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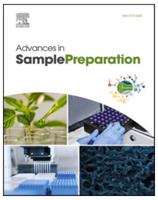

Recent cutting-edge approaches to the integration of solid-liquid extraction with deep eutectic solvents: Toward a greener procedure for biomass valorization

Niluh Indria Wardani [a,1], Thidarat Samkumpim [a,1], Waleed Alahmad [a,*], Andrew William King [a], Pakorn Varanusupakul [a], Andrey Shishov [b], Noorfatimah Yahaya [c], Nur Nadhirah Mohamad Zain [c,*]

[a] Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand
[b] Department of Analytical Chemistry, Institute of Chemistry, Saint Petersburg State University, SPbSU, 7/9 Universitetskaya nab., St. Petersburg 199034, Russia
[c] Department of Toxicology, Advanced Medical and Dental Institute, Universiti Sains Malaysia, 13200 Kepala Batas, Pulau Pinang, Malaysia

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ABSTRACT

As the global demand for sustainable and renewable resources intensifies, there is an imperative to explore innovative technologies for biomass valorization. This review delves into a promising avenue, providing an overview of green approaches that combine solid-liquid extraction (SLE) with a type of solvent known as deep eutectic solvents (DESs) in a synergistic manner. SLE, a conventional method for isolating bioactive compounds from biomass, is recognized for its effectiveness in sample preparation. However, it often involves the use of environmentally harmful solvents. Subsequently, DESs have emerged as an eco-friendly alternative to traditional solvents. Composed of naturally occurring and benign components, these DESs exhibit unique properties that render them suitable for various extraction processes. The integration of SLE with DESs introduces a novel approach to biomass valorization. This review explores the synergistic effects between SLE and DESs to optimize extraction yields, improve selectivity, and reduce overall energy consumption. Furthermore, the nature of DESs aligns with the principles of green chemistry, positioning them as a sustainable alternative to traditional solvents.

Introduction

In contemporary laboratories, primary consideration is given to renewable and sustainable practices. In the past, chemists prioritized achieving the highest yield in a reaction without regard for toxicity or pollution. However, after several decades of flourishing scientific endeavors, pollution has become a global issue, with traditional chemistry being a significant contributor. The utilization of renewable materials derived from waste or byproducts in reactions has been proposed as a solution to these environmental problems [1]. Biomass is a key component of renewable resources and holds great importance in the field of chemistry. It can be sourced from various origins, including both human and natural activities. The value of biomass lies in its composition, as it contains valuable compounds that can serve as essential precursors or be incorporated directly into the synthesis of complex products. This versatility makes biomass a promising alternative to traditional chemical feedstocks [2]. When biomass derived from waste is valorized, it can yield a wide range of valuable products. By extracting these valuable compounds from biomass, we can avoid the negative environmental impacts associated with incineration or landfill disposal [3], which can have negative environmental impacts.

Valorization is the process of converting biomass into valuable products, such as chemicals, materials, and fuels. Biomass refers to organic matter, such as plant material or agricultural waste, that can be used as a renewable resource [4]. The transformation of biomass into value-added products is increasing worldwide due to several key factors. The typical method of the valorization of biomass starts with obtaining and pretreating waste biomass resources. Then, extraction is undertaken before hydrolysis to facillatate the solid and liquid product recovery [5, 6]. There are various extraction techniques for the recovery of value-added products from biomass resources, such solid-liquid extraction, ultrasound, microwaves, etc. all of which are used for valorization

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* Corresponding authors.
E-mail addresses: waleed.al@chula.ac.th, waleed.alahmad.cu@gmail.com (W. Alahmad), nurnadhirah@usm.my (N.N.M. Zain).

[1] These authors contributed equally to this work.

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Solid-liquid extraction (SLE), as a widely used method in the field of valorization, allows for the separation of components from solid matrices. This process involves the use of organic solvents, such as methanol, ethanol, and acetone, to extract the desired compounds. However, it is important to consider the implications of using organic solvents in SLE, as they can have both positive and negative effects on extraction efficiency and pose potential risks to human health and the environment.

To address the concerns associated with the use of organic solvents in SLE, researchers have been exploring alternative methods and strategies. One approach is the use of green solvents, such as deep eutectic solvents (DESs) that are a class of green solvents. A significant advantage of DESs is that the synthesis is straightforward, does not require any solvents, nor does it produce byproducts. DESs can be used in various fields such as biomass valorization, chemical reactions, catalysis, synthesis, metal extraction and recovery, etc. due to their unique characteristics. DESs are alternative solvents that can replace toxic organic solvents and in some studies the use of DESs can lead to an increased yield. This can be attributed to the unique properties of DESs, such as their ability to enhance solubility and improve mass transfer rates [8].

Next generation valorization of biomass combines DESs with SLE. This combination of SLE and DESs is greener and more sustainable for biomass valorization. The study of SLE with DESs is important to open the view of biomass valorization. In particular the combination of SLE and DESs needs to be further studied to find proper conditions and analytes. The perspective and combination of SLE and DESs in biomass valorization was discussed in this review. It is crucial to explore its potential benefits and drawbacks to fully understand its applicability.

Biomass valorization techniques

Biomass valorization is the value-adding process of using biomass feedstock to produce certain products, materials, or energy. By effectively combining various biomass processing techniques and procedures to transform biomass into a finished product, as depicted in Fig. 1, biobased products are made ready for financially feasible application. Biomass is commonly converted using a variety of valorization methods, including thermochemical, biological, and chemical processing [9–12].

Under the thermochemical conversion pathway biomass can be converted, depending on the reaction conditions, into liquid fuels like hydrocarbon fuels and bio-oils, solid fuels like hydrochars or biochars, or gases like syngas. The categories of thermochemical conversion pathways can be further divided into three groups based on the main product obtained: biomass-to-gas processes (BTG) (including hydrothermal gasification, HTG, and conventional gasification); biomass-to-liquid (BTL) processes (including hydrothermal liquefaction (HTL), fast pyrolysis, and flash pyrolysis); and biomass-to-solid (BTS) processes (including torrefaction, hydrothermal carbonization (HTC), and slow pyrolysis) [13].

The biological conversion process includes anaerobic digestion (AD) and syngas fermentation. Anaerobic digestion consists of several processes that break down complex organic matter in the absence of oxygen. To summarise the main biological conversions; hydrolysis, converts complex organic matter into soluble monomers; acidogenesis, converts soluble monomers into short-chain volatile fatty acids and alcohol; acetogenesis, converts volatile fatty acids into acetate (the main intermediate), hydrogen, and carbon dioxide; methanogenesis, converts acetate and other intermediates into methane using acetoclastic methanogenic archaea as a mediator. Any biomass that contains sulfate can also undergo sulphidogenesis, which converts it into gaseous H_2S. Fig. 2 shows the entire procedure. Moreover, syngas fermentation is a promising technology that generates basic chemicals and fuels by acetogenic bacteria from a gas mixture of CO, H_2, and CO_2 into acetic acid, ethanol, or other organic compounds [12,13].

Additionally, a variety of chemical processing techniques can be distinguished, including solid phase extraction (SLE) with DESs, SLE with organic solvents, SLE with ionic liquids, ozonolysis, acid hydrolysis, and alkaline hydrolysis. Cleaner valorization products, a high reaction rate, little inhibitor formation, low temperatures, and pressure, as well as the ability to adhere to the green chemistry principles when using a green solvent, are all benefits of appropriate chemical processing. On the other hand, some chemical biomass valorization processes have several drawbacks, including reactor corrosion issues, neutralization requirements, a lengthy reaction time, low digestibility enhancement, the need to remove alkali, a high cost for alkaline catalysts, a high cost for the large amount of ozone required, flammability, toxicity, a high cost of energy, explosion risk, and environmental harm [12].

Traditional biomass valorization methods, which include thermochemical, biological, and chemical processes use organic solvents, ozonolysis, acid hydrolysis, and alkaline hydrolysis and as a result are hazardous, time-consuming, non-environmentally friendly, and involve large amounts of toxic solvents. It also takes a long time to extract materials and produces low extraction yields and selectivity. However, more recent methods of biomass valorization have shown promise in achieving green chemistry concepts. These new methods of extracting chemicals from biomass include pulsed electric field (PEF), pressurized fluid extraction (PLE), ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), and green solvent-based solid-liquid extraction (SLE-ionic liquid and SLE-DESs). Recent advancements in biomass valorization provide advantages such as increased yields, shorter processing times, the use of lower amounts of solvents, and the extraction of biologically active compounds without compromising their effectiveness [14].

Deep eutectic solvents

Deep eutectic solvents (DESs) are a unique type of solvent mixture characterized by a significantly lower deep eutectic point temperature compared to the ideal liquid mixture temperature ($\Delta T_2 > 0$). The definition of DESs in terms of temperature depression (ΔT_2) focuses on the difference between the ideal ($T_{E,\ ideal}$) and real (T_E) eutectic point temperatures, distinct from the temperature deviation (ΔT_1) between the melting points of pure compounds ($T_{m,1}$ and $T_{m,2}$) and the real eutectic point (T_E). Unlike eutectic solvents, DESs maintain a liquid phase at the operating temperature ($T_{operating}$), making them a distinct subclass of eutectic solvents. The solid-liquid equilibria phase diagram of eutectic solvents and deep eutectic solvents is illustrated in Fig. 3 [15,16].

The study of the physicochemical properties of DESs is very important in the development of these solvents. These properties can be identified by the measurement of a solid-liquid equilibria phase diagram that shows the ideal solubility line and the relation between the thermophysical properties of pure components and phase behavior at a range of compositions and temperatures (Fig. 3(b)). The primary physicochemical properties of DESs are phase behavior, viscosity, surface

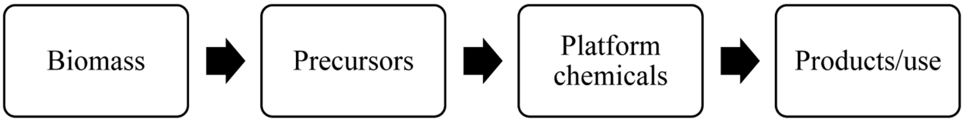

Fig. 1. The schematic diagram of biomass valorization [10].

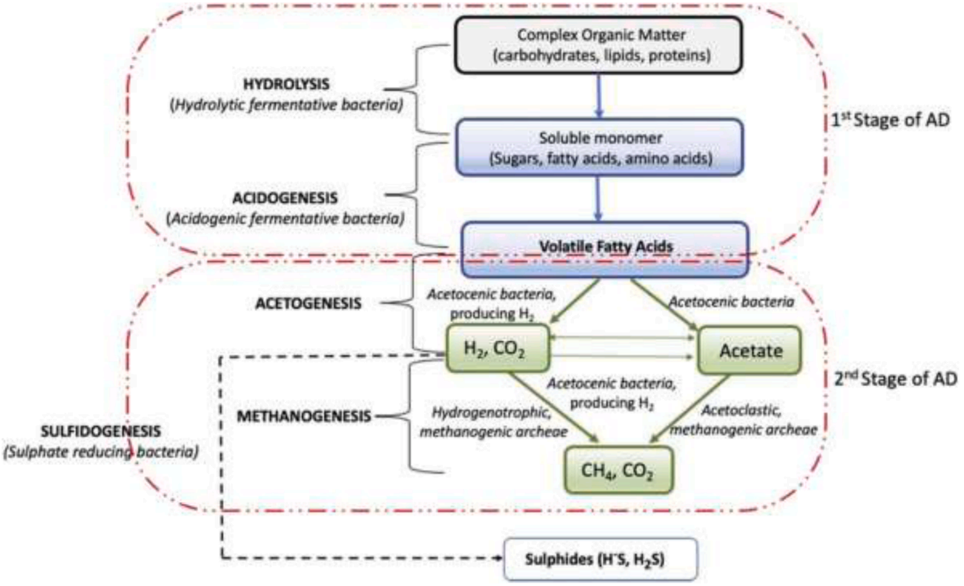

Fig. 2. Anaerobic digestion route. The image is reprinted in its entirety from the original source, without any modifications with permission from publisher [13].

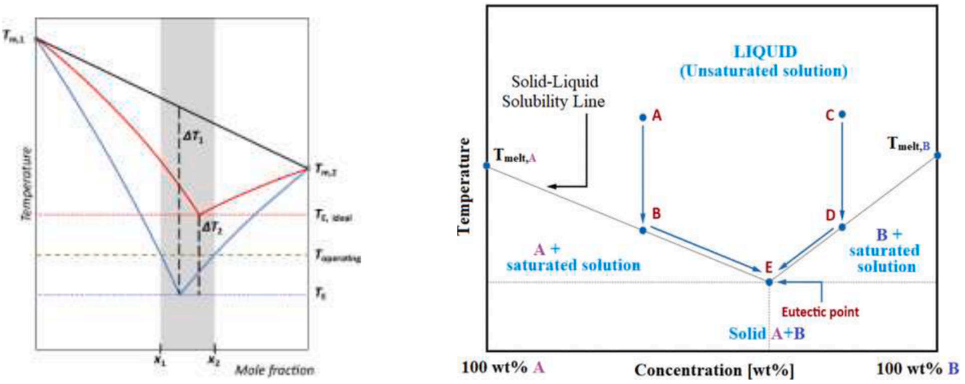

Fig. 3. (a) The solid-liquid equilibria phase diagram of a simple ideal eutectic mixture (red line) and a deep eutectic mixture (blue line) (b) The solid-liquid equilibria phase diagram of a binary mixture. Tm,1 is the melting point of component 1, and Tm,2 is the melting point of component 2. The images are reprinted in their entirety from the original sources, without any modifications. Source: [15,17].

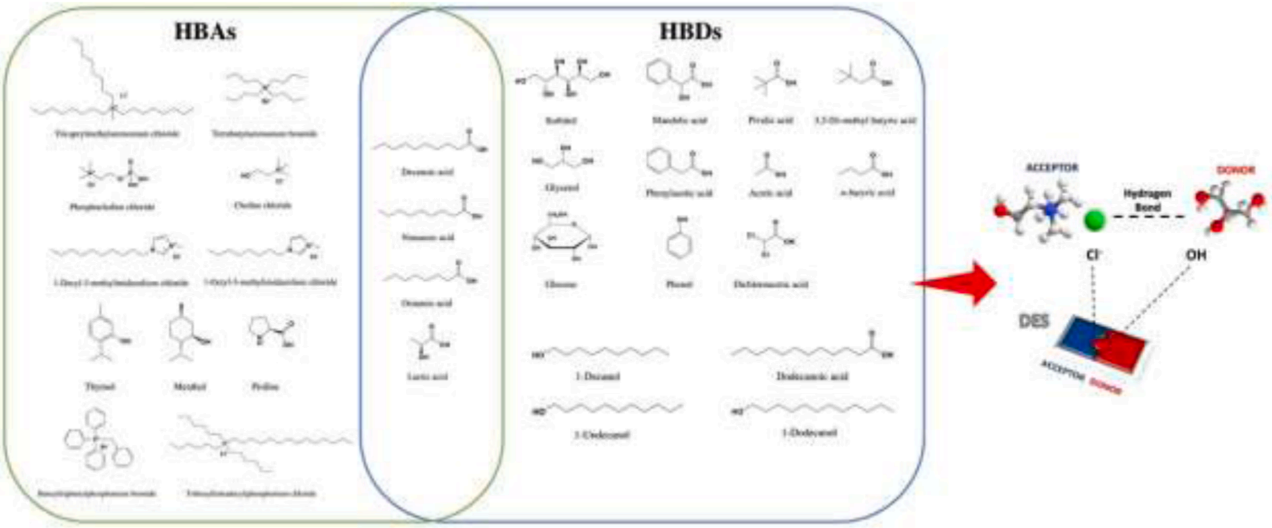

Fig. 4. The components of DESs. The image is a combination of two images sourced from [19,20].

tension, density, ionic conductivity, and polarity. In general, DESs have low volatility, low vapor pressure, are chemically and thermally stable, non-flammable, and chemically tunable [15,18].

DESs are a mixture of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA). The HBD and HBA components are bonded to each other at certain mole fraction ranges by very strong hydrogen bonding and complex formation, as summarized in Fig. 4. The general formula of DESs is Cat$^+X^-$zY where Cat$^+$ is a cation (e.g., ammonium, phosphonium, or sulfonium), X^- is a Lewis base (e.g., halide anion), and Y is a Lewis or Brønsted acid with z composition. Based on this HBA and HBD component, DESs are classified into several types. Type I DESs use non-hydrated metal halides ($Y = MCl_x$; $M =$ Zn, Sn, Fe, Al, Ga, In) with suitable low melting points, but the scope of this type of salt is constrained. Nevertheless, by using hydrated metal halides ($Y = MCl_x.yH_2O$; M = Cr, Co, Cu, Ni, Fe) and choline chloride (type II DESs), the range of DESs can be expanded. Many hydrated metal salts are relatively inexpensive, and their inherent resistance to air and moisture makes their use in large-scale industrial processes viable. Type III DESs have attracted interest as they have the ability to dissolve a variety of transition metal species and are created from organic salts (e.g., choline chloride) and hydrogen bond donors ($Y = RZ$; Z = $CONH_2$, COOH, OH). The broad variety of hydrogen bond donors in type III is well-developed, which makes this type of DESs adjustable. Furthermore, the type IV DESs are a combination of metal halides and hydrogen bond donors. The metal salts that are used are commonly nonionizable in nonaqueous media. Type V, developed by Abranches et al., are composed of non-ionic HBA and HBD [15,16,18,21].

DESs are classified not only as type I-V but also have another subclass of natural deep eutectic solvents (NADESs) that emerged in 2011 by Choi et al. This subclass is fully regarded as green chemistry being nontoxic, sustainable, and safe for the environment. NADESs could be included in the type III and V classes when they use natural biodegradable chemicals such as sugar, alcohol, amino acids, and carboxylic acids. Additionally, almost all DESs components in types I-IV are hydrophilic. The hydrophilic DESs are not stable in an aqueous solution and limit their application in high water-content environments. Therefore, in 2015, Kroon et al. developed hydrophobic DESs for the first time that consisted of decanoic acid and various quaternary ammonium salts. The increased alkyl chain length in these DESs increased their hydrophobicity. All the DESs classifications are shown in Fig. 5. DESs can be synthesized to satisfy the demands of the intended purpose by adjusting the water content, hydrogen bond donors and acceptors, and their molar composition [18,22–25].

The synthesis procedures for DESs are both easy and simple. These synthesis methods are determined by the availability of apparatus, personal choice, and water-reducing capacity. There are several kinds of synthesis methods for DESs, such as the heating and stirring method, vacuum evaporation, grinding, and freeze-drying methods. The heating-stirring method is the most popular because it needs no additional solvent, no purification steps, and is economically efficient. This technique involves combining the components of the DESs while applying heat and stirring [17].

DESs are versatile solvents that can be used for many applications, such as metallurgy, electrodeposition, gas separation, biocatalysis, synthesis, and biomass processing. One of the foremost applications of DESs is biomass processing, as it can facilitate the valorization process to convert raw biomass into useful chemicals (Table 1). DESs in biomass processing could be a viable green solvent in solid-liquid extraction (SLE) [17,26].

Solid-liquid extraction

Solid-liquid extraction (SLE) is a commonly used method in industries such as pharmaceuticals, cosmetics, and food additives [27,28]. It is employed to extract compounds from solid samples by dissolving them in a liquid solution. [29,30]. The principle of SLE is based on the extraction of analytes from a solid phase to a liquid phase by using an appropriate solvent [31,32]. Then the solid and liquid phases can be separated by centrifugation. The efficiency of SLE depends on the solvent type, pH, temperature, particle size, and solid-liquid ratio. An appropriate solvent will provide high efficiency with regards to extraction because each compound has a different solubility in the organic solvent due to solvent polarity [33].

There are several different types of SLE (maceration, reflux

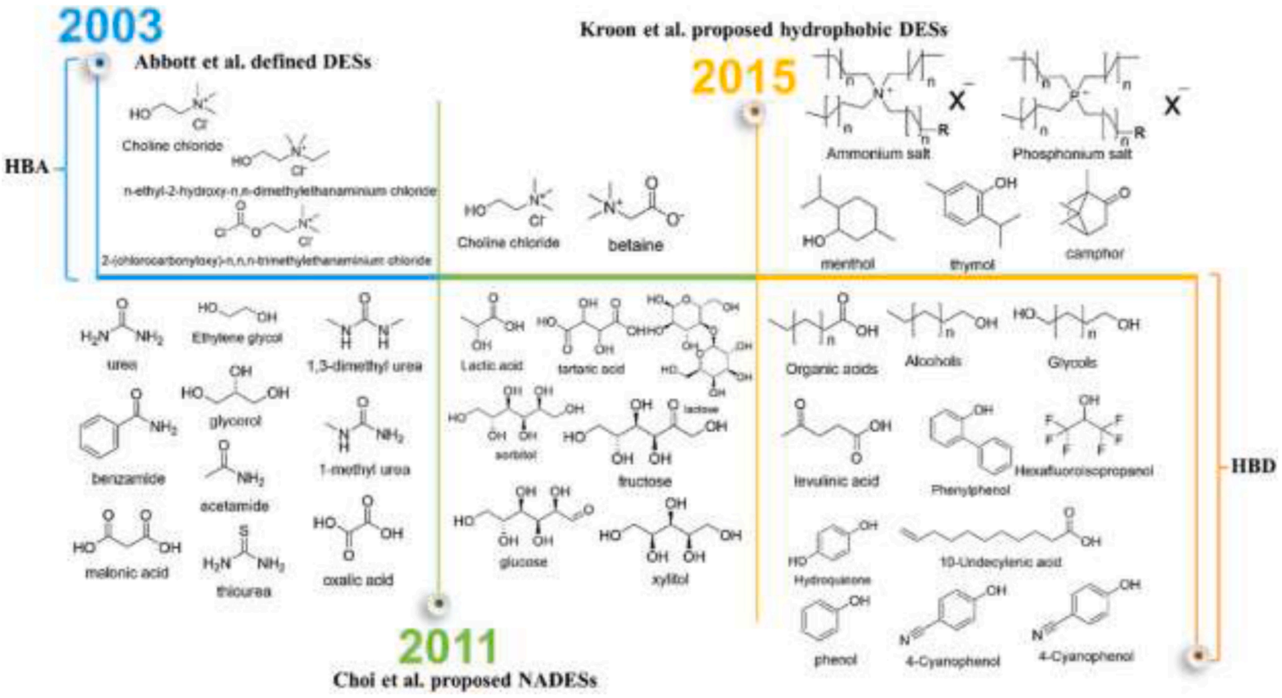

Fig. 5. The HBA and HBD components of hydrophilic, hydrophobic, and natural DESs. The image is reprinted in its entirety from the original source, without any modifications, with permission from the authour [23].

Table 1
The use of deep eutectic solvents in biomass valorization.

DESs composition		Molar ration	Solid sample	Process	Result	Refs.
Sodium hydroxide, potassium hydroxide, lithium hydroxide	ethylene glycol Polyethylene glycol-200 polyethylene glycol-300 polyethylene glycol-400 polyethylene glycol-600 1,4-butyl glycol 1,2-Propylene glycol	1:2 – 1:10	poplar wood	A DES-based lignocellulose pretreatment for enzymatic hydrolysis	bioethanol produced	[41]
ChCl	ethylene glycol/ p-toluenesulfonic acid	1:0.5:1	bamboo wood	pretreatment of bamboo wood	removal of more than 93.36 % xylan and 90.32 % lignin, and preservation of cellulose	[44]
ChCl	p-hydroxybenzoic acid	NA	poplar wood	Delignification of wood	69 % of delignification	[45]
ChCl	lactic acid	1:4 – 1:14	poplar wood	extraction of lignin from wood	antioxidant activities of lignin fractions were better than butyl hydroxyanisole	[46]
ChCl	ethanolamine, glycerol, malic acid	1:1 1:6 1:2	bamboo residue	extraction of lignin from wood for its further use	lignin fractions assemble into lignin nanoparticles and have excellent antioxidant activity	[47]
ChCl	levulinic acid	1:2 1:3	acacia wood	extraction of lignin from wood for its further use	extracted lignin has a high content of phenolic -OH groups, which favor its reactivity	[48]
ChCl	glycerol, 1,2-propylene glycol, 1,4-butanediol, $ZnCl_2$, $AlCl_3$, $CuCl_2$, $FeCl_3$	NA	pinus sylvestris	extraction and production of lignin with light color and low condensations	addition to physical sunscreens	[45]
ChCl	lactic acid	1:2	bulk wood sample	delignification and functionalization of wood	solar-driven sewage purification	[46]
ChCl	urea, glycerol, oxalic acid, acetic acid	NA	picea orientalis	impregnation of wood samples	Deep eutectic solvent wood modification	[47]
ChCl, betaine	acetic acid, oxalic acid	NA	scots pine	wood modification	the improvement in the accelerated weathering performance	[48]
ChCl	lactic acid	1:9	birch biomass	delignification and functionalization of wood	wood-based cellulose-rich membranes	[49]
ChCl	oxalic acid dihydrate	1:1	balsa wood samples	delignification	oil-absorbent wood material	[75]
ChCl	oxalic acid dihydrate	1:1	natural wood slice	delignification	wood-based filtration device	[53]
$ZnCl_2$	lactic acid	1:10	balsa wood	A DES has a dual role as a lignin removal agent and ZnO precursor	ZnO-coated carbon foams for CO_2 adsorption and oil absorption	[55]
ChCl	citric acid	1:1	pinus radiata	A DES pretreatment and subsequent temperature-assisted compression	densified wood	[56]
ChCl, histidine, proline	lactic acid malic acid oxalic acid	NA	different wood samples	delignification	softened wood	[58]
ChCl	lactic acid	1:5	populus tomentosa Carr.	removing lignin and hemicellulose	compressible cellulose wood	[59]
ChCl	acrylic acid	1:2	balsa wood slice	delignification and functionalization of wood	conductive, flexible, and transparent wood	[51]
ChCl	oxalic acid dihydrate	1:1	waste wood flour	microwave-assisted treatment of waste wood flour	production of cellulosic residue	[62]
ChCl	oxalic acid, glucose, tartaric acid, citric acid, malic acid, malonic acid, urea, and glycerin	NA	fruits of Litsea cubeba (Lour.) Pers.	extraction of plant essential oil		[76]
Sulfamic acid	urea	1:2	wood sawdust	mechanical milling using a planetary ball mill device	production of anionic sawdust nanofibers	[77]
ChCl	lactic acid	1:9	microfibril cellulose	functionalization of cellulose	A DES pretreated microfibril cellulose	[78]
ChCl	lactic acid, levulinic acid	1:2	Artemisia annua L.	extraction of artemisinin		[79]
ChCl	urea, formamide, acetamide, glycerol, ethylene glycol, diethylene glycol, triethylene glycol, Acetic acid, citric acid, formic acid, lactic acid, malic acid, propionic acid, succinic acid, xylitol	NA	pine wood powder	the pretreated biomass for enzymatic saccharification	reducing sugar	[80]

NA: Not Applicable.

extraction, and soxhlet extraction). Maceration is a simple classical SLE process. The mechanism of maceration is based on diffusion and osmosis. Solid samples are soaked in mild solvents (i.e., water or ethanol) for several days at room temperature to perform the extraction. However maceration is rarely used nowdays. Reflux is a simple extraction method where a mixture of solvent and biomass are placed in a vessel and heated up to the boiling point of the solvent. The reflux method provides a high yield, but produces a large amount of solvent waste and takes a long time. Another classical solid-liquid extraction (SLE) method is the Soxhlet extraction (SE). This method involves applying heat to the distillation flask, facilitating operation at elevated temperatures. During SE, the sample encounters the solvent, which is recycled and gradually enriched with analytes.

Although SLE is a time-consuming procedure, these conventional extractions have been utilized for many years. However, some analytes are not suitable for SLE because they cannot be sustained in the solution for an extended time [35]. SLE also requires large amounts of toxic organic solvents such as dichloromethane, chloroform, benzene, etc., which can evaporate and cause loss of selectivity.

Application of SLE in biomass processing

Biomass is a complex bioactive matrix that contains various natural products such as fatty acids, steroids, essential oils, phenolics, flavonoids, tannins, anthocyanins, etc. The conventional SLE is widely used for biomass extraction, such as the extraction of phenolic polymers (i.e., Lignin) [34] and bioactive compounds (i.e. antioxidant compounds). SLE also has an impact on the management of solid waste, especially in factories. In processing of treatment waste, the solid waste needs to be extracted to obtain valuable substances. Renewable biomass from a factory, such as wastewater, can be renewed as more valuable substances [35]. Biomass waste (e.g., animal manure, sewage sludge, municipal solid waste, and food waste) can be a source of organic fertilizer, impacting waste minimization and agricultural enhancement [36]

Integration of SLE and DESs for biomass valorization

Due to its efficiency, solid-liquid extraction has found widespread use in biomass processing, both to extract valuable compounds and as a method of pre-treatment of raw materials. For example, heavy metals can be extracted and purified from hazardous contaminants. It can also facilitate the decomposition of raw material matricies, such as lignin, and can provide a more efficient extraction of target components during fermentation stages. SLE is also widely used to extract bioactive compounds from plant medicinal materials, such as oils from oilseeds (e.g., sunflower) or proteins from algae. SLE can also be used for pre-delignification of lignocellulosic biomass before its conversion into biofuels. Solid-liquid extraction uses a variety of solvents and technologies, depending on the target compound and the type of biomass. Traditional solvents include water, ethanol, methanol, hexane, and supercritical fluids (e.g., supercritical carbon dioxide). The choice of solvent, temperature, pressure, and other conditions has a decisive influence on the efficiency and selectivity of the extraction process.

It is worth noting that, although solid-liquid extraction is a powerful tool for biomass processing, the choice of solvent and method can have environmental implications. Consequently, there is an interest in developing environmentally friendly extraction methods and using environmentally friendly solvents, such as deep eutectic solvents. In recent years, DESs have been increasingly used, and is already used actively in biomass processing. In this review, the emphasis is on SLE, and therefore the processing of solid samples is considered, although DESs can also be used when working with liquid biomass.

Integrating deep eutectic solvents into solid-liquid extraction methods for processing natural feedstocks offers a number of advantages. Among them, we can highlight improved solubility of both target analytes and interfering components, when necessary, increased environmental friendliness when processing raw plant materials, biocompatibility or low toxicity of the resulting extracts, and a number of other advantages.

Since their appearance, DESs have been widely used for processing raw plant materials and biomass (Table 1). In this direction, two vectors of technology development for using DESs can be distinguished. The first is associated with the extraction of biologically active molecules from raw medicinal plant materials. Several reviews are devoted to this area [37,38], therefore this area is not considered in this review. The second direction is associated with the use of DESs for the delignification of biomass in order to extract cellulose. Some reviews are also devoted to this area [39,40]. However, delignification not only makes it possible to extract cellulose for its further use but also opens up new opportunities for obtaining modified biopolymers for their use in many fields of science and technology. This section will be devoted to the new opportunities that DESs opens when used in the processing of biomass.

Synergistic effect of delignification and the use of deep eutectic solvents

The processing of natural raw materials, a fundamental aspect of sustainable green chemistry, holds paramount importance in fostering environmentally conscious practices. Delignification, as a key process within this framework, plays a pivotal role in unlocking the potential of renewable resources. Delignification of biomass is necessary for efficient cellulose recovery. The extracted lignin itself can act as an environmentally safe fuel or raw material for the production of various functional materials, for example, effective sorbents. This approach aligns with the principles of sustainable chemistry, emphasizing the efficient use of resources, reduced environmental impact, and the creation of new solutions for a more sustainable and greener future. Delignification of plant materials not only makes it possible to directly separate biopolymers and extract cellulose for further use, but also to prepare wood to obtain useful molecules and new materials. Thus, pre-treatment of raw plant materials with DESs allows not only for the extraction of lignin, and therefore obtaining high-purity cellulose, but also leads to easier subsequent fermentation of the resulting delignified raw materials to obtain bioethanol [41]. These bioethanols can be obtained using eutectic solvents based on polyols and alkali metal hydroxides or to obtain sugars by DESs-based choline chloride/ethylene glycol/p-toluenesulfonic acid (1/0.5/1) [44] and choline chloride/p-hydroxybenzoic acid (3/2) [45].

On the other hand, lignin isolated by a DES (choline chloride/lactic acid from 1/4 to 1/14) can be used as a medicinal product or for the production of environmentally friendly packaging of products [42]. A number of studies have shown that lignin extracted from raw materials using deep eutectic solvents, exhibits antioxidant activity [43] and has a high content of phenolic -OH groups, that contributes to its reactivity and use [44]. The extracted lignin, in some cases, can be lighter and at the same time exhibit useful properties such as UV filtration, which allows it to be added to sunscreen [45]. This effect is observed when using DESs as an extractant, which includes choline chloride and various hydrogen bond donors, such as glycerol, 1,2-propylene glycol, 1,4-butanediol, and the salts $ZnCl_2$, $AlCl_3$, $CuCl_2$, and $FeCl_3$.

In these examples, the raw materials were subjected to complete delignification, however, works have shown the possibility of treating only the surface of plant raw materials in order to obtain modified wooden surfaces. For example, the possibility of developing a device for wastewater treatment and seawater desalination based on natural wood, the surface of which was partially delignified using a DES (choline chloride /lactic acid 1/2) and coated with black polypyrrole [46]. Surface modification with DESs selectively removed most of the lignin from the surface of the material, which increased the hydrophilic moisture content of the wood to effectively transport water from below to the solar interface. Selective lignin removal reduced the thermal conductivity of the evaporator, facilitating heat distribution at the gas-liquid interface for efficient steam production. Another example of treating only the surface of a material is to partially extract lignin and replace it with DESs (choline chloride /urea, glycerol, oxalic acid, acetic acid) itself, which gives the surface antifungal properties [47]. Additionally, when using eutectic mixtures based on choline chloride and betaine as hydrogen bond acceptors and acetic or oxalic acids as donors it also contributes to better protection of the material from weathering and ultraviolet irradiation [48].

Not only can isolated lignin be used for the further production of functional materials, but delignified biomass also finds very wide applications. For example, for the manufacture of membranes [49] and filters for both water samples and atmospheric air. Membranes modified with metal-organic frameworks (MOF) that can remove particulates, have been obtained from eutectic solvent-treated ($ZnCl_2$/lactic acid) plant materials, and the authors suggest that their membranes can be further improved to capture hazardous gases and adsorb volatile organic compounds [50].

As another example, a natural material for the cleanup of water from oil spills was created by the delignification of biomass with a DES (choline chloride/acrylic acid 1/2) to produce a hydrophobic material that when subsequently treated with hexadecyltrimethoxysilane (HDTMS) created a hydrophobic coating on its surface allowing for effective oil cleanup [51]. It has also been shown that pre-treatment of plant materials with a DES (choline chloride/lactic acid 1/9) increases the uniformity of cellulose-based membranes. These membranes showed increased retention and decreased permeability values [52]. Natural sorbents based on delignified wood have also been proposed for purifying water from dyes [53], such as methylene blue [54].

Another example is the delignification of wood using a deep eutectic solvent (DES) consisting of $ZnCl_2$ and lactic acid. Here, the DES plays a dual role as a lignin removal agent and as a ZnO precursor to produce ZnO-coated carbon foam (Fig. 6). This composite material was used for CO_2 adsorption and oil absorption. The results showed that the resulting sorbents exhibited an excellent CO_2 adsorption capacity of 3.03 mmol/g (25 °C, 1 bar). In addition, this material had a high absorbtion ability for oil from both heavy and light fractions [55].

Processed raw materials, with extracted lignin, are widely used not just for cellulose production but also for other materials like densified wood [56]. Thus, a method for the production of dimensionally stable densified wood has been proposed, involving a DES (choline chloride/citric acid 1/1) pretreatment and subsequent thermal compression. The resulting densified wood showed high mechanical properties, such as flexural strength.

In another study, processing raw plant materials preserved the structure of the wood fibers. The tightly arranged fibers after compaction allow for the creation of reinforced wood with high mechanical properties. The resulting reinforced wood was 8 times stronger than the original wood and comparable to commonly used structural materials such as concrete, stainless steel, aluminum alloys, and magnesium alloys [57].

Not only high-strength materials can be obtained from raw plant materials through delignification, but also elastic materials based on natural polymers [58] after treating them with deep eutectic solvents (histidine, proline, and choline chloride as HBA and lactic, malic, and oxalic acids as HBD).

Wang et al. demonstrated that treating wood with a DES improves its elasticity and long-term compressibility. This is achieved by removing lignin and hemicellulose, thinning cell walls, and creating a stable honeycomb structure for compression and rebound. This wood had versatile properties like elasticity, durability, and sustainability, making it suitable for applications in fields such as sensors, water purification, and tissue engineering [59]. Another use case for flexible wood is to create "green electronics" [60]. The authors developed a simple approach to creating liquid metal-wood anisotropic (LMWA) conductors by integrating gallium-based LMs and delignified flexible wood. This material can be used to create flexible conductive structures and sensors.

Another example of using delignified wood to produce innovative materials is the creation of transparent wood. Delignification can remove the light-absorbing chromophore group from natural wood. Thus by impregnated the wood with a deep eutectic solvent a transparent wood can be created through photoinitiated polymerization. This transparent wood has excellent tensile strength, flexibility, and tensile strength. In addition, this transparent wood also has good electrical conductivity and the ability to sense temperature, which allows the material to be used in the creation of temperature sensors [51].

From the point of view of directly implementing the process of SLE of biosamples using DESs, the most widely used approaches are with heating [61]. However, there are more effective methods of solid-liquid extraction using DESs, for example, by treating the sample with microwave radiation [62,63], which opens up microwave-assisted autohydrolysis options [64]. Mechanochemical methods for intensifying the extraction have also been proposed, for example, using a ball mill [65] and twin-screw extrusion [66]. Thus, the integration of DESs into the delignification processes of raw plant materials in SLE procedures has multifaceted applications, including the production of bioethanol, the use of isolated lignin, and the modification of wood itself to obtain innovative materials. Table 1 briefly summarizes the different compositions of eutectic solutions and their use for a variety of biomass processing applications. From Table 1, we can conclude that, at present, the well-studied environmentally safe and accessible choline chloride is predominantly used as a hydrogen bond acceptor. Acids are most often used as hydrogen bond donors due to their greater activity during delignification processes. On the one hand, this shows that these DESs have proven themselves well for solving various problems of biomass processing, primarily delignification. On the other hand, it becomes obvious that most research has been focused on the use of a limited range of eutectic solvents, which could indicate a current limitation in this area. This can limit the introduction of new, innovative atypical eutectic solvents and confirms the need for more detailed study and implementation of them in real technological processes.

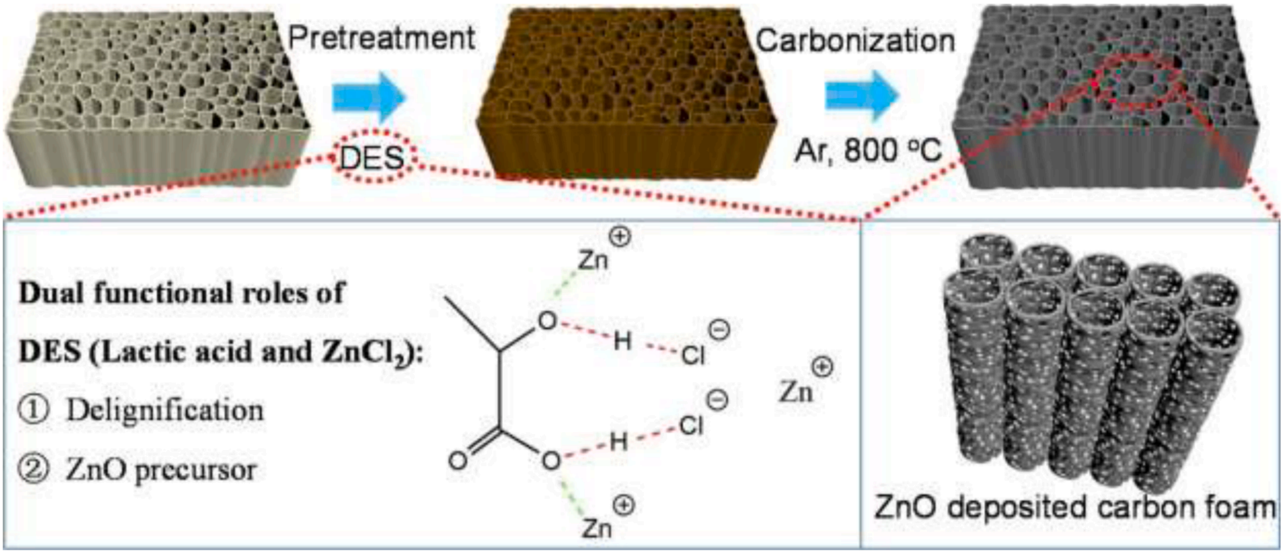

Fig. 6. Schematic illustration of the preparation process of ZnO deposited carbon foam copied from [55]. The figure is taken entirely from the original source.

New possibilities for processing food crops using deep eutectic solvents

In the field of processing plant crops, useful resources such as proteins, oils, and biologically active substances are traditionally extracted. Many reviews have been devoted to the work of extracting biologically active substances using eutectic solvents, so this review will only cover work on the extraction of proteins and oils from plant materials. There are two main approaches used to extract oils from plants. The first is to squeeze fruits or seeds of plants to obtain the healthier oils that have not been subject to thermal or dry processing. The resulting biomass contains high concentrations of residual oil, which is most often recovered by extraction into hydrocarbons, such as hexane. Hexane is a low-boiling flammable substance, which leads to the need to search for alternative oil extraction technologies. Several works have been proposed in this direction using DESs. A method for extracting essential oils from Chinese angelica Radix using microwave hydrodistillation into a eutectic solvent based on choline chloride and citric acid is described in previous work [67]. In that work various extraction options such as hydrodistillation (HD), microwave hydrodistillation (MHD), and DESs combined with hydrodistillation were studied and it was found that the combination of DESs and the hydrodistillation method provided the highest oil yield (1.2 % oil compared to 0.4 % obtained simply by hydrodistillation without the use of DESs). Another DES based on choline chloride and lactic acid was used in a similar system to extract oils from clove buds [68]. The authors also demonstrated the greater efficiency of using deep eutectic solvents in combination with hydrodistillation compared to unmodified hydrodistillation. The yield of essential oils was 4.5 % when using DES and 1 % without. DESs based on choline chloride and several hydrogen bond donors such as glucose, oxalic tartaric, citric, malic, malonic acids, urea, and glycerol have been used to extract essential oils from Litsea Cubaba fruit [69]. In this case, the microwave hydrodistillation method for sample preparation was also used. Among all the solvents studied, DES based on oxalic acid was found to be the best.

In another work, the authors used DESs based on choline chloride, alcohols (glycerol, ethylene glycol, diethylene glycol, and triethylene glycol) as well as urea and glucose not as the only solvent for extracting oil from flax seeds, but as an additive to hexane. This method increased the oil yield and lowered the temperature of the extraction process. This is important both from an economic point of view and from the point of view of preserving the beneficial properties of the oil [68]. In addition to experimental work, modeling the properties of DESs remains relevant not only from the point of view of studying their structure but also for solving applied problems, such as oil extraction. Many studies have been done in this area, for example, in [69] a DES based on tetraethylene glycol and choline chloride was synthesized and studied. Their physicochemical properties, such as conductivity, freezing point, density, surface tension, and viscosity, were studied, and by modeling using the COSMO-RS program, the dissolution of unsaturated fatty acids in this DES was predicted. This approach opens up a new perspective in chemistry, lipids, biofuel production, food processing, and vegetable oil extraction.

Dry and wet separation approaches are commonly used to extract proteins from plant materials. Dry testing involves sifting the sample to separate it into fractions of different protein contents. In the case of wet extraction, the protein is dissolveed into a solution with a pH far from the isoelectric point. Both methods are widely used, but they are economically expensive and, in the case of wet extraction, require large volumes of extractants. This led to the introduction of eutectic solvents to solve similar problems. In this area, acidic DESs have found widespread use due to the interaction of carboxyl groups in DESs and the amino groups of proteins, which leads to the effective extraction of the latter. Also, as in other areas, microwave [70] and ultrasonic sample processing [71] are used for more efficient protein extraction; however, in this direction, such methods of intensifying the extraction process are also implemented, such as pressurized liquid extraction [72] as well as high voltage electrical discharges (HVED) [73]. The proposed approaches made it possible not only to achieve high extraction yields but also to significantly reduce the costs of implementing the process.

In the described approaches, the traditional version of solid-liquid extraction was implemented by mixing the extractant and the sample, however, in the case of using eutectic solvents, it becomes possible to implement protein extraction in aqueous biphasic systems [74]. This procedure consists of the formation of a two-phase system, where the first phase is a solution enriched with DESs, and the second phase is an aqueous solution saturated with salt to exhibit a salting-out effect. In such a system, the distribution of proteins is observed, which allows them to be isolated and concentrated, however, this process can be classified as liquid-liquid extraction and is beyond the scope of this review.

In general, we can conclude that it is possible to implement various methods to extract substances from natural objects using DESs with SLE. Substances can either be completely extracted by the destruction of the sample or can be extracted from the surface layer. In both methods useful substances are concentrated in the DESs, and result in a significant change in the source material. From the point of view of the nature of the DESs used, the most widely used solvents are those based on choline chloride and polar hydrogen bond donors, such as acids (lactic, tartaric, and citric), urea, and glycerol. Extraction processes can be intensified by both traditional methods, such as heating, and microwave processing, and more modern ones, such as pressurized liquid extraction, as well as high voltage electrical discharges. Low toxicity, low volatility, and biodegradability of eutectic solvents in combination with various physical methods for intensifying the extraction process led to the gradual substitution of conventional solvents like alcohols and hydrocarbons in addressing a diverse range of problems solved by the SLE method. This ongoing transition is anticipated to actively introduce DESs in resolving various technological challenges in the near future. This shift towards DESs is poised to make a significant contribution to environmental sustainability and resource conservation by diminishing emissions and optimizing resource utilization.

Challenges and future directions

The utilization of biomass for producing value-added products and energy has garnered significant attention from researchers. However, the commercialization of biomass processing technologies faces challenges related to costs, biodegradability, and toxicity issues. Conventional solid-liquid extraction, employing organic solvents to facilitate extraction is commonly used for of high-value-added products. The choice of solvents is critical for efficient extraction. Typically, methanol or ethanol is used as the solvent, which often requires large volumes for efficient extraction, leading to cost concerns and ecotoxicity issues. In contrast, DESs have emerged as promising alternatives for biomass volarization due to their unique physicochemical properties and versatile applications. DESs are currently attracting widespread scientific and technological interest as an alternative to conventional ILs. In principle, DESs are a mixture of two or more compounds with a melting point lower than that of either of its components [81]. DESs possess many advantages compared to ILs: (i) they are simple to synthesize since the components are salts, and hydrogen bond donor (HBD)/ complexing agent that can be easily mixed and converted to DESs without the need for further purification; (ii) they have a low production cost due to the low cost of raw materials; and (iii) DESs are expected to have good biocompatibility when using quaternary ammonium salts such as choline chloride (ChCl), which is currently being used as an additive in chicken feed [82]. Moreover, DESs appear to be a less toxic alternative to ILs. The toxicity of DESs is affected by its composition, viscosity, and concentration. The concentration of any DESs has a significant impact on its toxicity, as indicated by the LC50 (lethal concentration at 50 %) value. Also, aqueous DESs were found to be less harmful to *Cyprinus carpio* than their individual constituents. There is also a discussion of the component's type and how it interacts with the organism's cell type. It was observed that Type I (containing organic salt and metal salt) and Type II DESs (containing organic salt and hydrate metal salt), due to the presence of metal salts, are more toxic than Type III DESs, which are made up of organic salts. In contrast to ILs, the toxicity level of DESs depends on the individual salt and its HBD, with a stronger hydrogen bond contributing to lower toxicity [83].

Despite the potential benefits of DESs in biomass processing, challenges persist in discovering renewable energy resources with lower energy consumption and operational costs, along with achieving high processing efficiency. It is crucial to emphasize these points in the context of biomass handling and green solvents, despite the potential shown by DES in biomass processing.

The development of green DESs alternatives for conventional solvents is a promising approach to sustainable chemistry. However, conducting in-depth research and development efforts focused on understanding the structure-property relationships of solvents, as well as their interactions with biomass components, is essential for informed solvent design. Researchers need to utilize advanced analytical techniques, computational modeling, and experimental validation to gain insights into the underlying mechanism governing solvent behavior and performance.

The recyclability of DESs is one of the major future issues to be addressed due to the difficulty of its purification after the reaction process. The challenges related to purifying DESs can be particularly limiting when attempting to scale up the use of DESs in industrial processes. The inefficiency of purification processes can make large-scale DESs applications less practical and cost-effective.

Viscosity, an essential property of liquids, significantly impacts mass transport and conductivity, thereby influencing functionality in various applications. DESs exhibit high viscosities owing to the continuous network of hydrogen bonding among their constituents, which restricts the mobility of free species within the DESs mixture. The decrease in viscosity with increasing temperature is attributed to the considerable reduction in hydrogen bonding interactions in DESs at higher temperatures [84]. For instance, the dissolution of rice straw biomass in carbohydrate-based DESs increases the viscosity of the mixture, leading to a lower dissolution ratio. However, the introduction of water (up to 10 wt%) to DESs with different molar ratios facilities the dissolution of lignin [85]. Dissolution slows down considerably as the solution becomes viscous. The viscosity of DESs decreases with an increase in water content. DES with a water content of 5 wt% increases biomass digestion, allowing dissolved lignin to be easily released into the DESs solvent [86]. Viscosity plays a critical role in industrial applications, particularly when DESs establish strong hydrogen bonding networks. Most DESs exhibit moderate viscosities ranging between 173 and 783 mPa.s at 25 °C. The wide range in viscosity is associated with the interaction strength between the HBD and the HBA. Trends in viscosity show that longer alkyl chains result in higher viscosity, and larger anions (such as Br^{-}) have higher viscosity than similar anions (such as Cl^{-}) [87]. This viscosity trend in DESs is akin to that observed in most ionic liquids.

There are issues regarding the thermal stability of ChCl due to volatilization of its HBA and/or HBD components. Thermal stability analysis of DESs revealed that these solvents primarily decompose into HBA and HBD through the weakening and breaking of hydrogen bonds. In general, two decomposition steps are observed for DESs components. The first step is a volatilization that occurs to the component with a lower boiling point or poorer stability (usually HBD). The second step is the volatilization or decomposition of the other component of the DESs at a higher temperature (usually HBA). Furthermore, Marchel et al. [88] reported that hydrogen bonds play a crucial role in the thermal stability of DESs since they prevent molecules from "escaping", requiring more energy to break the bonds compared to pure HBA and HBD. The analysis showed that when a ChCl:glucose DESs was heated at 80 °C for 2 h that there were no significant changes. However, at 100 °C, the DESs started to decompose and with more time and a higher temperature it underwent further decomposition, as indicated by additional peaks in the HPLC-UV chromatograms. This suggests that the stability of ChCl: glucose DESs decreases at higher temperatures and over extended periods. The study highlights the importance of using stable materials for DESs to achieve higher T_{onset} values. The typical temperatures applied for biomass extraction or treatment vary depending on the specific process and desired outcomes. Generally, temperatures can range from ambient to elevated temperatures, typically between 50 °C and 200 °C. Temperature plays a crucial role in facilitating biomass breakdown, solubilization of target compounds, and altering biomass structure to enhance downstream processing. Moreover, temperature influences the selectivity and yield of extracted components, as well as the overall energy consumption and environmental impact of the process. Thus, exploring the temperature ranges and their implications is essential for evaluating the effectiveness of various extraction and treatment methods.

Conclusion

The integration of SLE and DESs represents a transformative stride toward a more sustainable and environmentally conscious approach to biomass valorization. The adoption of deep eutectic solvents, with their eco-friendly composition, significantly mitigates the environmental impact, aligning with the principles of green chemistry. Recent research findings underscore the feasibility and benefits of this greener approach. Moreover, comprehensive analysis, incorporating experimental investigations, computational modeling, and life cycle assessments, adds depth to our understanding of the environmental implications, reinforcing the sustainability of the proposed methodology. While the combination of SLE and DESs shows promise in biomass valorization, further research is needed to explore its potential benefits and drawbacks. The difficulty in selecting an analyte that is compatible with DESs is one of its drawbacks. Therefore, it is crucial to study the combination of SLE and DESs more extensively in the future to fully understand its applicability and optimize its use in biomass valorization processes.

As the global demand for sustainable resources intensifies, this review contributes not only valuable insights to the scientific community but also offers a tangible solution for industries seeking more eco-friendly alternatives. The pursuit of a greener approach for biomass valorization through the integration of SLE and DESs signifies a pivotal step toward a future where renewable resources are harnessed efficiently and responsibly, fostering a harmonious coexistence with the environment. This review will inspire the researchers to evolve biomass utilization practices that are both economically viable and ecologically sound.

CRediT authorship contribution statement

Niluh Indria Wardani: Writing – original draft, Investigation, Formal analysis. **Thidarat Samkumpim:** Writing – original draft, Investigation, Formal analysis. **Waleed Alahmad:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Andrew William King:** Writing – review & editing. **Pakorn Varanusupakul:** Project administration. **Andrey Shishov:** Writing – original draft. **Noorfatimah Yahaya:** Conceptualization. **Nur Nadhirah Mohamad Zain:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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