulosic biomass under relatively mild operating conditions, making DESs attractive alternatives to conventional organic solvents and ionic liquids for sustainable biomass processing and green chemical production [4].

DESs are generally prepared by combining a Hydrogen Bond Acceptor (HBA), commonly choline chloride, with a Hydrogen Bond Donor (HBD) such as organic acids, polyols, amides, or sugars. Strong hydrogen-bond interactions between these components significantly reduce the melting point of the mixture, producing a stable liquid with excellent dissolution capability for lignocellulosic biomass [5]. One of the principal advantages of DESs is their flexibility in solvent design, allowing their acidity, polarity, viscosity, and hydrogen-bonding capacity to be tailored according to

the characteristics of different biomass feedstocks and target products. Compared with conventional pretreatment chemicals, DESs are relatively inexpensive, easy to synthesize without complex purification steps, and can often be recovered and recycled, thereby reducing chemical consumption and environmental impacts [6]. These advantages have established DESs as promising designer solvents capable of supporting sustainable biomass fractionation while adhering to the principles of green chemistry and circular bioeconomy development [7], [8].

Lignocellulosic biomass constitutes the largest renewable carbon reservoir on Earth and includes agricultural residues, forestry by-products, dedicated energy crops, food-processing residues and municipal organic waste [9]. However, efficient utilization of lignocellulosic biomass remains challenging because of its complex and recalcitrant structure. Cellulose microfibrils are embedded within a matrix of hemicellulose and lignin through extensive hydrogen bonding and lignin-carbohydrate complexes, which restrict enzyme accessibility and reduce biomass digestibility. Consequently, pretreatment has become the most critical stage of biomass conversion because it directly influences cellulose accessibility, lignin removal, enzymatic hydrolysis efficiency,

fermentable sugar production, and overall biorefinery performance [1], [10].

Conventional pretreatment technologies, including dilute acid hydrolysis and alkaline treatment have demonstrated considerable effectiveness in reducing biomass recalcitrance [11]. Nevertheless, these technologies often require harsh reaction conditions, corrosive chemicals, extensive wastewater treatment, or costly solvent recovery systems, thereby increasing operational costs and environmental burdens. In contrast, DES-assisted pretreatment offers a greener and more selective alternative by disrupting lignin-carbohydrate complexes while preserving cellulose integrity and minimizing degradation of valuable biomass components. Recent investigations have demonstrated that DES pretreatment significantly enhances lignin extraction, cellulose enrichment, enzymatic digestibility, and fermentable sugar recovery while simultaneously reducing inhibitor formation during downstream fermentation. Such improvements contribute directly to increased bioethanol productivity and improved overall biomass conversion efficiency [6], [10].

Recent advances have further improved DES pretreatment through high-solids processing, which reduces solvent consumption and enhances the commercial viability of

biomass fractionation. High-solids DES pretreatment enables greater biomass loading without compromising lignin removal efficiency or cellulose preservation, thereby lowering reactor volume, energy demand, and solvent recovery costs. In addition, process intensification strategies, including surfactant-assisted pretreatment, ultrasound irradiation, microwave heating, catalytic fractionation, and continuous-flow processing, have significantly enhanced solvent penetration, biomass wettability, and selective delignification. These developments improve cellulose accessibility, shorten pretreatment duration, reduce energy consumption, and increase enzymatic hydrolysis efficiency. Furthermore, optimization of DES composition, biomass loading, temperature, reaction time, and solvent recycling has demonstrated significant potential for improving both environmental sustainability and economic feasibility of integrated biorefinery operations [7]–[10].

The application of DESs extends beyond biomass pretreatment and plays a pivotal role in enabling integrated circular biorefineries. Cellulose-rich solids generated after DES pretreatment can be enzymatically hydrolyzed into glucose and subsequently fermented into bioethanol and other bio-based products. Simultaneously, hemicellulose-



derived sugars, including xylose and arabinose, can be converted into high-value products such as Xylo-Oligosaccharides (XOS), xylitol, furfural, levulinic acid, lactic acid, succinic acid, and other microbial metabolites. Instead of being treated as a combustion residue, lignin recovered during DES pretreatment serves as a renewable aromatic feedstock for producing phenolic compounds, polymers, adhesives, carbon materials, catalysts, and advanced functional nanomaterials. Such integrated utilization of cellulose, hemicellulose, and lignin substantially improves carbon utilization efficiency, minimizes waste generation, diversifies product portfolios, and enhances the sustainability of circular bioeconomy systems. These integrated strategies are increasingly recognized as essential for achieving carbon neutrality and establishing economically viable lignocellulosic biorefineries [9].

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