Application of deep eutectic solvents in biomass valorization

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Abstract

High reliance on crude oil for energy consumption results in an urgent need to explore and develop alternative renewable sources. One of the most promising routes is the transformation of biomass into biofuels and value-added chemicals. The introduction of deep eutectic solvents (DESs) in 2004 has received considerable amount of attention across different research fields particularly in biomass processing. The effectiveness of DESs in breaking down the recalcitrant structure of lignin in biomass highlights its impact on transformation of biomass into various value-added products. In comparison with some common solvents used in biomass valorization, DESs are able to produce highly concentrated solutions of carbohydrates, sometimes liquid at approximately room temperature. Besides, DESs are widely regarded as a promising green solvent due to its low cost, low toxicity and biodegradable properties. In this paper, firstly some background information on lignocellulosic biomass and DESs were given. Then, the mechanism and role of DES in pretreating biomass were discussed such as the impacts of DESs on the selectivity of chemical processes and dissolution of biomass by DESs. This review also highlighted the advantages and limitations of DESs associated with its usage on biomass pretreatment.

1.0   Introduction

Of late, the depletion of crude oil reserves, ever increasing global energy demand and regional concerns over energy security have encouraged a global policy shift from fossil reserve to use of biomass as an alternative source of renewable energy [1]. Having a production rate of 170-200 billion tons annually, lignocellulosic biomass could be regarded as one of the most abundant and renewable feedstocks that is essential to create a sustainable global environment [2]. Instead of disposing this lignocellulosic biomass as waste, it could be converted into various value-added products such as bio-fuels, energy sources or chemicals [3]. Due to the fact that it is abundantly available, the transformation of lignocellulosic biomass into reducing sugars which could be subsequently transformed into bio-fuels or other value added-products could be the potential sustainable solution to the aforementioned global issue. To date, the production of bioethanol from lignocellulosic biomass is very popular and the annual production capacities of bioethanol derived from banana residual, corn and sugarcane are 0.019 million litres per year, 39.5 billion litres per year and 30 billion litres per year respectively [4-5].

Due to the recalcitrant structure of lignin content in lignocellulosic, a pretreatment stage is usually essential before biomass could be transformed into value-added products [6]. Without pretreatment stage, only 20% of sugar recovery was possible [7], but the sugar recovery could be increased up to 80-83% with a pretreatment process [8]. The purpose of the pretreatment stage is to alter the structure of the biomass by breaking the main protective barrier of the biomass, which is lignin. The microscopic view of the lignin content present in lignocellulosic biomass is shown in **Figure 1**. Lignin is a complex structure which is composed of various cross- linked polymers of phenolic monomers [10]. It is present in the cell wall and provides the structural support and resistance against microbial attack. Its crystalline structure inhibits the accessibility of hydrolytic enzymes into the polysaccharides [11]. Therefore, delignification of biomass is essential to break the condensed lignin layer to ease the penetration of enzymes to the polysaccharides, leading to greater percentage
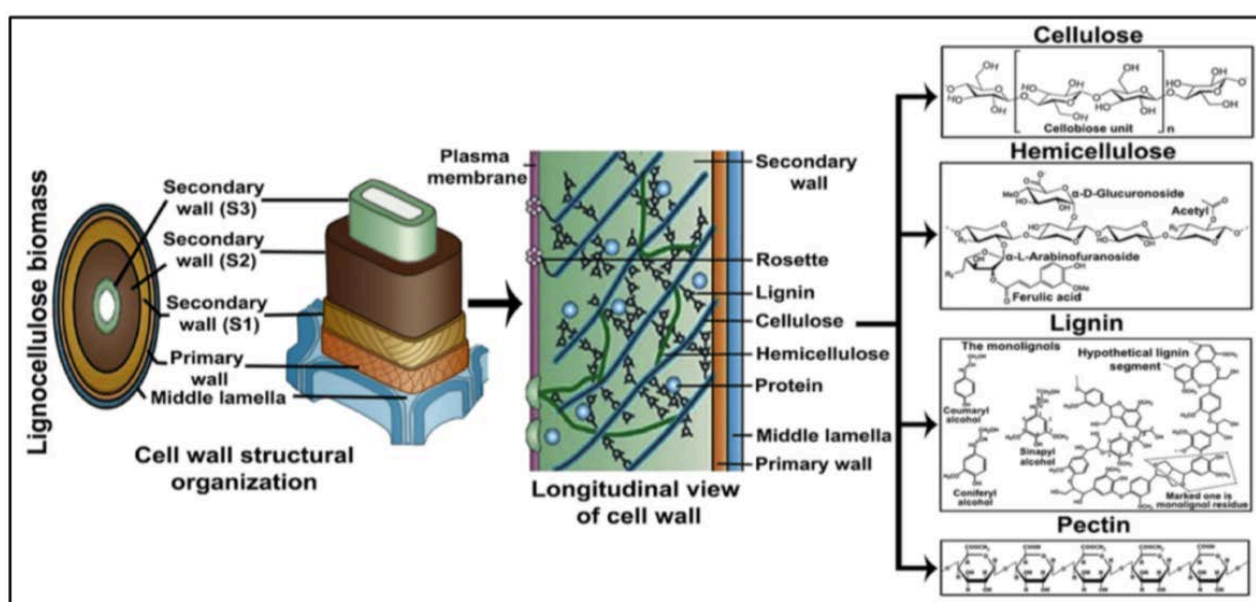
Fig. 1 Microscopic view of the structure and chemical composition of a typical lignocellulosic biomass [9]

of sugar recovery.

The percentage of lignin content in comparison with the hemicellulose and cellulose content in various biomass is shown in **Table 1**.

Table 1 Lignin, hemicellulose and cellulose content in various biomass [3]

Lignocellulosic material	Lignin (%)	Hemicellulose (%)	Cellulose (%)
Sugar cane bagasse	20	25	42
Sweet sorghum	21	27	45
Hardwood	18-25	24-40	40-55
Softwood	25-35	25-35	45-50
Corn cobs	15	35	45
Corn stover	19	26	38
Wheat straw	16-21	26-32	29-35
Grasses	10-30	25-50	25-40
Banana waste	14	14.8	13.2
Bagasse	23.33	16.52	54.87

For decades, various pretreatment methods on lignocellulosic biomass were studied such as physical methods (energy irradiation, ball milling), chemical methods (ionic liquid, inorganic salt, alkaline hydrolysis) and biological methods. Ionic liquid (ILs) seemed to be the most promising method in terms of delignifying lignocellulosic biomass in order to enhance the penetration of enzymes or solvents for the subsequent hydrolysis process. This was due to its special properties such as non-volatility and also its reagent could be varied according to the type of desired extractions [12]. The chemistry for lignin dissolution using ILs was rather complex and involves cleavage of more than one bond type such cleavage of β-aryl ethers and α-aryl ethers. The process of cleaving such bonds was carried out by a two-step reaction mechanism whereby the first step involves elimination of water followed by hydronium ion attack on the ether oxygen which formed a protonated ether [13]. In spite of being the most promising method, IL possessed several disadvantages such as high cost, high toxicity and long term recyclability concern [14].

Recently, the emergence of deep eutectic solvent (DESs) in lignocellulosic biomass pretreatment is becoming more significant as it is a greener solvent than ILs. Generally, DES is formed from the combination of two or three ionic compounds (usually cheap and safe compounds), forming a eutectic mixture with a melting point lower than its constituent components (Procentese et al., 2015). DES was more preferable over the conventional ILs pretreatment method because DES exhibited similar chemical and physical properties as ILs but possessed additional benefits such as it was easier to prepare, used renewable materials and also less

complicating purification method was needed [15]. According to Xu et al. (2016), the cost to synthesize a DES was only about 20% of the cost as compared to IL [16]. Even though DES possessed more benefits over IL, it was still not widely used because it was still relatively new in biomass processing. Hence, this review paper serves to highlight and discuss the effects of DES on the valorization of lignocellulosic biomass.

2.0   Preparation of DES

DES is defined as a new class of solvent which consists of ions and presents as liquid at temperature <100°C [17-18]. Its introduction was reported by Abbott and co-workers by mixing a hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) in a solid phase to form an eutectic mixture in a liquid phase upon gentle mixing at moderate temperature (60-80°C) [19]. This formation implied a large depression of melting point in DES as compared to either of its individual component [14, 17]. To differentiate DESs from ILs, the individual component opted for the formation of DES was often selected from safe and biodegradable components, such as choline chloride (ChCl), carbohydrates, carboxylic acids, amides and glycerol. Among the individual components selected to produce DES, ChCl (as HBA) combined with urea (as HBD) was the most common DES [20]. The synthesis of DES could be done via three common methods:

a.   Heating with agitation: The two-component mixture was placed in a beaker with a magnetic stirring bar and heated under literature temperature (60 - 120°C). This was done to the extent where a clear liquid solution was formed, which took about 60 to 90 min [19].

b.   Evaporating method: Using a rotatory equipment, the components were dissolved in water and evaporated at 50°C. The liquid obtained was kept in a desiccator with silica gel until a constant weight was achieved [21].

c.   Freeze drying method: The basis of this method was using the freeze-drying of aqueous solution which consisted of the individual components of the DES. However, this method was rarely utilized as compared to the former two methods [22-23].

3.0   Types and Properties of DES

By combining proper proportions of salts and HBDs, different types of DESs could be formed. **Table 2** tabulates different types of DESs identified based on the combinations of different chemicals used:

Table 2 General Formula for Classification of DESs [24]

Type	Terms	General Formula	Example
1	Metal salt + organic salt	$Cat^+ X^-$ $zMClx$; M = Zn, Sn, Fe, Al, Ga, In	$ZnCl_2$ + ChCl
2	Metal salt hydrate + organic salt	$Cat^+ X^-zMClx \cdot yH2O$; M = Cr, Co, Cu, Ni, Fe	$CoCl_2 \cdot 6H_2O$ + ChCl
3	Hydrogen bond donor + organic salt	$Cat^+ X^-$ zRZ; Z = $CONH_2$, COOH, OH	urea + ChCl
4	Zinc/Aluminium chloride + Hydrogen bond donor	$MClx + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}^-$; M = Al, Zn & Z = $CONH_2$, OH	$ZnCl_2$ + urea

The knowledge on DESs' physicochemical properties has been widely explored due to the need to accurately understand the properties in various industrial applications [18]. The main characteristics of DESs such as freezing point, density, viscosity, surface tension and conductivity were discussed as followed:

3.1 Freezing Point

The formation of DES could be completed through the mixing of two solids which are capable of producing a new solvent by self-association via hydrogen bonds. One of the main distinct and essential properties of DES was a lower freezing point as compared to its constituent components. **Figure 2** illustrates the eutectic point of DES on a two component phase diagram.
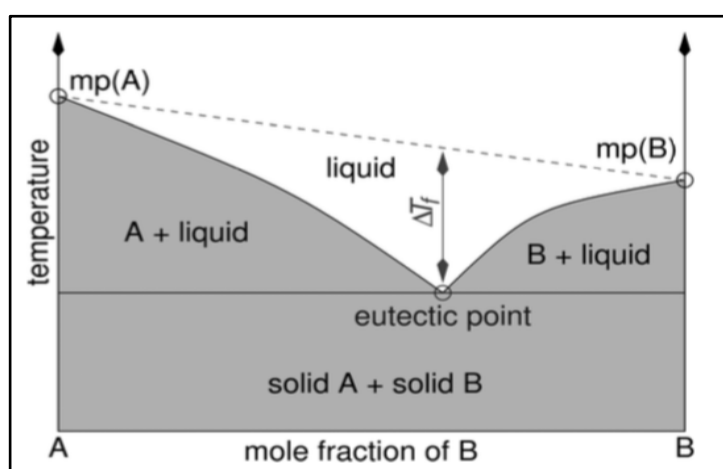
Fig. 2 Schematic representation of eutectic point on a two component
phase diagram [24]

For example, the combination of choline chloride and urea resulted in a DES mixture with a freezing point of 12°C, which was relatively lower that the freezing point of its constituent components (melting point of choline chloride and urea are 302°C and 133°C respectively). The properties that affected the freezing point of DESs would be the types of HBD and organic salt used during the synthesis [25]. The sharp decrease in freezing point of DESs was due to the delocalization of charge as a results of hydrogen bonding between HBD and a halide ion [17]. In addition, Smith et al. (2014) discovered that it was also dependent on the composition of HBD in the mixture. Several studies showed that the factors affecting the freezing point of DESs were internal energy of DESs molecule and also the change in entropy during the process of forming liquid [24, 26]. To date, all recent studies on DES showed that it exhibited a freezing point of below 150°C. However, only DES with a freezing point of below 50°C attracted interest since they were cheap and non-toxic, making them viable in various field of applications.

3.2 Density

Density of a solvent plays a very important role in studying its applicability in various field of studies. To date, most DESs exhibited a higher density as compared to water. For example, type IV DES ($ZnCl_2$/HBD)

possessed a density greater than 1.3 g/cm^3. However, different types of HBD led to a different density. For example, the density of ZnCl$_2$/Urea and ZnCl$_2$/Acetamide were 1.63 and 1.36 g/cm^3, respectively (Zhang et al., 2012). Since DESs were composed of holes, the density behavior was affected by the packing and arrangement of the DESs' molecules [25]. The hole theory described well the density property of DES. For instance, the combination of ZnCl$_2$ and urea, resulted in the decrease of the average hole radius, which in turn resulted in a decrease of DES density as compared to the pure urea [27]. Besides, Shahbaz et al. (2011) also discovered that an increase in temperature would lower the density of the DESs [28]. This was due to the accelerated motion of DES particles, creating more empty spaces within the molecule. Additionally, an increase in the water content in the DESs molecule would cause a decrease in its density [18].

3.3 Surface Tension

Surface tension arises from the reduction of surface area of the liquid's interface with other phases in contact with the liquid, which is caused by the cohesive tension resulted from the intermolecular attractive forces in the liquid. Generally, DES has a higher surface tension than most ILs because surface tension is closely associated with strength of intermolecular forces [14]. The effect of the type of cation on the surface tension is of great significance. It was proven that the hydroxyl group in cation would lead to a higher surface tension due to their hydrogen-bonding ability [17-18]. This statement was further supported by Hayyan et al. (2013), who reported that the surface tension of glucose-based DES were higher than those reported for carboxylic acids-based DES [29]. AlOmar et al. (2016) suggested that a decrease in surface tension was due to an increase of temperature. This was further explained by the gain of energy in the salt that broke up the intermolecular forces such as hydrogen bonding [30].

3.4 Viscosity

Viscosity is a critical property that must be accounted for equipment design and fluid flow calculation [30]. DESs possessed higher viscosity as compared to ILs at room temperature except ChCl-Ethylene Glycol [24, 31]. This property was mainly attributed to the relatively large ions size and free volume in the ionic systems [24]. Based on experimental result, the viscosity of DESs decreased with increasing temperature and ChCl amount, indicating the adoption of Arrhenius-like behavior shown in **Equation (1)** [29,30,32].

$$\mu = \mu^o e^{\frac{E_\mu}{RT}} \text{ ---------- Equation (1)}$$

Where μ is the dynamic viscosity (Pa.s), μ^o is the pre-exponential constant (Pa.s), E_μ is the activation energy (kJ mol^{-1}), R is the gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K).

In general, viscosity of DESs is mainly affected by the chemical nature of DES starting materials such as type of HBD and HBA, molar ratio of HBD and HBA, temperature and water content. Thus, the hole theory could again be employed to design DESs with low viscosity [27]. This method, for example, could be formulated using small cations HBD to lead to low viscosity DES [27].

3.5 Conductivity

Currently, the development of DESs in electrochemical applications has been rapid and extensive, which prompted great demand over their electrical conductivity [30]. The highly viscous property of DESs implied the low conductivity possessed by DESs. In addition, the electrical conductivity of DESs was highly dependent on the temperature, such as a notable increase of conductivity could be due to an increase of temperature [33]. Despite of its relative poor conductivity as compared to normal ILs, DES were still widely considered as good conductors in comparison to conventional organic solvent [33].

Table 3 tabulates a list of different combinations of ammonium salts and HBD that form Type III and Type IV DES, accompanied with their unique physico-chemical properties such as freezing point, density, viscosity, surface tension and conductivity:

4.0   Recent Development of DES in Biomass Processing

The use of DES in biomass processing is still in the preliminary stage as compared to the development of DES in other industries such as electroplating and biodiesel extraction. Thus far the mechanisms of DESs were focused on the extraction of phenolic compound from the lignocellulosic biomass and its ability to dissolve lignin in order to enhance the extraction of reducing sugars in the downstream process.

4.1   Extraction of Phenolic Compounds

The functional role of DES in extraction of phenolic compounds in the lignocellulosic materials highly relied upon its ability to donate and accept protons and electrons, which improved the chances of hydrogen bonds formation, thus increasing their dissolution capability [35]. Besides the selection of DES, temperature and extraction duration were the important parameters to be considered in order to achieve maximum yield of phenolic compounds. Cvjetko Bubalo et al. (2016) reported that ChCl-Oxalic acid with 25% water produced a maximum yield of phenolic compounds from grape skin, namely flavonoids which consisted of anthocyanins, (+)-catechin and quercetin-3-O-glucoside at the operating condition of 65°C and 50 min. The yields of anthocyanins, (+)-catechin and quercetin-3-O-glucoside were determined to be 17 mg g^{-1}, 26 mg g^{-1} and 30 mg g^{-1} of grape skin respectively [35]. Besides, DES demonstrated a higher extraction efficiency for (+)-catechin content with the presence of water in comparison with pure DES. Yao et al. (2015) explained that this phenomena could be devoted to the reduction of viscosity of DES via the addition of water, which adjusted the polarity and hence increased the solubility [36].

Wei et al. (2015) also performed the microwave assisted extraction of 14 phenolics from *C.cajan* leaves via different types of DESs [37]. The result showed that choline chloride-maltose DES produced the highest total yield of 14 active components at 30.63 mg g^{-1} of biomass. Furthermore, an addition of 20% (v/v) of water, the extraction efficiency of phenolic compounds markedly increased from 40 to 60% due to the effective decrease of viscosity of DES [37].

Xia et al. (2015) used different molar ratios of ChCl-based DESs in extracting phenolic acids (30 min, 80°C) such as rosmarinic acid and salviaflaside from *Prunella vulgaris* [38]. It was determined that the combination of ChCl and ethylene glycol at 1 : 4 molar ratio gave the best extraction yield at 2.87 mg g^{-1} and

0.92 mg g^{-1} of rosmarinic acid and salviaflaside, respectively [38]. From a molar ratio of 1:2 to 1:4, the extraction yield experienced a slight total decrease of 0.5mg g^{-1}, which could be explained by an increase in viscosity and surface tension of DES at 1:2 molar ratio [37].

Table 3 Summary of the properties of various DES combination

Hydrogen Bond Donor	Hydrogen Bond Acceptor	Molar ratio (HBD:HBA)	Freezing point (°C)	Density (g/cm^3)	Viscosity (cP)	Surface tension (mN m^{-1})	Conductivity (mS cm^{-1})	References
Urea	ChCl	2:1	12	1.25	750 (25°C)	52 (25°C)	0.75 (25°C)	[24, 27]
Ethylene Glycol	ChCl	2:1	-12.9	1.12	37 (25°C)	49 (25°C)	7.61 (25°C)	[24, 27]
Glycerol	ChCl	2:1	17.8	1.18	259 (25°C)	55.8 (25°C)	1.05 (25°C)	[24, 27]
2,2,2-Trifluoroacetamide	ChCl	2:1	Liquid at 25°C	1.342	77 (40°C)	35.9 (25°C)	-	[33]
Acrylic acid	ChCl	1.6:1	Liquid at 25°C	-	115 (22°C)	-	-	[33]
Malonic acid	ChCl	1:1	10	-	721 (25°C)	65.7 (25°C)	0.55 (25°C)	[27, 34]
1,4-Butanediol	ChCl	3:1	-32	1.06	140 (20°C)	47.17 (25°C)	1.64 (25°C)	[27, 34]
CF$_3$CONH$_2$	ChCl	2:1	51	1.342	77 (40°C)	-	-	[24, 27]
Imidazole	ChCl	7:3	56	-	15 (70°C)	-	12 (60°C)	[27, 34]
ZnCl$_2$	ChCl	2:1	-	-	85000 (25°C)	-	0.06 (42°C)	[24, 27]
Urea	ZnCl$_2$	3.5:1	9	1.63	11340 (25°C)	-	0.18 (42°C)	[24, 27]
MeCONH$_2$	ZnCl$_2$	4:1	-	1.36	-	-	-	[27]
Ethylene	ZnCl$_2$	4:1	-	1.45	-	-	-	[27]

Glycol								
Hexanediol	$ZnCl_2$	3:1	-	1.38	-	-	-	[27]
Imidazole	Bu_4NBr	7:3	-	-	810 (20°C)	-	0.24 (20°C)	[24, 27]
CF_3CONH_2	$EtNH_3Cl$	1.5:1	-	1.273	256 (40°C)	-	0.39 (40°C)	[24, 27]
Acetamide	$EtNH_3Cl$	1.5:1	-	1.041	64 (40°C)	-	0.688 (40°C)	[27, 34]
Urea	$EtNH_3Cl$	1.5:1	-	1.140	128 (40°C)	-	0.348 (40°C)	[27, 34]
Glycerol	Methyltriphenyl phosphonium bromide	3:1	-5.55	1.30	-	58.94 (25°C)	0.062 (25°C)	[33]
Ethylene Glycol	Methyltriphenyl phosphonium bromide	4:1	-49.34	1.23	-	51.29 (25°C)	1.092 (25°C)	[33]
Triethylene Glycol	Methyltriphenyl phosphonium bromide	5:1	-21	1.19	-	49.58 (25°C)	-	[33]
Urea	AcChCl	2:1	-	1.206	2214 (40°C)	-	0.017 (40°C)	[27, 34]

4.2   Solubilisation of Lignin

Although the development of using DES in dissolution of biomass is still infancy, the promising preliminary works showed the potential of using DES in pre-treatment processes of biomass. As the presence of lignin is in a form of phenolic compound, ChCl-based DES was particularly useful in separation of phenol. This was further aided by the short equilibrium time and stability exhibited by ChCl at a wide range of temperature [20]. DES was associated with delignification and reduction in cellulose crystallinity [14], mainly because DES was capable of donating and accepting protons and electrons. This characteristic of DES enabled the formation of hydrogen bond with other compounds which undoubtedly enhanced it dissolution capability [39]. However, most of the DESs have experienced failures in the attempt to dissolve cellulose within an acceptable concentration range [17]. As explained by Virgier et al. (2015), the reason could be the possession of strong hydrogen bond network by both cellulose and DES, in which dissolution of cellulose in DES requires 2 hydrogen bond networks to be dissociated to form a thermodynamically stable system [14]. Due to the strong cohesive energy of cellulose, the dissolution of cellulose in DES could be difficult. In spite of the negative results, some DESs have been suggested to possess significant impacts in dissolution of lignin, dissolving large amount of lignin with the cellulosic regions suspended in the supernatant liquid [17]. **Table 4** summarizes the comparison of DES with different established delignification methods on lignocellulosic biomass. Despite the potential shown by DES in biomass processing, the recyclability of DES and their thermal stability were the two major issues to be resolved in the future [14]. It was expected that the purification of DES at the end of the reaction to be difficult and energy consuming, indicating the constraints in scaling up of the extraction technology. Moreover, the issue regarding the thermal stability of ChCl, an important feedstock of DES synthesis, was needed to be addressed. This was attributed to the basic nature of ChCl, which might trigger a Hoffman elimination reaction at elevated temperature which released trimethylamine that proved to be a detrimental component for the industrial viability of the technology [14]. Thus, these limitations must be overcome before DES could be implemented in industrial scale for biomass processing.

5.0   Other Applications of DES

Although DES is still considered as a new solvent in biomass processing, its applications in other sectors have been widely explored and discussed. Firstly, the use of DES in biodiesel production has gained remarkable attention due to its environmental benefits and process improvements. As opposed to the use of IL in biodiesel production, DESs possessed different roles whereby they could be used as a catalyst or co-solvent in the biodiesel synthesis steps. Also, it could be used as extracting solvent in the biodiesel purification step [41]. Besides that, DES was used as a co-solvent by incorporation with other biocatalysts with the aim of improving their combined catalytic activity [42]. The utilization of DES as a catalyst in the biodiesel production step could be proven by the study done by Long et al. (2010), whereby DES was used as a Lewis acidic catalyst in the methanolysis process of soybean oil [43]. During the purification step, DES was found to be efficient in extracting glycerol from the crude biodiesel. For example, DES which was synthesized from ChCl and glycerol could be used in the purification of crude biodiesel from the methanolysis of rapeseed and soybean oil. It was found that the glycerol contents from rapeseed and soybean oil were reduced to 0.06 wt.% and 0.02 wt.%, respectively [44]. Next, the incorporation of DES with other catalyst was discovered to be efficient in the production   of   biodiesel.

Table 4 Summary of lignin solubilisation methods by different types of DES reagents

DES reagent	Mol ratio	Lignocellulosic Biomass	wt% Delignification	Solubilisation method	References
Lactic acid - Betaine	2:1		52 ± 6	At 5 wt% biomass solid loadings, respective concentrations of DES reagent were added to biomass contained in a screw capped conical flask. Reaction vessel was incubated at 60°C for 12 h with agitation at 100 rpm. The pre-treated solid biomass residue was separated from soluble lignin hydrolysate by low speed centrifugation at 5000 rpm for 30 min at room temperature.	[12]
	5:1		56 ± 3		
Lactic acid – ChCl	2:1	Rice straw	51 ± 1		
	5:1		60 ± 2		
	9:1		59 ± 3		
Formic acid – ChCl	-	Corn stover	23.8	DES reagent was added to a 1L three necked flask and heated to 130°C. 5.0 g of corn stover was added in and the reaction vessel was incubated at 130°C for 2 h with agitation of 100 rpm.	[16]
Imidazole – ChCl	2:1		70	The DES reagent synthesized was stirred at 500 rpm in an oil bath to form a homogenous liquid. Corncob was added in at a solid wt. ratio of 16:1 and the temperatures were set at 115°C under the same agitation for 15 h.	[40]
Urea – ChCl	2:1	Corncob	24.8		
Glycerol - ChCl	7:3		4.4		

For example, the ChCl:glycerol (2:1) enhanced the use of conventional CaO catalyst by eliminating the inactive layers of $CaCO_3$ and $Ca(OH)_2$ from the surface of the solid catalyst. The presence of DES in the methanolysis of rapeseed oil with the calcinated CaO has increased the ester yield from 87.3% to 95.0% [45].

For decades, DESs have been utilized extensively in the metal processing industry. The traditional electro finishing industry was based on aqueous system which could be attributed to the high solubility of electrolytes and metal salts in the water. However, this technology encountered drawback due to the narrow potential window of the water. This setback caused the deposition of some metals to be hindered by poor current efficiency of the substrate [24]. Therefore, DESs possessed the ability to replace the aqueous electrolytes in terms of incorporation of metal ions in the solution for metal deposition, metal dissolution and metal processing. Generally, DES is more preferable over aqueous solvent as the former exhibits higher solubility of metal salts, absence of water and higher conductivity [46]. The metal processing industry was divided into three sections namely metal electrodeposition, metal electropolishing and extraction as well as processing of metal oxides. In the metal electrodeposition process, as compared with the aqueous and organic based electrolyte, DESs possessed additional advantage as it exhibited higher solubility for metal salts. Also, the issue of passivation which inhibited the deposition of target metal could be prevented. Therefore, thicker metal films could be more easily deposited in the DESs. Furthermore, the issue with legal restriction could be prevented as DES did not contain any hazardous complexing agent [46]. Moving on to the electropolishing industry, the principle of this industry was to control the dissolution of metal on a surface with the purpose to reduce surface roughness, increase optical reflectivity, increase corrosion resistance, decrease wear, etc. The conventional method was based on aqueous phosphoric and sulphuric acid which were mixed with certain additive such as CrO_3. However, the drawback of this method was the corrosiveness and toxicity of the solution. Hence, DES was discovered to be the better alternative due to several advantages such as negligible gas evolution at the anode/solution interface, higher current efficiency and the benign yet non-corrosive properties.

The next widely used application of DES can be seen in the efficient absorption of sulphur dioxide, SO_2 which is the major pollutant due to the combustion of fossil fuel. Thus, the method of removing SO_2 has been the major topic of interest among researchers. Generally, the method of removing SO_2 is using limestone scrubbing but this technique possess several disadvantages such as low efficiency, irreversible process and production of undesired byproducts such as wastewater and $CaSO_4$ [47]. Besides that, the usage of various organic solvents such as ethylene glycol, 1,4 – dioxane and sulfolane for removal of SO_2 have been proven unsuccessful due to the fact that these solvents have the tendency to volatilize at high temperature [47]. In a study carried out by Yang et al. (2013), the ChCl-glycerol DESs were able to reduce the SO_2 content by 0.678 g SO_2 per g DES at 293 K and 1 atm [48]. This finding was agreed by Liu et al. (2013) in which they discovered that the absorption capacity of amide-thiocynates DESs was also as high as 0.588 g SO_2 per g DES at 293 K and 1 atm [49].

DES also received numerous attention in nanotechnology field mainly due to its properties of being an efficient dispersant and acting as a large scale media for chemical and electrochemical synthesis of advanced nanomaterials. Moreover, DESs also improved the size and morphology of nanomaterial during its synthesis

stage. In this field of study, the most common use of DES was its use as a solvent for chemical synthesis of gold nanoparticles. **Table 5** shows the uses and main roles of DES in nanotechnology.

Table 5 Roles of DES in nanotechnology [33]

DES	Molar ratio	Role
ChCl:Urea	1:2	Electrolyte (nanostructure sensor) Media for nanoparticles production by sputter Electrolyte (nanoparticle deposition) Dispersant
ChCl:1,3DU	2:1	Media for chemical synthesis of nanoparticles
ChCl:TU	1:2	Media for chemical synthesis of nanoparticles
ChCl:EG	1:2	Dispersant Electrolyte (nanoparticle deposition)
ChCl:CrCl$_3$.6H$_2$O	1:2	Electrolyte (nanoparticle deposition)
ChCl:PTSA	1:1	Structure-directing agent and media for chemical synthesis of nanoparticles
ChCl:HMP	1:1	Dispersant
ChCl:ZnCl$_2$	1:1	Nano-confinement
CA:DU	1:1.5	Nanocatalytic assembly

ChCl: choline chloride, U: urea, DU: dimethyl urea, TU: thiourea, EG: ethylene glycol, PTSA: para-toluene sulfonic acid, HMP: tris(hydroxymethyl) propane, CA: citric acid.

The dissolution of metal oxides has been extensively investigated over the past few years. This was attributed to the fact that DESs have the capability to donate and accept electrons or protons, forming hydrogen bonding which provides them excellent dissolution properties. For example, the most common DES (ChCl/Urea) possessed the ability to dissolve various compounds including water-soluble inorganic salt, salts that were partially soluble in the water, aromatic acids and amino acids. This ability to dissolve various types of metal oxides created a "green" method in separating and recycling of metals. For example, the difference in the solubility of metal oxides in DES was utilized in the process of recovering Zn and Pb selectively from the waste products generated by an electric arc furnace [27]. **Table 6** tabulates the solubility of various types of metal oxides in the DES (ChCl/Urea).

Table 6 Solubility of metal oxides in DES (ChCl/Urea) [27]

Metal Oxides	Melting Point (°C)	Solubility (ppm)
Al$_2$O$_3$	2045	<1
CaO	2580	6
CuO	1326	470
Cu$_2$O	1235	8725
Fe$_2$O$_3$	1565	49

Fe$_3$O$_4$	1538	40
ZnO	1975	8466

Table 7 Summary of various applications of DES in the industry.

No.	Application	Conventional method	Drawbacks of conventional method	Advantages of DES	Ref.
1.	Biodiesel production and purification.	Ionic liquid.	• Expensive. • High toxicity. • Non-biodegradable.	• Cheap. • Enhanced glycerol extraction from crude biodiesel. • Increased yield of biodiesel production.	[43-45]
2.	Metal electrodeposition.	Aqueous and organic based electrolytes.	• Passivation effects. • Legal issue due to presence of hazardous complexing agent.	• Higher solubility for metal salts. • Prevents passivation effects. • Thicker metal films can be deposited.	[24, 46]
3.	Metal electropolishing.	Aqueous sulphuric acid and phosphoric acid mixed with certain additives.	• Highly corrosive and toxic.	• Negligible gas evolution. • Higher current efficiency. • Benign and non-corrosive.	[24, 46]
4.	Absorption of sulphur dioxide, SO$_2$.	Limestone scrubbing.	• Low efficiency. • Irreversible process. • Production of undesired byproducts.	• Higher SO$_2$ absorption efficiency.	[47-49]
5.	Nanotechnology	Ionic liquid	• Expensive • High toxicity	• Excellent thermal stability • Good dispersibility • Wide electrochemical window	[33]
6.	Dissolution of metal oxides	N/A	• N/A	• Able to selectively recover metal • Enhance recycling of metal	

6.0 Conclusion

This review provided some insight on the increasing interest of DES which could be used as a "green" solvent over the past few years, especially for the purpose of pretreating lignocellulosic biomass. The commercialization of biomass pretreatment is often restricted by the costs, biodegradability, as well as toxicity issues. In this context, DES showed promising potential in the production of highly concentrated carbohydrates solutions, due to its distinct physicochemical properties and the ability to suit different uses. Hence, DES represented a sustainable alternative to existing and more common pretreatment technologies such as dilute acid and alkaline pretreatment. Despite being established for various industries such as metal finishing, biocompounds extraction, and synthetic applications, the use of DES in biomass pretreatment was relatively unexplored. One of the main concerns regarding the use of DES to pretreat biomass was the presence of minerals and impurities in the biomass which might affect its catalytic processes. Also, thermal stability and recyclability issues of DES were the other concerns if DES was to apply in biomass processing industrially. Nevertheless, information regarding the structure and molecular interaction between the components in DES with the lignocellulosic compounds remained unclear to date. Moreover, only a limited combinations of DESs have been utilized thus far. The vast possibility of different combinations of salts and hydrogen bond donors could prove to be an excellent opportunity to expand the application of these solvents in biorefinery processes. Therefore, further research on the application and scale-up processes using DES as a solvent is required to unlock its full potential as a 'green' solvent and contribute towards new horizons in the biomass pretreatment industry.

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References

[1] Clark, J., Deswarte, F.: Introduction to Chemicals from Biomass: Second Edition, Introduction to Chemicals from Biomass: Second Edition (2015).

[2] Luo, J., Fang, Z., Smith, R.L., Jr.: Ultrasound-enhanced conversion of biomass to biofuels. Progress in Energy and Combustion Science, vol. 41, no. 1, pp. 56-93 (2014).

[3] Iqbal, H.M.N., Kyazze, G. & Keshavarz, T.: Advances in the valorization of lignocellulosic materials by biotechnology: An overview. *BioResources*, vol. 8, no. 2, pp. 3157-76 (2013).

[4] Guerrero, A.B., Aguado, P.L., Sánchez, J. & Curt, M.D.: GIS-Based Assessment of Banana Residual Biomass Potential for Ethanol Production and Power Generation: A Case Study. *Waste and Biomass Valorization*, vol. 7, no. 2, pp. 405-15 (2016).

[5] Liguori, R, Amore, A. & Faraco, V.: Waste valorization by biotechnological conversion into added value products. *Applied Microbiology and Biotechnology*, vol. 97, no. 14, pp. 6129-47 (2013).

[6] Loow, Y.L., Wu, T.Y., Jahim, J.M., Mohammad, A.W., Teoh, W.H.: Typical conversion of lignocellulosic biomass into reusing sugars using dilute acid hydrolysis and alkaline pretreatment. *Cellulose*, DOI: 10.1007/s10570-016-0936-8

[7] Singhvi, M.S., Chaudhari, S. & Gokhale, D.V.: Lignocellulose processing: A current challenge. *RSC Advances*, vol. 4, no. 16, pp. 8271-7 (2014).

[8] He, Y., Zhang, J. & Bao, J.: Dry dilute acid pretreatment by co-currently feeding of corn stover feedstock and dilute acid solution without impregnation. *Bioresource Technology*, vol. 158, pp. 360-4 (2014).

[9] Loow, Y.L., Wu, T.Y., Tan K.A., Lim, Y.S., Siow, L.F., Jahim, J.M., Mohammad, A.W., Teoh, W.H.: Recent advances in the application of inorganic salt pretreatment for transforming lignocellulosic biomass into reducing sugars. *J Agr Food Chem* 63(8), 8349-8363 (2015).

[10] Kumar, P., Barrett, D.M., Delwiche, M.J. & Stroeve, P.: Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Industrial and Engineering Chemistry Research*, vol. 48, no. 8, pp. 3713-29 (2009).

[11] Manavalan, T, Manavalan, A & Heese, K.: Characterization of Lignocellulolytic Enzymes from White-Rot Fungi. *Current Microbiology*, vol. 70, no. 4, pp. 485-98 (2015).

[12] Kumar, A.K., Parikh, B.S. & Pravakar, M.: Natural deep eutectic solvent mediated pretreatment of rice straw: bioanalytical characterization of lignin extract and enzymatic hydrolysis of pretreated biomass residue. *Environmental Science and Pollution Research* (2015).

[13] Keskar, S.S., Edye, L.A., Doherty, W.O.S. & Bartley, J.P.: The chemistry of acid catalyzed delignification of sugarcane bagasse in the ionic liquid trihexyl tetradecyl phosphonium chloride. *Journal of Wood Chemistry and Technology*, vol. 32, no. 1, pp. 71-81 (2012).

[14] Vigier, K.D.O.D., Chatel, G.D. & Jérôme, F.: Contribution of deep eutectic solvents for biomass processing: Opportunities, challenges, and limitations. ChemCatChem, vol. 7, no. 8, pp. 1250-1260 (2015).

[15] Gunny, A.A.N., Arbain, D., Nashef, E.M. & Jamal, P.: Applicability evaluation of Deep Eutectic Solvents-Cellulase system for lignocellulose hydrolysis. *Bioresource Technology*, vol. 181, pp. 297-302 (2015).

[16] Xu, G.C., Ding, J.C., Han, R.Z., Dong, J.J. & Ni, Y.: Enhancing cellulose accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation. *Bioresour Technol*, vol. 203, pp. 364-9 (2016).

[17] Domínguez de María, P.: Recent trends in (ligno)cellulose dissolution using neoteric solvents: Switchable, distillable and bio-based ionic liquids. *Journal of Chemical Technology and Biotechnology*, vol. 89, no. 1, pp. 11-8 (2014).

[18] García, G., Aparicio, S., Atilhan, M.: Deep eutectic solvents: Physicochemical properties and gas separation applications. *Energy and Fuels*, vol. 29, no. 4, pp. 2616-2644 (2015).

[19] Abbott, A.P., Boothby, D., Capper, G., Davies, D.L., Rasheed, R. K., *J. Am. Chem. Soc.*, vol. 126, pp. 9142–9147 (2004).

[20] Tang, B., Zhang, H. & Row, K.H.: Application of deep eutectic solvents in the extraction and separation of target compounds from various samples. *Journal of Separation Science*, vol. 38, no. 6, pp. 1053-64 (2015).

[21] Dai, Y., van Spronsen, J., Witkamp, G.J., Verpoorte, R., Choi, Y.H.: Natural deep eutectic solvents as new potential media for green technology. *Anal. Chim. Acta* 766 pp. 61–68 (2013).

[22] Espino, M., de los Ángeles Fernández, M., Gomez, F.J.V. & Silva, M.F.: Natural designer solvents for greening analytical chemistry. *TrAC - Trends in Analytical Chemistry*, vol. 76, pp. 126-36 (2016).

[23] Gutierrez, M.C., Ferrer, M.L., Mateo, C.R. & Monte, F.D.: Freeze-drying of aqueous solutions of deep eutectic solvents: a suitable approach to deep eutectic suspensions of self-assembled structures. Langmuir 25 pp. 5509–5515 (2009).

[24] Smith, E.L., Abbott, A.P., Ryder, K.S.: Deep Eutectic Solvents (DESs) and Their Applications. *Chemical Reviews*, vol. 114, no. 21, pp. 11060-11082 (2014).

[25] Jörg Daub, P.D.W.K., Prof. Dr. Hubert Motschmann, Prof. Dr. Frank-Michael Matysik: Properties and Applications of Deep Eutectic Solvents and Low-Melting Mixtures.(2015)

[26] Abbott, A.: Deep Eutectic Solvents. *Leuven Summer School on Ionic Liquids (2010)*.

[27] Zhang, Q., De Oliveira Vigier, K., Royer, S. & Jérôme, F.: Deep eutectic solvents: Syntheses, properties and applications. *Chemical Society Reviews*, vol. 41, no. 21, pp. 7108-46 (2012).

[28] Shahbaz, K., Mjalli, F.S., Hashim, M.A. & Alnashef, I.M.: Prediction of deep eutectic solvents densities at different temperatures. *Thermochimica Acta*, vol. 515, no. 1-2, pp. 67-72 (2011).

[29] Hayyan, A., Mjalli, F.S., Alnashef, I.M., Al-Wahaibi, Y.M., Al-Wahaibi, T. & Hashim, M.A.: Glucose-based deep eutectic solvents: Physical properties. *Journal of Molecular Liquids*, vol. 178, pp. 137-41 (2013).

[30] AlOmar, M.K., Hayyan, M., Alsaadi, M.A., Akib, S., Hayyan, A. & Hashim, M.A.: Glycerol-based deep eutectic solvents: Physical properties. *Journal of Molecular Liquids*, vol. 215, pp. 98-103 (2016).

[31] Zhang, L.X., Yu, H., Yu, H.B., Chen, Z. & Yang, L.: Conversion of xylose and xylan into furfural in biorenewable choline chloride-oxalic acid deep eutectic solvent with the addition of metal chloride, *Chinese Chemical Letters*, vol. 25, no. 8, pp. 1132-6 (2014).

[32] Fischer, V.: Properties and Applications of Deep Eutectic Solvents and Low-Melting Mixtures, University of Regensburg (2015).

[33] Abo-Hamad, A., Hayyan, M., AlSaadi, M.A. & Hashim, M.A.: Potential applications of deep eutectic solvents in nanotechnology. *Chemical Engineering Journal*, vol. 273, pp. 551-67 (2015).

[34] Tang, B. & Row, K.H.: Recent developments in deep eutectic solvents in chemical sciences. *Monatshefte fur Chemie*, vol. 144, no. 10, pp. 1427-54 (2013).

[35] Cvjetko Bubalo, M., Radoševicˊ, K., Radojcˇicˊ Redovnikovicˊ, I., Halambek, J., Gaurina Srcˇek, V.: A brief overview of the potential environmental hazards of ionic liquids. *Ecotoxicol. Environ. Saf*, vol. 99 pp. 1–12 (2014).

[36] Yao, X.H., Zhang, D.Y., Duan, M.H., Cui, Q., Xu, W.J., Luo, M., Li, C.Y., Zu, Y.G. & Fu, Y.J.: Preparation and determination of phenolic compounds from Pyrola incarnata Fisch. with a green polyols based-deep eutectic solvent, *Separation and Purification Technology*, vol. 149, pp. 116-23 (2015).

[37] Wei, Z., Qi, X., Li, T., Luo, M., Wang, W., Zu, Y. & Fu, Y.: Application of natural deep eutectic solvents for extraction and determination of phenolics in Cajanus cajan leaves by ultra performance liquid chromatography, *Separation and Purification Technology*, vol. 149, pp. 237-44 (2015).

[38] Xia, B., Yan, D., Bai, Y., Xie, J., Cao, Y., Liao, D. & Lin, L.: Determination of phenolic acids in Prunella vulgaris L.: A safe and green extraction method using alcohol-based deep eutectic solvents, *Analytical Methods*, vol. 7, no. 21, pp. 9354-64 (2015).

[39] Paiva, A., Craveiro, R., Aroso, I., Martins, M., Reis, R.L., Duarte, A.R.C.: Natural deep eutectic solvents Solvents for the 21st century. *ACS Sustainable Chemistry and Engineering*, 2 (5), pp. 1063-1071 (2014).

[40] Procentese, A., Johnson, E., Orr, V., Garruto Campanile, A., Wood, J.A., Marzocchella, A., Rehmann, L.: Deep eutectic solvent pretreatment and subsequent saccharification of corncob. *Bioresource Technology*, vol. 192, pp. 31-6 (2015).

[41] Dragan Z. Troter, ZBT, Dušica R. Đokić-Stojanovićξ, Olivera S. Stamenković, Vlada B. Veljković: Application of Ionic Liquid and Deep Eutectic Solvents in Biodiesel Production: A Review. *Renewable & Sustainable Energy Reviews* (2013).

[42] Zhao, H. & Baker, G.A.: Ionic liquids and deep eutectic solvents for biodiesel synthesis: a review. *Journal of Chemical Technology and Biotechnology*, vol. 88, no. 1, pp. 3-12 (2013).

[43] Long, T., Deng, Y., Gan, S. & Chen, J.: Application of choline chloride·xZnCl2 ionic liquids for preparation of biodiesel. *Chinese Journal of Chemical Engineering*, vol. 18, no. 2, pp. 322-7 (2010).

[44] Abbott, A.P., Cullis, P.M., Gibson, M.J., Harris, R.C. & Raven, E.: Extraction of glycerol from biodiesel into a eutectic based ionic liquid. *Green Chemistry*, vol. 9, no. 8, pp. 868-72 (2007).

[45] Huang, W., Tang, S., Zhao, H. & Tian, S.: Activation of commercial CaO for biodiesel production from rapeseed oil using a novel deep eutectic solvent. *Industrial and Engineering Chemistry Research*, vol. 52, no. 34, pp. 11943-7 (2013).

[46] Smith, E.L.: Deep eutectic solvents (DESs) and the metal finishing industry: Where are they now?. *Transactions of the Institute of Metal Finishing*, vol. 91, no. 5, pp. 241-8 9 (2013).

[47] Sun, S., Niu, Y., Xu, Q., Sun, Z. & Wei, X.: Efficient SO absorptions by four kinds of deep eutectic solvents based on choline chloride. *Industrial and Engineering Chemistry Research*, vol. 54, no. 33, pp. 8019-24 (2015).

[48] Yang, D., Hou, M., Ning, H., Zhang, J., Ma, J., Yang, G. & Han, B.: Efficient SO2 absorption by renewable choline chloride-glycerol deep eutectic solvents. *Green Chemistry*, vol. 15, no. 8, pp. 2261-5 (2013).

[49] Liu, B., Wei, F., Zhao, J. & Wang, Y.: Characterization of amide-thiocyanates eutectic ionic liquids and their application in SO2 absorption. *RSC Advances*, vol. 3, no. 7, pp. 2470-6 (2013).

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