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POTENTIAL OF LIGNIN FROM OIL PALM BIOMASS USING DEEP EUTECTIC SOLVENT AS CARBON FIBRE PRECURSOR

(Potensi Lignin daripada Biojisim Kelapa Sawit Menggunakan Pelarut Eutektik Dalam sebagai Prekursor Gentian Karbon)

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Abstract

The modern composites industry heavily relies on carbon fibre as a raw material due to its high tensile strength, fatigue resistance, and temperature resistance. Thus, researchers are investigating the use of lignin extracted from biomass as a precursor for carbon fibre to reduce costs and environmental impact. Oil palm biomass is classified as a lignocellulosic compound due to its high cellulose, hemicellulose, and lignin content. Since lignin has a complex structure with numerous linkages between its monomeric components, it can be complicated to isolate it from lignocellulosic components. Deep eutectic solvents (DESs) are a promising new class of environmentally friendly solvents owing to their low toxicity, low production cost, and high biodegradability. Lignin valorisation has received much attention due to immense ability of DES to dissolve and extract lignin without condensation. This review aimed to provide a comprehensive and comparative analysis of the physicochemical and thermal properties of DES for utilisation in lignin extraction from biomass, with a focus on its potential as a precursor for carbon fibre.

Keywords: deep eutectic solvent, carbon fibre, lignin, precursor, oil palm biomass

Abstrak

Industri komposit moden sangat bergantung pada gentian karbon sebagai bahan mentah kerana kekuatan tegangan yang tinggi, rintangan kelesuan dan rintangan suhu. Oleh itu, penyelidik sedang mengkaji penggunaan lignin daripada biojisim sebagai prekursor yang lebih mesra alam dan kos efektif untuk gentian karbon. Biojisim kelapa sawit dikategorikan sebagai lignoselulosa, kerana kandungan selulosa, hemiselulosa dan lignin yang tinggi. Walau bagaimanapun, mengasingkan lignin daripada lignoselulosa memberikan cabaran kerana strukturnya yang rumit dan mempunyai pelbagai sambungan antara komponen monomeriknya. Pelarut Eutektik Dalam (DES) ialah generasi baharu pelarut hijau yang mudah disediakan, tinggi biodegrabiliti, kos pembuatan yang rendah dan ketoksikan yang rendah. Keupayaan DES yang luar biasa untuk melarutkan dan mengekstrak lignin tanpa pemeluwapan telah mencetuskan minat yang ketara dalam valorisasi lignin. Kajian ini bertujuan untuk menganalisis secara sistematik dan perbandingan sifat fizikokimia dan terma DES untuk pengekstrakan lignin daripada biojisim, dengan penekanan khusus pada penggunaannya sebagai prekursor untuk gentian karbon.

Kata kunci: pelarut eutektik dalam, gentian karbon, lignin, prekursor, biojisim kelapa sawit

Introduction

Advanced materials interest industrial strategists, economists, and policymakers due to their far-reaching potential and impact across various industries. Carbon fibre has a high strength-to-weight ratio and is lightweight, making it a desirable component in various high-tech and extensive applications. Bengtsson et al. [1] reported that a substantial amount (>96%) of carbon fibre is manufactured from the fossil-based polymer polyacrylonitrile (PAN), with the remainder coming from petroleum, coal-tar pitch, and rayon. The need for lightweight composites has led to the increasing popularity of carbon fibres. Hence, developing a more sustainable and cost-effective alternatives is necessary due to their high manufacturing costs and reliance on fossil-based resources.

Owing to its abundance and carbon neutrality, lignocellulosic biomass has the potential to replace fossil fuels as renewable feedstock. Lignin is a naturally occurring renewable raw material with exceptional chemical and physical properties. It is cheap and has the potential to replace feedstocks that are based on fossil fuels. Lignin extracted from palm oil biomass can be processed in several ways to yield various value-added carbon products [2]. However, physical and chemical heterogeneities of lignin render it a poor feedstock.

The hot and humid climate of Malaysia makes it ideal for growing oil palms, one of its most important crops. The palm oil milling industry produces millions of metric tonnes of waste annually. Oil palm fronds, mesocarp fibres, palm kernel shells, empty fruit bunches, and oil palm trunks are all renewable resources that make the palm oil industry a significant biomass producer [3]. Oil palm biomass is produced during milling, burned for energy recovery, or left to biodegrade in the plantation. Inefficient management practices exacerbate the production of harmful greenhouse gases. Oil palm biomass, with its high lignin content, may be able to replace PAN and pitch as carbon fibre precursors.

The environmental benefits of DESs as 'green solvents' have garnered widespread interest. DESs are compounds that contain at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) and form a transparent liquid eutectic mixture at temperatures ranging from 60°C to 80°C [4]. The hydrogen-bonding network formed between the components and the associated charge delocalisation causes the melting point of DES to be much lower than the melting points of the individual components [5]. Due to their low toxicity, high biodegradability, low production cost, and broad applicability, DESs have been used in various processes, such as metal extraction, bio-catalysis, CO_2 capture, and biodiesel synthesis [6].

As shown in Figure 1, several studies suggested that DESs may dissolve lignin from woody plants by disrupting the β-O-4 linkages between lignin and carbohydrates. Type III DES, which are commonly synthesised by reacting quaternary ammonium or phosphonium salts as HBAs with acids, alcohols, amines, or carbohydrates as HBDs, are the most explored for biomass treatment due to their cheap cost, non-reactivity with water, and biodegradability. However, their effectiveness depends on the specific DESs used and molar ratios. Due to their impact on biomass processing, especially the modes of action on cellulose, hemicellulose, and lignin, a complete understanding of the properties of DESs is crucial. Furthermore, lignin extracted with DES as a carbon fibre precursor has not been studied, and there have been no findings regarding its fundamental properties.

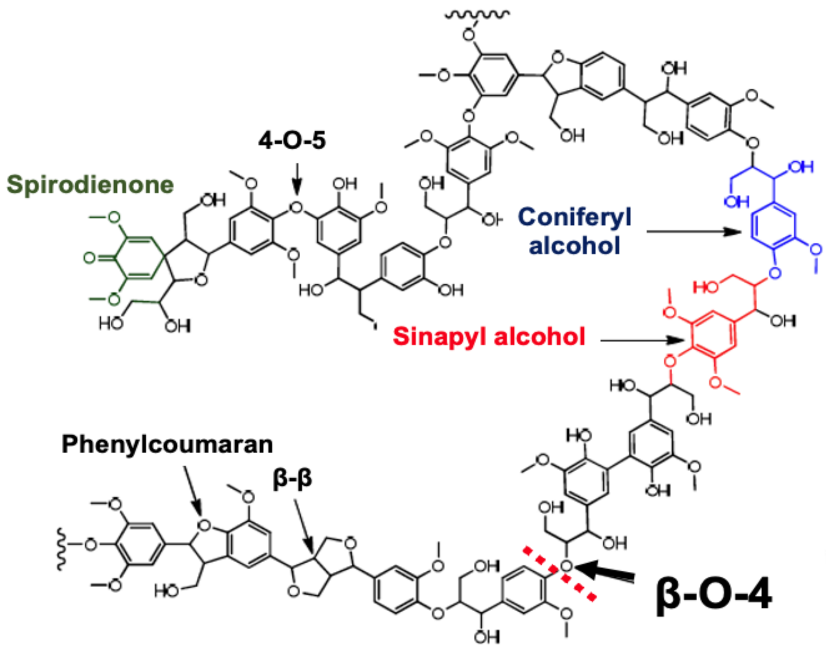

Figure 1. Selective cleavage of β-O-4 in lignin by DES

Deep eutectic solvents and its properties

DESs are eutectic mixtures of solid compounds that melt at lower temperatures than their components [7]. The hydrogen-bonding network between the components and the resulting charge delocalisation lowers the melting point. Abbott et al. [7], who discovered the dissolving power of DES mixtures, documented the first report on DESs. Understanding the HBA and HBD properties based on the functional group and mixing them in the precise molar ratios enables the synthesis of DESs to be accomplished quickly and efficiently. Finally, they have low toxicity and production costs when designed properly, particularly when produced from renewable sources.

DESs are solvents similar to ionic liquids (ILs), which are made up of a cation and an anion. ILs are widely used as solvents, although their hazardous effects on the environment and human health are well known [8]. In contrast to ILs, DES synthesis is a straightforward mixing procedure that can be scaled up to produce environmentally friendly and effective alternative solvents. Ca+X-zY is a common formula for DES, whereby Ca+ is the principal cation (typically ammonium, phosphonium, or sulfonium), and X- is a Lewis base (typically a halide anion). Figure 2 shows the interaction between the X- and z molecules of Y, where Y can be a Lewis acid or a Brønsted acid [9].

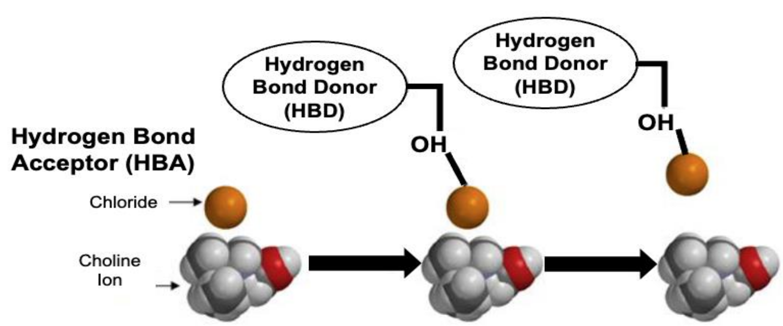

Figure 2. HBA and HBD components of DES

Table 1 shows the four distinct categories of DESs based on the chemicals used to produce them. The high melting temperatures of non-hydrated metal halides restrict the use of Type I DESs in biomass processing. On the other hand, Type II DESs are a much more cost-effective option for industrial processes because hydrated metal halides are cheaper. It is possible to tailor the physical properties of Type II DES to meet the needs of various applications by varying the HBD [8]. Type III DESs. On the other hand, Type III DESs are the most studied and investigated due to their low cost, non-reactivity with water, and biodegradability. Finally, Type IV DESs combine inorganic transition metals with urea to create eutectic mixtures, although metal salts do not typically ionise in non-aqueous media.

Table 1. Classification of DESs [8]

Type	Component	General Formula	Example
I	Metal salt organic salt	$Ca^{+} X^{-}$ zMClx; M = Zn, Sn, Fe, Al, Ga. In	$ZnCl_2$ + ChCl
II	Metal salt hydrate + organic salt	$Ca^{+} X^{-}$ zMClx.yH_2O; M = Cr, Co, Cu, Ni, Fe	$CoCl_2.6H_2O$ + ChCl
III	HBD + organic salt	$Ca^{+} X^{-}$ zRZ; Z = $CONH_2$, COOH, OH	Urea + ChCl
IV	Zinc/aluminium chloride + HBD	MClx + RZ = MCl_{x-1}^{+}. RZ+ MCl^{-}_{x+1}; M = Al, Zn & Z = $CONH_2$, OH	$ZnCl_2$ + ChCl

DESs are typically formed by reacting quaternary ammonium or phosphonium salts with HBD, such as acids, alcohols, amines, or carbohydrates [10]. Quaternary ammonium salts such as choline chloride (ChCl) are common HBAs, and metal salts, urea, carboxylic acids, and polyols are examples of HBDs, as shown in Figure 3 [11]. Selecting the most appropriate HBA and HBD with the right molar ratio allows for developing DESs tailored for specific applications. For example, Francisco et al. [10] observed that lactic acid:betaine (2:1) resulted a clear liquid of DES while lactic acid:histidine (2:1) showed no evidence of melting. This demonstrates that the specific molar ratio is dependent on the type of HBA and HBD combination.

Farooq et al. [12] reported that modifying the degree of basicity of hydrogen bonds in DESs can increase their efficacy. Based on their findings, the use of acidic carboxylic acids as HBDs with higher HBD:HBA molar ratios is proposed for high extraction efficiency with biomass [12]. Although a high extraction yield is desired, the fundamental properties of the extracted compounds may vary depending on the nature of the raw materials, particularly lignocellulosic compounds, which include various constituents. Information on the physiochemical and thermal properties of DES is required owing to the growing interest in this compound. The freezing point and decomposition temperature of DESs and physicochemical properties (viscosity, density, refractive index, and pH) vary with HBA and HBD combinations and molar ratios. The review on the physicochemical and thermal properties of DES is important because these properties are related to a potential lignin valorisation pathway, particularly as a carbon fibre precursor.

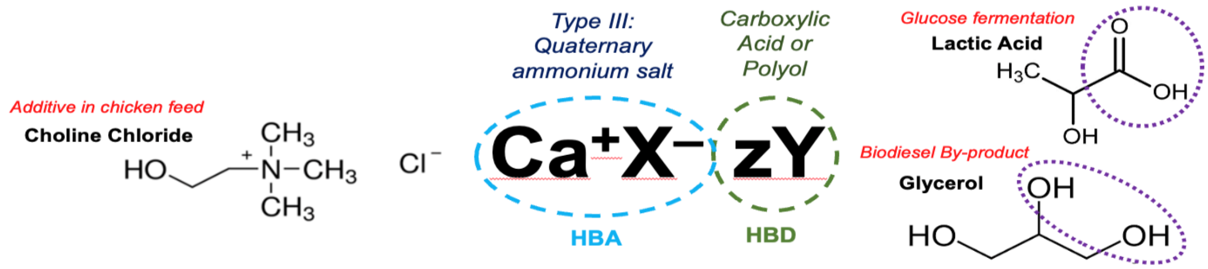

Figure 3. HBAs of quaternary ammonium salts (ChCl) and HBDs of carboxylic acids (lactic acid) and polyols (glycerol)

Viscosity

The viscosity of a fluid indicates the extent to which it resists its movement. The higher viscosity of DESs as compared to organic solvents makes handling, stirring, and filtration more challenging. The type of HBD, molar ratio, and temperature play a role in the viscosity of binary eutectic mixtures owing to hydrogen-bonding, Van der Waals, and electrostatic interactions [13]. Yusof et al. [14] reported that an increased number of hydroxyl groups produced higher viscosity due to the increased adhesive force between molecules provided by the increased number of hydrogen bonds. For example, citric acid, which has three carboxyl groups, forms stronger hydrogen bonds with ChCl owing to its larger molecular size. Therefore, the molecules in the ChCl:citric acid system are less mobile than those in the ChCl:malic acid system. Meanwhile, the hydrogen bond interaction between ChCl and lactic acid is weaker owing to its smaller molecular size [15].

Due to the sparse network between the different groups in DES, decreasing the salt molar ratio can decrease viscosity [16]. For instance, as the molar ratio of ChCl increased, the viscosity of ChCl:glycerol decreased, most likely due to the dissolution of intermolecular hydrogen bonds, resulting in molecular disruption [17]. Therefore, the frictional forces were diminished, and the molecular motion became less restricted. On the other hand, the viscosity of the DES increased as the molar ratio of HBD increased. For example, increasing the molar ratio of HBD causes the viscosity of ChCl:fructose to increase from 28.31 cP to 72.42 cP. This may be due to the increased hydrogen bond strength between the chloride ion and hydrogen atom due to the higher fructose concentration [15]. In addition, the viscosity significantly varies with temperature. Increasing the temperature caused the viscosity of the DES to decrease. Shear impact and thermal expansion can weaken the internal structure of DESs, leading to low viscosity [18]. Francisco et al. [19] stated that higher temperatures could increase the kinetic energy and reduce viscosity by weakening the attractive forces between molecules.

Density

The density influences the diffusion rate of the solvent and its ability to mix with other liquids. Density can be affected by various factors such as temperature, pressure, intermolecular interactions, and molecular weight. The density differences could be attributed to the different arrangements or packing of DES molecules [13]. Designing a DES without establishing a correlation between HBD and density is impossible. The density of DES is affected by the number of hydrogen bonds present in the solution [14, 20].

Fuad et al. [15] reported that DESs containing high-molecular-weight compounds have a greater density in the eutectic mixture than DES containing low-molecular-weight compounds. Since lactic acid had a relatively low-molecular-weight (90.08 g/mol), the ChCl:lactic acid mixture had a low-density of 1134 kg/m^3. On the other hand, ChCl:maltose density is 1431 kg/m^3 high molecular weight (342.3 g/mol) of maltose [15]. The density of a DES is also affected by the organic salt-to-HBD molar ratio. For instance, increasing the molar ratio of ChCl:glycerol from 1:1 to 1:4 resulted in an increase in density from 1160 kg/m^3 to 1210 kg/m^3

[21]. As the salt concentration relative to the HBD increased, the liquid became more structured, and the free volume decreased. When the free volume decreases, the molecular mobility decreases and the viscosity gradually increases [19].

Yadav and Pandey [22] stated that the DES density can be altered by the presence of water, making it less dense. For example, the density decreased from 1219.4 kg/m^3 to 1111.3 kg/m^3 when 50 vol% of water was added to the DES solution [23]. In addition, increasing the temperature reduced the DES density. Shahbaz et al. [24] reported that the rapid motion of DES particles increases the number of voids within the molecule as the temperature increases, making the DES less dense.

pH

The pH of a solution can affects chemical reactions in several ways, making it a crucial physical property. The applications of DESs in catalysis, biological activities, and metal treatment depend on the pH. Donor and acceptor acidity and basicity are responsible for the pH of DESs [25]. Hydrogen bonding and other molecular interactions between these ions and other species in the solvent affect the pH. For example, the ChCl:glycerol solution has a higher pH than the ChCl:malic acid solution (4.9 vs 2.4) [25]. This study demonstrated that DES acidity increased when acidic compounds were added to HBD.

Hayyan et al. [26] investigated numerous molar ratios of ChCl and fructose-based DES. They found that when the HBD content was reduced, the pH decreased as well. In addition, the pH value declined with increasing temperatures. For instance, at a molar ratio of 1:1, the pH of ChCl:fructose declined from 6.1 to 4.4 as the temperature increased from 25°C to 85°C [26]. Hypothetically, the slightly acidic pH of the DES aids lignin extraction. Although the acidity of the DES is important, it is not the most crucial factor for isolating lignin from lignocellulosic biomass. However, the extraction of lignin can be affected by factors such as the swelling of the material, the amount of carbohydrates bound to lignin, and the proportion of syringyl to guaiacyl units in the lignin structure [27].

Refractive index

The refractive index is important for understanding molecular interactions and free volumes, which heavily depend on the optical properties of the medium [28]. Salmaliyan et al. [29] found a positive correlation between the refractive index and density. Therefore, a DES with a higher refractive index is typically denser. Changes in the molar ratio, temperature, and chemical structure affect the refractive index of the DES. Chen et al. [30] observed that the refractive index of ChCl:lactic acid was 1.4590 at a molar ratio of 1:2 but declined to 1.4399 at a molar ratio of 1:4. Hence, it can be concluded that the higher the lactic acid concentration, the lower the refractive index of the DESs. A reduced concentration reduces the number of light-striking molecules, resulting in a lower refractive index ([31].

In contrast, DESs have a refractive index that decreases with temperature. For example, the refractive index of ChCl:ethylene glycol decreased from 1.468 to 1.4610 when the temperature increased from 298.15 K to 328.15 K [30]. At higher temperatures, the refractive index of the DES was reduced due to changes in its physical properties and the motion of its molecules [30]. In addition, the density and refractive indices of ChCl:ethylene glycol and ChCl:glycerol, as well as their aqueous mixes, were investigated at standard atmospheric pressure and temperatures between 298.15 K and 333.30 K [32]. A linear decrease in the density and refractive index with increasing temperature and an increase with increasing DES molar ratios were observed for pure and aqueous solutions. Furthermore, at constant molar ratios, DES with glycerol had a higher refractive index than DES with ethylene glycol.

Freezing temperature

Freezing temperature is also an important factor when assessing the liquidability of DES. All of the reported DESs have freezing points below 150°C, which are lower than their individual freezing points [13]. Donors such as carboxylic acids and sugar-derived polyols lower the freezing point of acceptor salts. The strength of hydrogen bonds is also affected by the composition of the salt owing to the charged shield [13]. In addition, the strength of the intermolecular interactions in the structure significantly affects the freezing point [33].

The freezing point of the DES mixture is typically lower than that of the individual HBAs and HBDs formed. For example, Abbott et al. [7] hypothesised that a ChCl:urea mixture with a molar ratio of 1:2 would have a freezing point of 12°C, which is lower than those of ChCl (303°C) and urea (133°C). DESs with freezing points lower than 50°C are preferable as solvents or liquids in various applications owing to their wide liquid range. Freezing point depression is proportional to the HBA and HBD interaction strength, which depends on their structures and molar ratios. Smith et al. [8] postulated that charge delocalisation due to hydrogen-bonding between the HBD and halide ion is responsible for the sharp decrease in the freezing point of DESs. Moreover, the freezing point of DES is affected by entropy change during liquid formation and the internal energy of DES molecules. Glycerol is one of the few HBDs that can yield a liquid DES at room temperature when combined with ChCl. This is possible due to the low eutectic melting point of −40°C at molar ratios of 1:2–1:4. Carboxylic acids, including levulinic acid, malonic acid, and phenylpropionic acid, have been shown to form liquid DES at room temperature [13].

For ChCl-based DES, the choice of the HBDs is decisive in producing a eutectic combination with a low melting temperature. Polyols such as glycerol or ethylene glycol HBD typically have lower freezing temperatures and may remain liquid below room temperature. This indicates that ChCl-based DESs using polyols as HBDs are viable alternatives to conventional solvents [34]. Qin et al. [35] suggested that the freezing points of DES are significantly affected by the molar ratio of HBA to HBD and that HBD compounds determine the lowest freezing point. It is theorised that freezing point depression is proportional to the molecular weight of the organic acids, with a larger effect for those with lower molecular weights.

Decomposition temperature

The decomposition temperature is the temperature range wherein the DESs are stable in the liquid phase. It is affected by various variables, including temperature, pressure, molar ratio, and heating rate. In addition, the constituent proportions and molar ratios influence DES stability and thermal behaviour [36]. However, analysis of thermal stability is relatively scarce. The robust hydrogen-bond networks of DESs may contribute to their thermal degradation characteristics. Hydrogen bonds hinder molecular escape, complicating DES decomposition. The maximum degradation temperature increased because the DESs required more energy to break bonds. Since the hydrogen bond interactions weaken with increasing temperature, DES separates into HBDs and HBAs. HBDs with lower thermal stability and boiling points then volatilise/decompose first, whereas HBAs volatilise/decompose at higher temperatures [37].

Florindo et al. [38] evaluated the decomposition temperature of various DESs. The decomposition temperature of DES was measured between 126.85°C and 226.85°C. The highest temperature at which ChCl:glutaric acid decomposed was 239.05°C, while the lowest was 124.68°C for ChCl:malic acid. In addition, Chemat et al. [39] found that the decomposition temperature of ChCl:urea+L-arginine increased from 215.38°C to 230.07°C as the molar ratio of L-arginine increased. A higher decomposition temperature resulted in a greater thermal stability. The Intermolecular interactions and coordination nature of the ions in the mixture may account for the enhanced thermal stability of ChCl:urea+L-arginine [39].

Delgado-Mellado et al. [40] found that ChCl:glycerol eutectic mixtures were stable due to the increased thermal stability of glycerol. These findings indicated that the thermal decomposition of ChCl and the vaporisation of glycerol simultaneously occurred in ChCl:glycerol, resulting in a single mass loss step due to the decomposition temperature of ChCl (250°C), which was close to the glycerol boiling point (290°C) [40]. Therefore, the higher decomposition temperature of DES may be attributed to the high thermal stability of glycerol, which ensures that the eutectic mixture never solidifies. As a result, HBD with low volatility and high thermal stability should be used to produce DES with high stability.

Lignin extraction from biomass by using DESs

Several obstacles must be overcome to extract lignin from biomass successfully. Pure lignin is difficult to extract from lignocellulosic biomass due to the highly linked structures of lignin and carbohydrates [41]. The condensation and oxidation of lignin also occur during isolation, thereby increasing the complexity of the process. In biomass, lignin and carbohydrate compounds form lignin-carbohydrate complexes (LCCs) with strong bonding strengths, which may affect their extraction [42]. There are eight types of lignin-carbohydrate bonds: benzyl ether, benzyl ester, glycosidic or phenyl glycosidic, hemiacetal or acetal linkages, and ferulate or diferulate esters. Tarasov et al. [43] found that LCCs facilitate bond cleavage and increase the accessibility of enzymes to biomass.

A thorough understanding of the LCC structure may help devise the best methods for breaking bonds to separate lignocelluloses efficiently and selectively. In recent years, there has been a surge in research and development of greener solvents for lignin isolation. DES can dissolve lignin from woody plants by rupturing lignin-carbohydrate bonds, thus liberating lignocellulose components [44]. The combination of HBA and HBD facilitates the breakdown of the ether bond between the phenyl propane units, resulting in low-molecular-weight lignin [45]. Evidence suggested that DES can improve the efficiency of biomass enzymatic saccharification despite its low polysaccharide solubility [46]. The rate of lignin extraction is affected by the structure of lignocellulosic biomass, which varies between species. The high solubility of lignin in DESs makes it an ideal solvent for isolating lignin from biomass. Therefore, the use of DESs to extract lignin holds great promise. Achieving biorefinery goals heavily relies on the efficient fractionation of biomass components. Several studies have demonstrated that different DES can be used to extract lignin from biomasses successfully (Table 2).

Understanding the relationship between the various types of functional groups in HBD is crucial to developing a DES capable of extracting lignin with specific properties. Although carboxylic acids and polyols are commonly used as HBAs, ChCl is more commonly used as a HBD. Alvarez-Vasco et al. [45] compared the effectiveness of DESs in extracting lignin from hardwood and softwood species. Four HBDs (glycerol, levulinic acid, lactic acid, and acetic acid) and ChCl were used in this study. DESs extracted 79% of lignin from hardwood poplar but only 58% from softwood Douglas fir (softwood). These results indicated that DESs can successfully extract lignin from plants with a purity of 95%. Chen et al. [44] investigated lignin extraction from poplar wood. A ChCl:lactic acid molar ratio of 1:9 was the optimal molar ratio for dissolving 95% of lignin from poplar wood at 120°C for 6 h, with a lignin purity of 98.1%. Tan et al. [47] reported that the extraction efficiency of DES is significantly affected by the functional groups present in the acid component. The HBD with a carboxylic acid double bond improved lignin extraction due to its short alkyl chain and OH group.

In the past, studies on DES have shown that they have the potential to be the most effective method for high-yield lignin extraction. The amount of lignin extracted depends on many variables, such as reaction time, temperature, and molar ratio. Increasing the reaction temperature is necessary to improve lignin extraction, thus decreasing the viscosity and improving DES diffusion into the lignocellulosic matrix [56]. Increasing the temperature enhances the molecular polarity and ionic properties of the DES. Therefore, it promotes the breakdown of the intermolecular hydrogen bond network to increase the solubility of lignin [10]. A higher acid concentration in the DESs promotes lignin extraction and leads to lower residue recovery [48]. This was corroborated by Tan et al. [47], who found that increasing the molar ratio of HBD to HBA in DES may have a synergistic effect, effectively increasing its ability to extract more lignin. The physicochemical and thermal properties of DESs, such as freezing point, density, surface tension, and viscosity, are also noteworthy because they can affect the isolation of lignin. In addition, the selectivity of HBD and HBA largely depends on their low cost and biocompatibility [57].

Table 2. Previous studies on lignin yield (%) with various reaction conditions

DESs	Molar Ratio	Feedstock	Reaction Temperature (°C)	Reaction Time (hr)	Lignin Yield (%)	References
ChCl: LA	1:2	Poplar	145	6	78.5	[45]
	1:2	Corncob	90	24	64.7	[48]
	1:5	Corncob	90	24	77.9	[48]
	1:10	Corncob	90	24	86.1	[48]
	1:15	Corncob	90	24	93.1	[48]
	1:5	Rice straw	60	12	60	[49]
	1:9	Poplar	120	6	95	[44]
	1:10	Willow	120	12	91.8	[50]
	1:5	Sugarcane bagasse	80	12	50.6	[51]
	1:10	Eucalyptus	110	6	80	[52]
ChCl:Glycerol	1:2	Corncob	150	15	59.0	[53]
	1:2	Switchgrass	110	1	76.6	[37]
ChCl:Ethylene Glycol	1:2	Corncob	90	24	87.6	[48]
ChCl:Oxalic Acid	1:2	Rice straw	120	1	75.9	[54]
	1:1	Corncob	90	24	98.5	[48]
ChCl: Urea	1:2	Corncob	80	15	27.1	[53]
	1:2	Rice straw	130	8	44.7	[55]

Lignin extraction from wheat straw increased from 48.76% after 2 h to 73.75% after 12 h [58]. On the other hand, the amount of lignin extracted increased from 90°C to 145°C but declined when the temperature was increased to 180°C. Lignin is most efficiently extracted from poplar and Douglas fir at 145°C with ChCl:lactic acid [45]. Moreover, lignin extraction was affected by the molar ratio of ChCl to carboxylic acid. The lactic acid:ChCl molar ratio increased the lignin extraction rate from 64.7% to 93.1% [48]. In addition, when the ChCl:lactic acid ratio increased from 1:1 to 1:15, the percentage of lignin extracted increased from 33% to 61%. [47].

The hydrophilic amorphous fractions of cellulose and hemicellulose facilitate extensive interactions between the fibres and solvents. Owing to their relatively high chloride ion concentration and activity, DESs are anticipated to play a crucial role in dissolving lignin. As shown in Figure 4, DES can break down LCC linkages due to the hydrogen-bonding interactions between the HBA anion and the hydroxyl group in the LCCs [9]. Several studies have found that DESs affect cellulose solubility, which is likely the cause of the observed interactions [59-61]. To dissolve cellulose, the hydrogen bonds between cellulose molecules and their intramolecular bonds must be broken. In addition, the inherent charge of the fibre may need to be considered [60]. During lignin extraction, the chemical bonds between cellulose, lignin, and hemicellulose are broken, leading to the formation of cellulose pulp. Thus, lignin degradation products are soluble in DES.

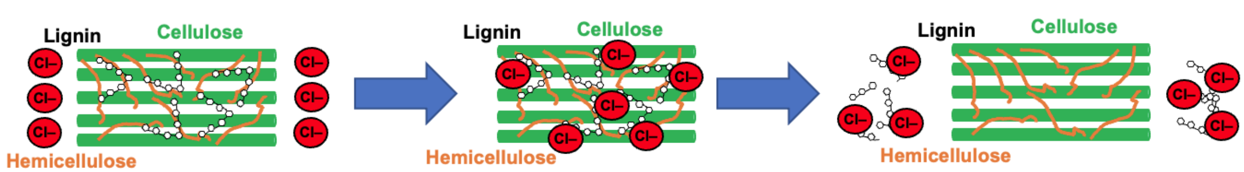

Figure 4. Isolation of lignin from the LCCs

Lignin extraction from oil palm biomass

Lignin from oil palm biomass can be extracted by using DESs. These studies have been performed to remove lignin from cellulose and hemicellulose [62-64]. However, it should be noted that these studies explored the possibility of removing lignin from LCCs. However, since lignin was not the primary focus of these studies, there are few studies on the fundamental properties, structures, or functional groups of the isolated lignin.

New et al. [23] obtained oil palm fronds delignification rate of 16.31% with a ChCl:urea molar ratio of 1:2 at 120°C for 4 h. Tan et al. [65] focused on the delignification of empty fruit bunches by using ChCl as the HBA and various types of HBD, including carboxylic acid and polyol. The study discovered that acids could extract a significant amount of lignin from empty fruit bunch (EFB), with ChCl:lactic acid yielding 88%. However, the near-neutral pH of the eutectic system is thought to be responsible for the 22% lower yield observed in lignin extraction using ChCl:glycerol [65]. Lignin can be extracted more efficiently with DES at an acidic pH than with DES at a neutral pH. Cl- in DES form's hydrogen bonds with hydroxyl groups in lignocellulose, cleaving LCC and releasing the constituent lignin and hemicellulose [66].

Tan et al. [47] examined the effects of different acidic hydroxyl groups, including lactic, malic, citric, formic, and acetic acids, on lignin extraction from EFB under the same conditions (120°C and 8 h). The lignin yield from ChCl:lactic acid was 33.5% at a molar ratio of 1:1, which increased to 61% at a molar ratio of 1:15. Lignin is more readily obtained using ChCl:lactic acid (monocarboxylic acids) than using ChCl:citric acid (dicarboxylic acid) or other HBD types. This was consistent with the findings of Hou et al. [54], who discovered that the delignification efficiency of dicarboxylic acids for rice straw pre-treatment was lower than that of monocarboxylic acids. ChCl:malic acid and ChCl:citric acid was significantly more viscous than ChCl:lactic acid. Lower extraction efficiencies could have resulted from a lack of solvent interactions with lignin due to low molecular mobility [47].

Lignin extraction from empty fruit bunches by using ChCl:lactic acid and ChCl:glycerol is efficient, with a lignin yield of 74.61% [67]. They found that a high HBD molar ratio and prolonged reaction time facilitated the lignin extraction. They concluded that DES could reveal biomass recalcitrance and increase the surface area for more efficient lignin extraction. However, ChCl:lactic acid was more effective than ChCl:glycerol in disrupting aromatic-dominated lignin linkages and cellulose crystallinity associated with β-(1,4)-glycosidic linear bonds. Despite having multiple HBD sites (-OH), the longer hydrocarbon site chain in glycerol molecules resulted in a lower hydrogen-bonding capacity and solubilising ability [67, 68].

The chemical structure and composition of lignin significantly differ depending on its origin, type, and extraction method. Lignin in oil palm biomass must be characterised for this reason. The chemical structure of lignin has been investigated by using various analytical methods. Thus, the most beneficial lignin modification can be identified and evaluated via structural elucidation. Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical composition and functional properties of the extracted lignin. The primary functional groups in lignin include hydroxyl, methoxy, and carbonyl groups [69]. The FTIR spectra of lignin extracted from oil palm biomass using various DES have been reported by Tan et al. [47]. The FTIR analysis showed that all spectra contained guaiacyl lignin units, G (1269 cm^{-1} and 850 cm^{-1}), and syringyl, S (1328 cm^{-1} and 1118 cm^{-1}). The peaks at 1421 cm^{-1}, 1508 cm^{-1}, and 1593 cm^{-1} belong to aromatic skeleton vibrations (C-C). The peak between 850 cm^{-1} and 650 cm^{-1} was characteristic of aromatic C-H bending. Peaks at 3371 cm^{-1} and 1365 cm^{-1} were also identified as phenolic and aliphatic OH in lignin, respectively. Unconjugated C=O was detected at 1700 cm^{-1}. The number of lignin functional groups is affected by the HBD type. The potential of lignin as an aromatic feedstock is related to its aromatic structure and hydroxyl and carbonyl groups. This suggested that DES-extracted lignin, which retains all necessary structures and high intensities, may be particularly suitable for manufacturing aromatic chemicals.

The phenolic hydroxyl group (PhOH) content indicates the reactivity of lignin for further modification because PhOH is the most reactive functional group in lignin [70]. The solubility and derivatisation potential of lignin are significantly affected by the presence of PhOH groups. The PhOH content in lignin from EFB was found to be the highest when using ChCl:lactic acid, as opposed to ChCl:malic acid, ChCl:formic acid, or ChCl:citric acid [47]. However, the PhOH content declined from 3.72 mmol/g to 3.33 mmol/g when the molar ratio of ChCl:lactic acid was increased to 1:15. Increasing the acidity of the solvent caused lignin condensation, which reduced PhOH content [47].

Lignin as carbon fibre precursor

Carbon fibres have high tensile strength, fatigue resistance, and heat tolerance despite their lightweight. Carbon fibre is an important and promising raw material for fibre-reinforced composites, particularly for high-performance applications. Nonetheless, the precursor materials significantly affected the final carbon fibre properties. Approximately 90% of the raw material for carbon fibres is PAN, making it the most widely used precursor. The remaining 10% were rayon or petroleum pitches. PAN-based carbon fibre-reinforced composites have been singled out by the US Department of Energy as a material with immense potential for use in lightweight vehicles with a 60% weight reduction [71]. While conventional carbon fibre-reinforced composites are inexpensive, PAN-based carbon fibres can be up to ten times more expensive. In addition, the time and energy spent on the thermal treatment necessary to convert PAN into carbon fibre considerably increases the cost of the process.

The high cost of fossil-based PAN precursors accounts for a significant portion of the cost of producing carbon fibre, making it necessary to develop cost-effective precursors, preferably from renewable sources. The prominence of lignin arises from its potential as a cheap carbon fibre precursor and its abundance and sustainability [72]. In addition, lignin is the most appealing renewable precursor for carbonaceous materials due to its aromatic properties and high carbon content (> 60%) [2]. Because lignin has a low decomposition temperature, partially oxidised properties, and high carbon content, it can be melt-spun and stabilised at a higher heating rate [73]. They are non-petroleum-based and, therefore, more environmentally friendly resources.

Compared to alternative materials, the production cost of carbon fibre made from lignin is lower. However, impurities in isolated lignin and complex structures may compromise the mechanical properties and carbon fibre construction. A study was conducted to identify differences between unmodified and modified lignin carbon fibres. Untreated lignin was found to have a tensile strength of 0.38 GPa and a yield of 31%, while treated lignin carbon fibre achieved tensile strengths of 0.710 GPa and yields of 41% [71].

Highly pure lignin with precisely controlled properties is essential for producing high-performance carbon fibres. Highly pure lignin is required to produce carbon fibres with exceptional characteristics and minimal impurities (ash, volatile, and particulate matter). High carbon content, narrow molecular weight distribution, and sufficiently high glass transition temperature all play important roles in the conversion of lignin into carbon fibre through spinning, thermal stabilisation, and carbonisation [2]. Oak Ridge National Laboratory developed a set of specifications to evaluate the potential of lignin as a precursor to carbon fibre [74]. Table 3 presents the specifications.

Table 3. Lignin as carbon fibre precursor

Criteria	Value (wt.%)
Lignin Purity	99
Ash Content	< 0.1
Volatile Matter	< 0.5
Particulate Matter	100% removal of matter >1 µm in diameter
Carbon content	> 60

A lignin purity greater than 99% is required as a carbon fibre precursor. Carbon fibre relies on its high purity to maintain its mechanical properties. Nonetheless, the extraction and use of lignin are complicated by its structural complexity and heterogeneity, primarily linked by aryl ether bonds and C-C bonds. The ability of DES to break β-O-4 aryl ethers and specific lignin-carbohydrate covalent bonds has been reported to increase lignin solubilisation significantly compared to conventional pre-treatment methods [75]. Many studies have successfully used DES to extract high purity lignin from biomass as shown in Table 2. In their study of lignin extraction from poplar using various DESs, Chen et al. [44] found that increasing the reaction temperature from 100°C to 130°C resulted in a higher purity of lignin (98%) due to the breakdown of hemicellulose. Furthermore, lignin purity of 95% from willow was achieved by using ChCl:lactic acid at a molar ratio of 1:10 [76]. These results confirmed the viability of ChCl:lactic acid for efficient isolation and extraction of high purity lignin. Li et al. [50] extracted lignin with high purity (94.46%) using a ChCl:lactic acid eutectic mixture with a molar ratio of 1:10 for 12 h at 120°C.

Ash is the residue remaining after the high-temperature (900°C) combustion. Most ash is composed of minerals found in biomass, such as calcium, magnesium, and potassium. The amount of inorganic matter in the recovered lignin must be kept to a minimum because it affects the mechanical properties of the carbon fibre. Therefore, it should be less than 0.1 wt.%. The stability of a polymer is determined by its volatility. The volatile matter content was determined by comparing the mass of the samples before and after 6 h of heating at 250°C. The volatile matter content of lignin must be less than 5 wt.% for no volatiles to be released during carbonisation. Carbonisation changes porosity [2]. As a result, the high volatile content of lignin could lead to a flaw on the surface of the carbon fibre.

Carbon fibre extracted from lignin was superior due to its low solid particle content. Lignin extraction removes solid particles larger than 1 μm in diameter [77]. Particles, such as sand or clay, are the main cause of impurity precipitation during the extraction process [78]. These impurities must be eliminated because they alter the mechanical properties of the carbon fibre, especially its fibre breakage point, by decreasing its modular and tensile strengths [74].

The extracted lignin should have a carbon content of at least 60 wt.%. The carbon content of commercial lignin is typically 59% to 61% [79]. Since lignin loses mass during carbonisation, the precursor must have a high carbon content and a low amount of non-carbon elements. High-quality carbon fibre requires a carbon content of at least 92 wt.% after the carbonisation of the precursor. A study has shown that ChCl:lactic acid at a molar ratio of 1:10 produced lignin with a high carbon content of 60.08% and negligible nitrogen (0.41%), hydrogen (5.50%), and oxygen (33.50%) content [76].

Furthermore, a uniform structure in carbon fibre is formed after carbonisation only if its molecular weight distribution is narrow [71]. Therefore, it is essential to determine the average molecular weight of lignin and its glass-transition temperature. The average molecular weight is essential for analysing the heterogeneity of long-chain lignin [80]. There is a correlation between the average molecular weight and glass transition temperature, the temperature at which lignin becomes brittle when cooled and soft when heated. However, the melt-spinning process requires a high glass transition temperature to prevent decomposition during the fibre-spinning process. Alvarez-Vasco et al. [45] reported that lignin extracted using ChCl:lactic acid has a low and narrow molecular weight range of 490 g/mol to 2600 g/mol, with an average molecular weight of approximately 890 g/mol. Results showed that DES depolymerises native lignin by selectively cleaving ether linkages without condensation. Lyu et al. [76] investigated the characteristics of lignin extracted from willow using ChCl:lactic acid at a 1:10 molar ratio. They observed that the average molecular weight decreased from 1806.7 to 1042.5 g/mol with a longer reaction time. The rate of lignin macromolecule degradation increases over time owing to the absence of intermolecular lignin bonds [81].

Conclusion

This mini review showed that DESs have the potential to be used as solvents in biomass processing. Organic acid-based DESs have shown promise for biomass processing due to their ability to extract lignin in a simple, single-stage process while maintaining high purity. Many industrial processes would benefit from the use of DESs owing to their low density, low viscosity, and high thermal stability. Selecting appreciate HBD functional groups and molar ratio is important as it affects the physicochemical and thermal properties of the compounds through intermolecular interactions. On the other hand, the composites and polymer industries have recognised the value of carbon fibre, prompting researchers to explore lignin from biomass for its potential as a low cost, more environmentally friendly and economically viable precursor. More studies are needed to investigate the application of DES with varied functional groups of HBA to HBD for lignin extraction from oil palm biomass, with a particular focus on the effect of varying molar ratios and other operating conditions such as temperature and reaction time. Furthermore, to assess its feasibility as a carbon fibre precursor, the fundamental properties of lignin-derived oil palm biomass must be established, which are critical in establishing whether the isolated lignin is viable as a carbon fibre precursor.

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