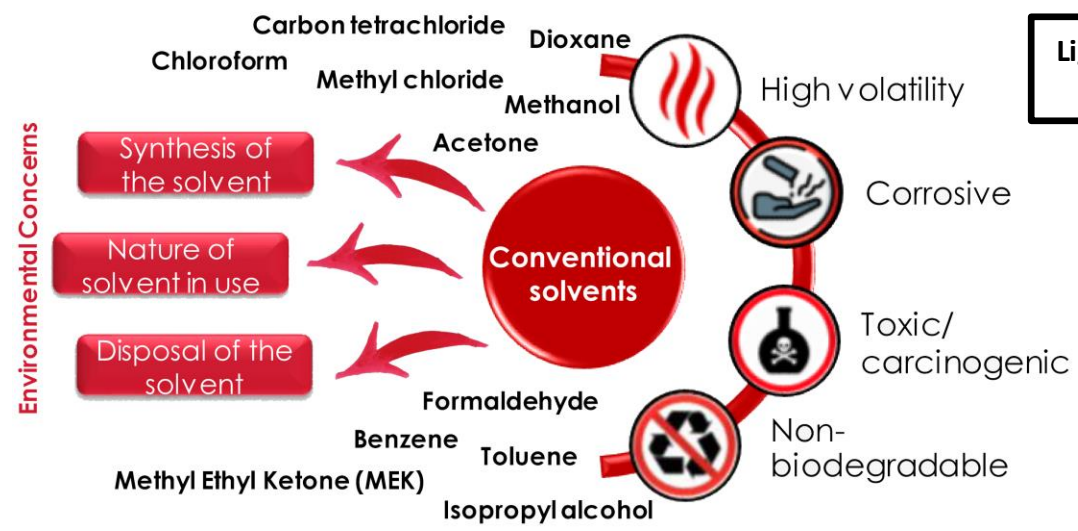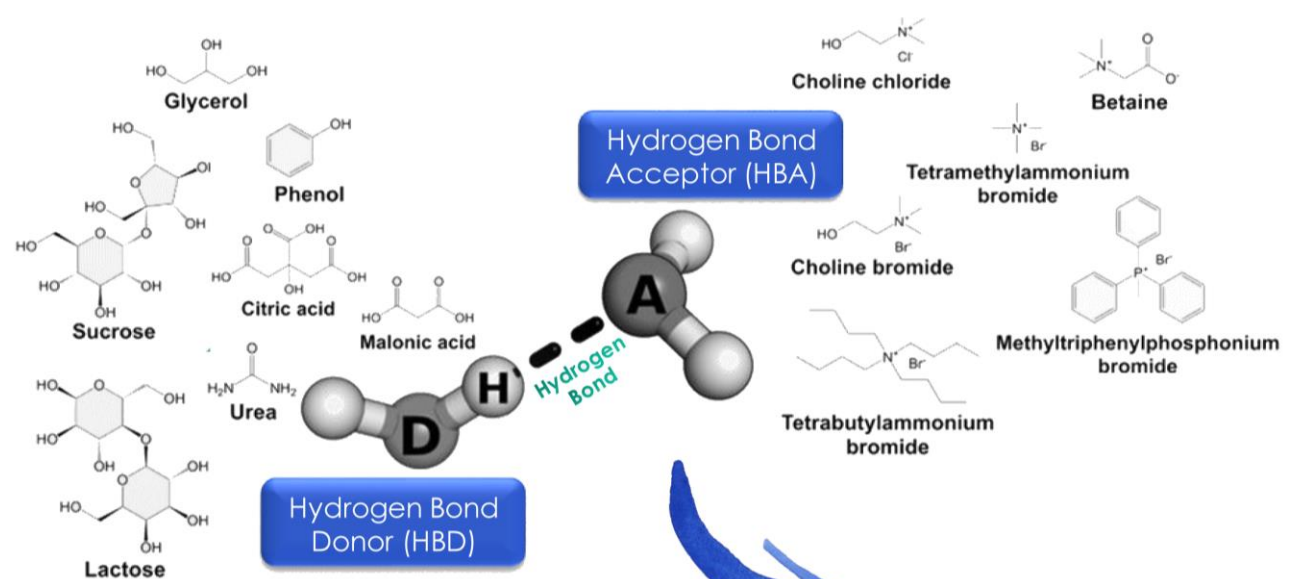# Bioresource Technology

Recent advances in green solvents for lignocellulosic biomass pretreatment: Potential of choline chloride (ChCl) based solvents

--Manuscript Draft--

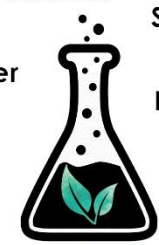|	
Manuscript Number:	BITE-D-21-01652R2
Article Type:	Review article
Keywords:	lignocellulosic biomass; pretreatment; green solvents; choline chloride; biomass-to-energy
Corresponding Author:	CHUNG LOONG YIIN, Ph.D Universiti Malaysia Sarawak (UNIMAS) Kuching, Sarawak MALAYSIA
First Author:	CHUNG LOONG YIIN, Ph.D
Order of Authors:	CHUNG LOONG YIIN, Ph.D
	Kok Liang Yap
	Andrian Zi En Ku
	Bridgid Lai Fui Chin, Ph.D
	Serene Sow Mun Lock, Ph.D
	Kin Wai Cheah, Ph.D
	Adrian Chun Minh Loy, MSc
	Yi Herng Chan, Ph.D
Abstract:	Biomass wastes exhibit a great potential to be used as a source of non-depleting renewable energy and synthesis of value-added products. The key to the valorization of excess lignocellulosic biomass wastes in the world lies on the pretreatment process to recalcitrant barrier of the lignocellulosic material for the access to useful substrates. A wide range of pretreatment techniques are available and advances in this field is continuously happening, in search for cheap, effective, and environmentally friendly methods. This review starts with an introduction to conventional approaches and green solvents for pretreatment of lignocellulosic biomass. Subsequently, the mechanism of actions along with the advantages and disadvantages of pretreatment techniques were reviewed. The roles of choline chloride (ChCl) in green solvents and their potential applications were also comprehensively reviewed. The collection of ideas in this review serve as an insight for future works or interest on biomass-to-energy conversion using green solvents.

Highlights

- Identified green solvents of current interest for biomass pretreatment

- Discussed formation, types, materials and design methodologies of green solvents

- Reviewed potential applications of choline chloride (ChCl) based green solvents

- **Existing challenges of green solvents are emphasized for future research**

1   **Recent advances in green solvents for lignocellulosic biomass pretreatment: Potential of**

2   **choline chloride (ChCl) based solvents**

3   Chung Loong Yiin[1a*], Kok Liang Yap[2a], Andrian Zi En Ku[3a], Bridgid Lai Fui Chin[4b], Serene

4   Sow Mun Lock[5c], Kin Wai Cheah[6d], Adrian Chun Minh Loy[7e], Yi Herng Chan[8f]

5   [a]Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering,

6   Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan 94300, Sarawak, Malaysia.

7   [b]Department of Chemical Engineering, Faculty of Engineering and Science, Sarawak Campus,

8   Curtin University Malaysia, Miri 98009, Sarawak, Malaysia

9   [c]CO$_2$ Research Center (CO$_2$RES), Department of Chemical Engineering, Universiti Teknologi

10   PETRONAS, 32610 Seri Iskandar, Malaysia.

11   [d]Energy and Environment Institute, University of Hull, Cottingham Road, Kingston upon Hull

12   HU6 7RX, United Kingdom.

13   [e]Chemical Engineering Department, Monash University, 3180, Victoria, Australia.

14   [f]PETRONAS Research Sdn. Bhd. (PRSB), Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan

15   Institusi Bangi, 43000 Kajang, Selangor, Malaysia.

16   [1*]E-mail address (Corresponding author): clyiin@unimas.my; Tel: +6082-583268

17   [2]E-mail address: kokliang1@live.com.my

18   [3]E-mail address: andrianku@live.com

19   [4]E-mail address: bridgidchin@curtin.edu.my

20   [5]E-mail address: sowmun.lock@utp.edu.my

21   [6]E-mail address: K.Cheah@hull.ac.uk

22   [7]E-mail address: adrianminh@gmail.com

23   [8]E-mail address: chan.yiherng@petronas.com.my

Abstract

Biomass wastes exhibit a great potential to be used as a source of non-depleting renewable energy and synthesis of value-added products. The key to the valorization of excess lignocellulosic biomass wastes in the world lies on the pretreatment process to recalcitrant barrier of the lignocellulosic material for the access to useful substrates. A wide range of pretreatment techniques are available and advances in this field is continuously happening, in search for cheap, effective, and environmentally friendly methods. This review starts with an introduction to conventional approaches and green solvents for pretreatment of lignocellulosic biomass. Subsequently, the mechanism of actions along with the advantages and disadvantages of pretreatment techniques were reviewed. The roles of choline chloride (ChCl) in green solvents and their potential applications were also comprehensively reviewed. The collection of ideas in this review serve as an insight for future works or interest on biomass-to-energy conversion using green solvents.

Keywords

lignocellulosic biomass; pretreatment; green solvents; choline chloride; biomass-to-energy

1. Introduction

Biomass is often renowned as one of the cheapest and largest sources of non-depleting energy in the world, attributed with great potentiality for continuous and sustainable supply of energy in the form of biofuels and various value-added products in the near future (Zoghlami & Paës, 2019; Kumar et al., 2020). Vast amount of lignocellulosic biomass is available for immediate global exploitation. Nonetheless, majority of the nations have yet to fully utilise and derive energy, chemicals and materials from the abundant biomass waste resources. For instance, in Malaysia, there are five major sectors that contribute to the generation of biomass wastes in the country, both

47 directly and indirectly, namely forestry or so-called wood products, rubber cultivation, cocoa

48 cultivation, sugar cane cultivation, and most importantly oil palm cultivation sector (Ratnasingam

49 et al., 2015). Malaysia is currently ranked the world second largest palm oil producer which

50 relatively accounts for the production of 7 million tonnes of crude palm oil. The country produces

51 approximately 20 tonnes per hectare (t ha^{-1}) of biomass residues from this sector every year (Yiin

52 et al., 2019).

53 Lignocellulosic biomass is mainly composed of polysaccharides (cellulose and

54 hemicelluloses) and an aromatic polymer (lignin), from which typical lignocellulosic biomass

55 consists of 30-60% cellulose, 20-40% hemicellulose and 15-25% lignin (Dahadha et al., 2017).

56 Nevertheless, the respective lignocellulosic contents in lignocellulosic biomass can be varied in

57 accordance with the source and physical properties of the biomass, where some typical

58 compositions of selected lignocellulosic biomass reported across several literatures are shown in

59 **Table 1**. Valorizing, instead of disposing these biomass wastes is utterly important as these

60 biomass wastes can serve as alternative feedstocks in place of the depleting fossil fuels, as well as

61 to be transformed into various value-added products such as bio-derived fine chemicals and bio-

62 fuels. Most importantly, they serve as inexpensive energy sources for the production of enzyme

63 which are beneficial for microbial fermentation (Anwar et al., 2014; Yiin et al., 2018). As such,

64 lignocellulosic biomass has indeed caught the interests of many researchers in recent times due to

65 their nature of being renewable and cheap. However, the major limitation that impedes the

66 valorisation of lignocellulosic biomass is mostly ascribed to the recalcitrance of plant cell walls to

67 biochemical and biological decomposition, conferred by the heterogeneous polyphenolic structure

68 of lignin (Zoghlami & Paës, 2019). Therefore, the pretreatment of these lignocellulosic materials

69   is introduced in order to unleash the trapped potential in lignocellulosic biomass and to promote

70   the valorization of biomass waste.

71   The pretreatment of biomass has been extensively discussed in existing review papers such as

72   in Baruah et al. (2018) and Zabed et al. (2016) which presented the conventional pretreatment

73   approaches including physical, chemical, biological, and physicochemical pretreatment methods.

74   Generally, it can be concluded that most of the conventional pretreatment techniques possess some

75   of the disadvantages suchlike high energy requirement, high cost of equipment, low-scale

76   applications, formation of inhibitors as well as non-environmentally friendly. Consequently,

77   Baruah et al. (2018) highlighted the need for low cost, energy-effective, environmentally

78   sustainable approach which are outseen as the bottlenecks for biomass valorization. Thus, this

79   review provides a comprehensive review of pretreatment of lignocellulosic biomass by evaluating

80   the conventional techniques, followed by the recent advances of green solvents in terms of current

81   interest, chemistry behind, designing, challenges and future prospects as well as roles of ChCl in

82   green solvents. Besides, the mechanism of actions, advantages and disadvantages associated with

83   all the pretreatment approaches were also evaluated. This review article aims to come up with

84   notable information for researchers who are dealing with the pretreatment of lignocellulosic

85   biomass for waste-to-energy transformation.

86   **2. Conventional approaches for lignocellulosic biomass pretreatment**

87   The recalcitrance of plant cell walls to biochemical and biological decomposition, conferred by

88   the heterogeneous polyphenolic structure of lignin, is deemed as the main concern when it comes

89   to utilize the simple substrates trapped within the lignocellulosic biomass. In this sense, the

90   pretreatment of lignocellulosic biomass plays a crucial role to ensure the recovery of cellulosic

91   content from these lignin-based biomasses. As such, the lignin barrier in lignocellulosic biomass

92   is disintegrated and broken down during the pretreatment process in order to recover the cellulose

93   (Anwar et al., 2014). Additionally, the degree of polymerisation and crystallinity of cellulose are

94   also altered, in which there is a reduction in both aspects (Chen et al., 2017). During the

95   pretreatment process, the compact structure of lignocellulose is disrupted to overcome the

96   recalcitrance through the combination of chemical and structural changes to the lignin and

97   carbohydrates, exposing the cellulose fibers to allow enzymatic hydrolysis (Amin et al., 2017). All

98   the advantages and disadvantages of various pretreatment methods are summarised in **Table 2.**

99   *2.1   Physical pretreatment*

100   It is essential for lignocellulosic biomass to undergo size reduction through mechanical

101   processing. Physical pretreatment can be classified into several methods such as milling,

102   microwave, extrusion and ultrasonication (Baruah et al., 2018). The main objective of physical

103   pretreatment is to reduce and minimise the particle size. Correspondingly, this leads to the increase

104   in the surface area, decrease in the degree of polymerisation as well as reduction in crystallinity

105   (Rajendran et al., 2018). Apart from that, the processes also can be carried out smoothly and

106   effectively. These pretreatment methods are deemed as environmental-friendly as they hardly

107   produce toxic materials which would pollute the environment (Shirkavand et al., 2016).

108   *2.1.1   Milling*

109   Milling is implemented in order to reduce the crystallinity and particle size of lignocellulosic

110   biomass up to approximately 0.2 mm. Nevertheless, biomass with particle size of less than 0.4 mm

111   oftentimes has no notable effect on the rate and yield of hydrolysis (Baruah et al., 2018). Numerous

112   milling methods have been introduced in which the types of milling method used will eventually

113   determine the reduction in particle size and crystallinity. Moreover, the processing time and type

114   of lignocellulosic biomass used would also has an impact on the particle size and crystallinity of

5

115   the respective biomass. A research conducted by Bai et al. (2018) stated that the effective reduction

116   in the particle size and decrease in crystallinity bring about high surface contact as well as pore

117   volume of the biomass. In addition, the respective biomass has a low thermal degradation

118   temperature.

119   ### *2.1.2   Microwave irradiation*

120   Microwave irradiation in general terms is an unconventional heating method for the

121   lignocellulosic biomass pretreatment by the means of electromagnetic field. This method utilises

122   dielectric polarisation to induce molecular collisions and further generates thermal energy which

123   results in the disruption of the complex structure of lignocellulosic biomass (Aguilar-Reynosa et

124   al., 2017). Microwave irradiation brings about disintegration of cellulose fibers through molecular

125   collision with the use of dielectric polarisation. There are two types of microwave irradiation

126   pretreatment namely atmospheric and high-pressure treatment. The microwave pretreatments

127   under high pressure are usually carried out in a closed reactor at temperatures between 150 to 250

128   °C (Li et al., 2016). In recent years, most researchers have discovered that microwave pretreatment

129   can actually be implemented along with other available pretreatment methods as an upgraded

130   attempt.

131   ### *2.1.3   Extrusion*

132   Extrusion as the conventionally used physical pretreatment method often utilises a tight barrel

133   which is equipped with temperature control in order to carry out the pretreatment of lignocellulosic

134   biomass (Duque et al., 2017). In this method, the lignocellulosic materials are to be passed through

135   the barrel at a temperature of greater than 300 °C. The recalcitrant structure of the lignocellulosic

136   biomass is disintegrated attributable to the high operating temperature. Additionally, the rotating

137 screw blades in the barrel produces shear forces which in return would also disrupt the structure

138 (Kumar & Sharma, 2017)

2.1.4 Ultrasonication

140 The pretreatment of lignocellulosic biomass via ultrasonication often utilises the ultrasonic

141 radiation which is in accordance with the principle of cavitation (Ravindran & Jaiswal, 2016). In

142 this method, shear forces is generated from the cavitation which causes the complex network

143 structure of lignocellulosic biomass to rupture. This will hence ease the extraction of desired

144 cellulose, hemicellulose or lignin. There are numerous factors suchlike the ultrasound frequency,

145 sonication power as well as the duration and temperature of sonication which tend to influence the

146 efficiency of ultrasonication (Liyakathali et al., 2016).

2.2 Chemical pretreatment

148 Chemical pretreatment describes the involvement of organic or inorganic compounds that are

149 known for their dissolvability of lignin, through interactions with the intrapolymer or interpolymer

150 bonds of lignin, hemicellulose, and cellulose, leading to the disruption of the recalcitrant structure

151 of the lignocellulosic materials (Jędrzejczyk et al., 2019). In general, the chemical pretreatment of

152 lignocellulosic biomass can be classified into acid pretreatment, alkaline pretreatment, organosolv

153 pretreatment, and ozonolysis.

2.2.1 Acid pretreatment

155 Fundamentally in the acid pretreatment, the presence of acid causes cellulose and

156 hemicelluloses in the lignocellulosic biomass to be hydrolysed into monosaccharides. This is

157 mainly due to the fact that the glucosidic bonds between these polysaccharides are susceptible to

158 acid. The hydronium ions from acid catalyst disaggregates the long polysaccharide chains into

159 sugar monomers. The enzymatic hydrolysis of cellulose and hemicelluloses can be carried out

160 more easily after the acid pretreatment (Baruah et al., 2018). Acid pretreatment can be further

161 categorised into concentrated acid pretreatment and dilute acid pretreatment. Conventionally,

162 concentrated acid pretreatment is conducted at a percent acidity of 30-70 % as well as at a

163 temperature of lower than 100 °C. On the other hand, dilute acid pretreatment (0.1-10 %) is carried

164 out at a higher temperature in the range of 100-250 °C. Nevertheless, both of the pretreatment

165 methods have a similarity in which the pretreatment process depends on the characteristics of

166 lignocellulosic biomass used (Baruah et al., 2018).

167 ### *2.2.2   Alkaline pretreatment*

168 Alkaline pretreatment in general utilises the working principle of solubilisation of lignin in

169 alkali solution. Researches have stated that among all the alkaline reagents suchlike potassium

170 hydroxide, calcium hydroxide and ammonium hydroxide used for the pretreatment process, it is

171 found out that sodium hydroxide functions most effectively (Kim et al., 2016). In this pretreatment

172 technique, the linkages between hemicelluloses and lignin are segmented and dissociated due to

173 the saponification process (Sun et al., 2016). The solubilisation of lignin and hemicellulose further

174 lead to the enhanced enzymatic hydrolysis of cellulose. Furthermore, the pretreatment with

175 alkaline reagents also cause swelling in cellulose which indirectly changes the structure of

176 lignocellulosic biomass. Subsequently, there will be a reduction in the crystallinity, decrease in the

177 degree of polymerisation, increase of surface area as well as porosity of lignocellulosic biomass.

178 ### *2.2.3   Organosolv pretreatment*

179 Organosolv pretreatment in general terms is the utilisation of organic solvents to pre-treat

180 various lignocellulosic biomass. Organic solvents such as methanol, ethanol, acetone, organic acid,

181 organic peracid as well as ethylene glycol tend to break down the linkages between lignin and

182 hemicellulose. The removal of lignin and solubilisation of hemicellulose cause an increase of

183　surface area and pore volume of cellulose, thus making cellulose more accessible to enzymatic

184　hydrolysis (Zhang et al., 2016). Commonly, the addition of mineral acids, bases and some other

185　salts which act as catalysts will lower the pretreatment temperature and boost the delignification

186　process (Borand & Karaosmanoğlu, 2018).

187　　*2.2.4　Ozonolysis*

188　　In this process, ozone gas brings about the breakdown of both lignin and hemicelluloses which

189　further results in the increase of accessibility of cellulose fibrils to enzymatic hydrolysis. The

190　ozone gas used in this technique is known as a strong oxidant and soluble in water (Mood et al.,

191　2013). Besides, the process is conducted at ambient condition and only forms a low amount of

192　inhibitors.

193　*2.3　　Biological pretreatment*

194　　Biological pretreatment utilises microorganisms such as fungi to convert lignocellulosic

195　biomass into more accessible compounds. This is related to the fact that some fungi are capable of

196　producing enzymes which help in the degradation of lignin (Sindhu et al., 2016). There are

197　different lignin-degrading enzymes available, however fungi are suitable for biological

198　pretreatment as they have the potentiality to disintegrate lignocellulosic materials. Additionally,

199　fungi play a crucial role in the removal of antimicrobial substances. White-rot, soft-rot, and brown

200　fungi are known for lignin and hemicellulose removal with a very little effect on cellulose

201　(Nauman Aftab et al., 2019). As compared to brown-rot and soft-rot fungi, white-rot fungi are

202　widely used in the breakdown of lignin and hemicelluloses in biological pretreatment owing to its

203　high sugar yield (Baruah et al., 2018). Hydrolytic system and ligninolytic system are among the

204　two extracellular enzymatic systems involved in the pretreatment with microorganisms. However,

205　the main difference between the two systems is that the disintegration of both cellulose and

206   hemicelluloses occur in hydrolytic system. Meanwhile, ligninolytic system is accountable for the

207   dissolution of lignin (Wagner et al., 2018). Generally, a reduction in the particle size and an

208   increase in the moisture content would bring about high efficiency of biological pretreatment. The

209   efficiency of biological pretreatment also increases with increasing pretreatment time and

210   temperature.

211   *2.4   Physicochemical pretreatment*

212   Physicochemical pretreatment is a technique that operate in a hybrid approach, affecting both

213   the physical parameters as well as their chemical bonding (bond cleavage) and intermolecular

214   interactions (Wei Zhao et al., 2012). Predominantly, physicochemical pretreatment can be

215   classified into steam explosion, ammonia fiber explosion, carbon dioxide (CO_2) explosion as well

216   as liquid hot water pretreatment.

217   *2.4.1   Steam explosion pretreatment*

218   The pretreatment of lignocellulosic biomass through steam explosion utilises both mechanical

219   forces and chemical effects. Operating conditions such as high-pressure saturated steam in the

220   range of 0.69-4.83 MPa as well as temperature of approximately 160-260 °C are implemented in

221   order to allow the water molecules penetrate through the substrate structure of the lignocellulosic

222   biomass. The water molecules are forced to escape in an explosive way through a sudden reduction

223   of pressure in the system (Baruah et al., 2018). This phenomenon results in major parts of the

224   lignocellulosic biomass to be splitted into fibers. Furthermore, the glycosidic bonds in cellulose

225   and hemicellulose as well as the segmentation of hemicellulose-lignin bonds are also broken down

226   due to the relatively high operating pressure and temperature of steam explosion pretreatment

227   (Chen & Liu, 2015). Hemicelluloses are also hydrolysed into respective glucose and xylose

228   monomers throughout this pretreatment method (Singh et al., 2015). The factors which affect the

229   pretreatment process are steam temperature, residence time, the size and moisture content of

230   lignocellulosic biomass.

231   ### *2.4.2 Ammonia fiber explosion (AFEX)*

232   In AFEX, liquid ammonia is used to heat the lignocellulosic biomass in a closed vessel at a

233   ratio of 1:1. Commonly, AFEX is conducted under high pressure of 1.72-2.06 MPa along with a

234   moderate temperature around 60-100 °C (Brodeur et al., 2011). This pretreatment process is lasted

235   for approximately 5 to 30 min. Similar to the steam explosion technique as discussed previously,

236   AFEX also undergoes a sudden reduction of pressure (Shirkavand et al., 2016). This results in the

237   disruption of the fibrous structure of lignocellulosic biomass and reduction in cellulose

238   crystallinity. Thus, the enzymatic hydrolysis of lignocellulosic biomass can be further enhanced.

239   AFEX pretreatment is influenced by several factors such as the operating temperature, blowdown

240   pressure, residence time, ammonia loading as well as water loading (El-Naggar et al., 2014).

241   ### *2.4.3 Supercritical CO_2 explosion*

242   In supercritical CO_2 explosion pretreatment, CO_2 molecules are allowed to diffuse through the

243   lignocellulosic biomass under a considerably high pressure which causes the disintegration of

244   hemicellulose and lignin structure of lignocellulosic biomass. The carbonic acid which formed

245   from the dissolved CO_2 in water promotes the hydrolysis reaction of hemicellulose (Baruah et al.,

246   2018). The cellulose crystalline structure of lignocellulosic biomass can also be broken down

247   through the sudden release of pressurised gas which increased the accessibility of cellulose fibers

248   to enzymatic hydrolysis (Capolupo & Faraco, 2016). A higher rate of penetration of the CO_2

249   molecules into the cellulosic pores can be achieved by increasing the operating pressure which

250   brings about a high glucose conversion (Baruah et al., 2018).

251   ### *2.4.4 Liquid hot water (LHW)*

252   LHW pretreatment utilises water to conduct the pretreatment process with a high operating

253   temperature in the range of 170-230 °C and a pressure of within 5 MPa. The lignocellulosic

254   biomass is set to expose to the hot water for roughly 15 min residence time. Hemicellulose is

255   hydrolysed by LHW through the removal of lignin and the discharge of acetyl groups in

256   hemicellulose which enhance the accessibility of cellulose fibers to enzymes (Zhuang et al., 2016).

257   LHW pretreatment is conducted at the pH of 4 to 7 in order to prevent the degradation of sugar as

258   well as the formation of inhibitors (Baruah et al., 2018).

2.5   Green solvents pretreatment

260   In recent years, green solvents have been introduced and implemented for the pretreatment of

261   lignocellulosic biomass in replacement of other conventional pretreatment techniques mainly due

262   to its environmentally friendly nature. Predominantly, there are various types of green solvents

263   available for biomass pretreatment which include ionic liquids (ILs), deep eutectic solvents (DESs)

264   and low-transition-temperature-mixtures (LTTMs).

2.5.1   Ionic liquids (ILs)

266   ILs are classified as organic salts which are made up of both cations and anions with a melting

267   point of lower than 100 °C (Baaqel et al., 2020; Baruah et al., 2018). Besides, ILs show the

268   potential to dissolve lignin and carbohydrates contemporaneously. The formation of strong

269   hydrogen bonds between the ILs' non-hydrated ions and the hydroxyl protons of sugars contributes

270   to the disruption of crystalline structure of cellulose as well as dissolution of hemicelluloses and

271   lignin. Several factors such as the cations, anions, operating temperature and treatment time tend

272   to show an impact on the overall pretreatment process (Yoo et al., 2017). Generally, lignocellulosic

273   biomass that is pre-treated with ILs results in an increased porosity and amorphous structure of

274   cellulose. Accordingly, its accessibility to enzymatic hydrolysis by cellulases can be increased (Li

275   et al., 2016).

276   ### 2.5.2   Deep eutectic solvents (DESs)

277   DESs are considered as a different class of green solvents which are comparable to ILs from

278   the perspective of their physicochemical properties. DESs have been extensively acknowledged as

279   analogues of ILs and developed as the new representative for green solvents (Hussin et al., 2020).

280   The term DES was introduced back in 2003 by Abbott et al. which encompass a new class of

281   designer solvent system that comprises of natural and renewable starting materials that are widely

282   available and near inexhaustible in nature. DESs are often constituted of two components which

283   are connected to each other by strong hydrogen bonds. The eutectic mixture formed has a melting

284   point lower than each individual component. DESs are simply made up of one hydrogen bond

285   donor (HBD) and one hydrogen bond acceptor (HBA). Besides, the respective solvents are usually

286   liquids at temperature below 100 °C (Baruah et al., 2018). The pretreatment of lignocellulosic

287   biomass with DESs promotes the disruption and disintegration of the complex structure of

288   lignocellulosic materials. Xu et al. (2016) reported that the acidic HBD of DES tends to improve

289   the overall efficiency of delignification and the dissolution of hemicellulose.

290   ### 2.5.3   Low-transition-temperature-mixtures (LTTMs)

291   The original term DESs does not provide a thorough description to delineate the new class of

292   solvents due to the fact that many of these solvents actually demonstrate glass transitions instead

293   of eutectic (melting) points. Hence, Francisco et al. (2013) coined the term LTTMs to describe the

294   solvents that are synthesized by mixing two or more solid components capable of establishing

295   hydrogen bond interactions which results in liquid solvents with much lower melting point than

296 any of its respective constituents. However, most literatures used both terms, LTTMs and DESs,

297 interchangeably.

298   LTTMs in general can be regarded as one of the newly designed green solvents which are

299 effective for the pretreatment of lignocellulosic biomass through delignification process. LTTMs

300 are quite comparable with DESs in which these types of solvents are also composed of one HBD

301 and one HBA (Kottaras et al., 2017). In addition, the pretreatment with LTTMs is capable of

302 achieving a higher extraction yields as compared to conventional solvents (Kottaras et al., 2017).

303 For instance, a study conducted by Yiin et al. (2018) involving the pretreatment of lignocellulosic

304 biomass with malic acid-based LTTMs demonstrated high delignification selectivity, and

305 improved enzymatic hydrolysis, as well as thermal degradation of biomass.

306 **3. Recent advances in green solvents**

307   Traditionally, the pretreatment of lignocellulosic biomass rely heavily on conventional

308 solvents and the intensive use of conventional solvents worldwide is often regarded as a threat to

309 the environment, where the concerns arise in three main areas: the synthesis of the solvent, the

310 nature of the solvent in use, and the disposal (Welton, 2015). Most conventional solvents are

311 considered damaging due to the large quantities in use and these solvents are often associated with

312 their properties of being highly volatile, corrosive, toxic or carcinogenic, non-biodegradable, etc.

313 (Mallakpour & Dinari, 2012). In this context, growing research on green solvents actively seeks

314 to explore environmentally friendly and tunable solvents that meet both the economic demand and

315 technological demand, specifically on the performance of the green solvents that are intended to

316 replace existing solvents.

317 *3.1. Green solvents of current interest*

14

318   Green solvents encompass those which are non-toxic, non-volatile, recyclable, biodegradable,

319   low-cost and preferably made from materials that are readily available (Das et al., 2017). Solvents

320   of current interest that are recognized as green solvents include water, supercritical fluids, organic

321   carbonates, ILs, DESs, and bio-based solvents (Welton, 2015). Among these classes of green

322   solvents, ILs emerged as a competitive candidate which finds a versatile application in various

323   fields such as bio-catalysis, separation process, electrochemical and biopolymers processing. ILs

324   are molten salts in form of liquid at room temperature and exhibits interesting characteristics,

325   which includes their physicochemical properties (melting point, density, surface tension, refractive

326   index, viscosity, electrical conductivity, polarity, water and cosolvent miscibility, etc.) that can be

327   tailored to needs by the combination of different cations and anions (Mallakpour & Dinari, 2012;

328   Paiva et al., 2014). The ILs which are of high thermal stability and low vapor pressure also offer

329   advantages such as easy containment or storage, final product recovery, and recyclability of the

330   solvent (Mallakpour & Dinari, 2012).

331   Despite the promising characteristics of ILs as solvent, the widespread use of ILs in the

332   industry is impeded by economic and environmental imperatives that are commonly associated

333   with their controversial ecotoxicological data, flammability, high cost, complex synthesis method

334   and purification process, etc. (Durand et al., 2015; Taylor et al., 2019). The "greenness" of ILs are

335   often questioned due to their limitations in terms of poor biodegradability, biocompatibility, and

336   solvent recoverability as well as their economic viability since the cost of ILs are relatively

337   expensive compared to conventional solvents (Francisco et al., 2012). Furthermore, ILs are

338   commonly derived from materials that use fossil resources, whereby the complex synthesis process

339   involves the use of different reagents, other volatile organic compounds and create a large amount

340   of chemical waste (Ratti, 2014).

341   On another note, it is worth mentioning that an alternative approach that is capable of

342   overcoming the aforementioned drawbacks is the development of choline-based ILs wholly

343   originated from biomaterials which have attractive features of low toxicity, relatively high stability

344   and fewer negative effects on the environment, pioneered by Fukaya et al. (2007) and known as

345   "Bio-ILs". The idea was adopted to create novel acetylcholine-carboxylate bio-ionic liquids for

346   catalytic fixation of CO_2 to produce fine chemicals (Wenfeng Zhao et al., 2019). In another

347   instance, choline-based bio-ILs were applied in nanomaterials and polymers field (Noshadi et al.,

348   2017). However, further studies are limited and could be of another interesting topic awaiting

349   exploration.

350   DESs/LTTMs that can be easily synthesized from natural and readily acquirable raw materials,

351   came up as an inexpensive and promising alternative to conventional ILs. The wide liquid range

352   and befitting physicochemical properties evinced the key qualities of DESs/LTTMs suitable to be

353   used as solvents. The strong hydrogen bond interactions are accredited for the similar benefits

354   exhibited by DESs/LTTMs as compared to ILs while at the same time overcome the limitations of

355   conventional ILs. Although both DESs/LTTMs and ILs present highly similar core characteristics,

356   DESs/LTTMs are deemed a more complete representation of the green chemistry benchmarks,

357   rendering LTTMs a compelling interest as the more favourable alternative compared to their

358   analogue ILs (Silva et al., 2019).

359   ***3.2. Chemistry behind*** DESs/LTTMs

360   ***3.2.1.   Overview on formation of DESs***

361   DESs are system of eutectic mixtures formed between a HBA, most dominantly quaternary

362   ammonium salts; and a HBD from a wide range of components such as alcohols, acids, amines,

363   carbohydrates, among others. DESs are generally described by the following formula (Smith et al.,

364   2014).

365      $$Cat^+X^-zY$$

366   where

367   Cat^+ refers to any ammonium (NR_4^+), phosphonium (PR_4^+), or sulphonium cation (SR_3^+)

368   X is a Lewis base, generally a halide anion (F^-, Cl^-, Br^-, I^-, etc.)

369   Y is either a Lewis or Brønsted acid

370   z refers to the number of molecules Y that interact with the anion

371   The complex anionic species forms between the halide anion X^- with another Lewis or

372   Brønsted acid Y, resulting in the charge delocalization between anion and the HBD compounds.

373   The hydrogen-bonding interactions between a compatible pair of HBA and HBD is suggested to

374   be responsible for the formation of the eutectic mixture (Francisco et al., 2013).

375   DESs/LTTMs constitute of a group of easily tunable eutectic mixtures that are adjustable to

376   suit for specific applications, ascribed to their high number of HBDs present in the mixture

377   (Bernasconi et al., 2017). Although the formation and functioning of these green solvents are not

378   fully understood at their molecular level, the hydrogen bonds between the two hydrogen bonding

379   constituents (HBA and HBD) are known to be responsible for the formation of DESs/LTTMs. The

380   existence of hydrogen bond formation between the HBA and HBD in DESs/LTTMs can be

381   verified through proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy or Fourier-transform

382   infrared spectroscopy (FTIR) (Haraźna et al., 2019). In this context, analyzing the changes in FTIR

383   spectra of the synthesized DESs /LTTMs in comparison with the individual starting materials able

384   to identify the chemical bonds and functional groups based on the assigned characteristic range of

385   wavenumbers. Similarly, the trend of chemical shift in terms of ^{1}H-NMR interpretation of the

386 DESs/LTTMs in comparison with the individual constituents can be taken as the indicator for the

387 formation of hydrogen bonds and changes in hydrogen bond strength. The extensive hydrogen

388 bonding interaction renders the depression in the melting/freezing point of LTTMs.

389 ### *3.2.2. Types of DESs*

390 Depending on the nature of its constituents, there are four dominant types of DESs with the

391 addition of type V DESs as a new idea that was proposed recently as shown in Table 3. Type I

392 eutectics comprise of quaternary ammonium salts and non-hydrated metal halides, including a

393 wide range of eutectic mixtures from chloroaluminate or imidazolium to less common 1-ethyl-3-

394 methylimidazolium chloride (EMIC), with different metal halides well studied in the 1980s

395 (Bernasconi et al., 2017). The range of suitable non-hydrated metal halides with low melting point

396 to form type I DESs is limited, giving rise to type II eutectics, where many metal salts hydrates

397 were coupled with quaternary ammonium salts following their inertness to air or moisture.

398 Most DESs are built on the fundamental of type III eutectics, where the most typical starting

399 materials involve quaternary ammonium salts such as ChCl and HBDs such as glycol, ethylene

400 glycol, urea, carboxylic acids, amides, and etc. (Zhekenov et al., 2017). Type III eutectics have

401 been of great interest due to their solvation ability across a wide range of transition metal species,

402 including chlorides, and oxides derivatives (Smith et al., 2014). These eutectic mixtures

403 demonstrated high inertness with water to the extent of being almost unreactive, making them

404 relatively easy to prepare and handle.

405 While most ILs and DESs involve a quaternary ammonium salt as the cationic component,

406 giving a sense of quaternary ammonium salts being a requirement to form eutectics. However, it

407 has been confirmed that the mixture of metal chloride hydrate and HBDs such as simple amides

408 ($-CONH_2$) or alcohols ($-OH$) forms a metalliferous solution composed of cations and anions via

18

409   disproportionation processes (Abood et al., 2011). These DESs composed of metal chloride salts

410   and HBDs without organic quaternary ammonium cations are the most recent class of DESs well

411   established so far, known as type IV eutectics.

412   Type V DESs composed of non-ionic species are the most recent breakthrough. These non-

413   ionic hydrophobic eutectics offset the limitations associated with hydrophobic eutectics based on

414   quaternary ammonium salts, specifically their higher cost, hydrophobicity, viscosity, and also

415   shown potential for the recovery and regeneration of the DES by evaporation, attributed to their

416   non-ionic nature (Abranches et al., 2019). However, type V DESs is an area of research that is

417   relatively new, hence still immature to support different scientific research.

418   ***3.3. Designing green solvents***

419   ***3.3.1. Starting materials of DESs/LTTMs***

420   The vast library of feasible constituents for the starting materials grants ubiquity to

421   DESs/LTTMs ascribed to the ability in controlling and fine-tuning the physicochemical properties

422   and phase behavior simply by altering the composition of the DESs/LTTMs. Apart from that, the

423   solvation ability of DESs/LTTMs on solutes with different natures can also be tweaked for task-

424   specific applications. DESs/LTTMs can easily be synthesized from readily available natural

425   sources, simply by mixing two solid starting materials at moderate temperature without the need

426   for further purification steps to form liquid eutectics by hydrogen bond interactions.

427   Theoretically, there is a near infinite number of combinations that could be rendered out of the

428   numerous HBA and HBD constituents available. However, the compatibility of the mixture

429   prepared by simple mix-and-match approach is not always guaranteed. In this sense, successful

430   formation of DESs/LTTMs are characterized by solution that remains stable, homogenous, and

431   colourless after cooled down to room temperature (Hussin et al., 2020).

3.3.2. Design methodologies

432

433 Despite the ease to synthesize DESs/LTTMs as compared to ILs, the designing of DESs/LTTMs

434 are rather difficult. The potential constituents of ILs are limited to bulky or asymmetric ions, by

435 which the fixed molar ratio of the ions in ILs is defined by the electroneutrality of the solution

436 (Mainberger et al., 2017). In contrast, the complexity in designing DESs/LTTMs is ascribed to the

437 wide array of possibilities in formulating the molar ratio of the components in DESs/LTTMs that

438 could be of any value (Alhadid et al., 2020). The time and cost for the synthesis and testing of such

439 an impossibly large number of DESs/LTTMs poses a scientific challenge, given that the area of

440 research is relatively new and lacks a comprehensive framework for the optimal design of

441 DESs/LTTMs.

442 Most of the published works to date adopts the trial and error methodology in designing the

443 DESs/LTTMs, where the preselected components are mixed at several molar ratios, typically 1:1

444 or 1:2, and mixtures that remain liquid at room temperature are documented for further studies

445 (Alhadid et al., 2020). However, making selections based on the trial-and-error method can be very

446 limiting and have a high chance to overlook good candidates (Rodriguez-Donis et al., 2018). It

447 was emphasized that the trial-and-error method was too time consuming and costly (Azmin et al.,

448 2015). To offset the limitations of the trial-and-error approach, Zhou et al. (2020) mentioned two

449 categories of solvent selection and design methods, namely database screening, and molecular

450 design.

451 Predictive design methodologies make use of the valuable experimental data from traditional

452 trial-and-error approach for the screening of solvents. Rigorous modelling of predictive models

453 can be implemented to compute the properties of the target molecules to reduce the exhausting and

454 costly experimental efforts, and allowing more feasible designs to be explored. A pre-specified set

455 of solvent candidates are screened based on the prediction of properties to identify the best solvent

456 with matching specifications from a known set of candidates (Zhou et al., 2020).

457   The advancements in theoretical and modelling methods today, synchronous with robust

458 computing power, enabled the possibility to incorporate computational methods in the selection

459 and design of solvents (Kovács et al., 2020). Reverse design methodology is an innovative and

460 systematic approach that combines the predictive capability of solvent properties with computer-

461 aided molecular design (CAMD) tools to support the design of novel solvents that meet target

462 specifications (Bergez-Lacoste et al., 2014).

463   The chronology of DESs/LTTMs development are similar to other solvents from the state of

464 infancy to maturity, starting from the widely used trial-and-error approach to investigate the

465 fundamental correlations, before predictive models can be developed for the prediction of

466 molecular properties, then further advanced to involve the use of computational tools as seen in

467 the reverse design methodology (Bergez-Lacoste et al., 2014). Still in its infancy, DESs/LTTMs

468 are not well characterized and understood to pursue for advanced design strategies due to the

469 limitations in providing a comprehensive description of their physicochemical properties as the

470 pre-requisite for advanced modelling and computational approaches.

471 **4. Roles of choline chloride (ChCl) in green solvents**

472   The emergence of LTTMs can be traced back to the early years in the 21st century when Abbott

473 et al. (2003) discovered that ChCl and urea forms a homogeneous solution at ambient temperature

474 and pioneered the idea on DESs. Since then, ChCl appeared to be the most dominant quaternary

475 ammonium salt to be used as the HBA in DESs/LTTMs-related studies. The vast interest in ChCl

476 sparked an exponential growth of the studies on ChCl-based DESs over the years. Apart from

477 being popularized by the original author, the other contributing factors to the popularity of ChCl

478 being used as the HBA in DESs/LTTMs are its relatively low cost, and other natures such as

479 biodegradable, non-toxic, etc., that satisfies the green chemistry metrics.

480 *4.1. ChCl-based solvents for lignocellulosic biomass pretreatment*

481   ChCl-based green solvents find applications in a wide array of fields where lignocellulosic

482 biomass pretreatment is regarded one of its most prospective use. Some of the ChCl-based solvents

483 used in the pretreatment of lignocellulosic biomass for further valorization were reviewed and

484 summarised in **Table 4**.

485 *4.2. Other applications of ChCl-based solvents*

486   DESs/LTTMs find versatile applications in various fields and are not limited only to be used

487 as solvents. DESs/LTTMs can be used as cheaper and environmentally benign alternatives to

488 substitute for the use of conventional solvents in extraction, purification, or other separation

489 processes. The applications of DESs/LTTMs were also reported in fields of chemical and polymer

490 synthesis, metal electrodeposition, nanomaterials, CO_2 capturing, biomass and biofuels processing,

491 biomedicine, pharmaceutics, food processing, cosmetics, etc. (Ezgi Ünlü & Takaç, 2020; Marcus,

492 2019; Paiva et al., 2014; Silva et al., 2019). Some other applications of ChCl-based solvents

493 include:

494   i.   Microalgal biomass pre-treatment for the extraction of cellular components by using

495   ChCl/1,2-Propanediol/Water (Cicci et al., 2017),

496   ii.   Pretreatment and fractionation of keratinous waste biomass by using ChCl/Oxalic acid

497   (Wang et al., 2018; Wang & Tang, 2018), separation of aliphatic-aromatic mixtures by

498   using ChCl/Malonic acid (Samarov et al., 2018)

499   iii.   Extraction of phenolic compounds from wood-apple pulp by using ChCl/Oxalic acid

500   (Saha et al., 2019)

501 iv. Extraction of polyphenols from palm samples by using ChCl/Formic acid,
502   ChCl/Glycerol, ChCl/Acrylic acid, ChCl/Ethylene glycol, ChCl/Malonic acid,
503   ChCl/Citric acid, ChCl/Xylitol, ChCl/Phenol, ChCl/Urea, and ChCl/Oxalic acid (Liu
504   et al., 2019)

505 v.   Hydrogen sulfide (H_2S) absorption by using ChCl/Formic acid, ChCl, Acetic acid, and
506   ChCl/Propionic acid (Wu et al., 2019)

507 vi. Solvent extraction of phenolic constituents from olive leaves by using ChCl/Lactic
508   acid, ChCl/Oxalic acid, ChCl/Tartaric acid, ChCl/ 1,4-Butylene glycol, ChCl/Ethylene
509   glycol, ChCl/Xylitol, ChCl/1,2-Propylene glycol, ChCl/Maltose, and ChCl/Urea
510   (Alañón et al., 2020),

511 vii. CO_2 capturing by using ChCl/Ethylene glycol, and ChCl/Glycerol as solvents in
512   absorption column (Alkhatib et al., 2020)

513 viii. NH_3 absorption and separation by using DES formed from ChCl and dihydric alcohols
514   (1,4-butanediol,2,3-butanediol, and 1,3-propanediol) (Deng et al., 2020)

515 ix. Extraction of crude oil from contaminated soil (Duan et al., 2020)

516 x.   Pretreatment and extraction of polyphenols from chestnut shell waste ChCl/Ethylene
517   glycol, ChCl/1,4-Butanediol, ChCl/Oxalic acid dihydrate, ChCl/Malic acid,
518   ChCl/Citric acid hydrate, ChCl/Maltose 1:1, ChCl/Glucose 1:2 (Husanu et al., 2020)

519 xi. Extraction of oat protein by using ChCl/ 1,2-Butylene glycol, ChCl/1,4-Butylene
520   glycol, and ChCl/2,3-Butylene glycol (Yue et al., 2020), and etc.

521 Considering the large possibilities for applications of ChCl-based solvents across a wide array

522 of fields especially in biomass pretreatment for further processing, ChCl demonstrates high

523 potential as the representative constituent of green solvents. The reported studies on biomass

524   pretreatment using ChCl-based solvents delivered promising results on the delignification

525   efficiency in several lignocellulosic biomass samples. For instance, delignification of tortoise-shell

526   bamboo (*Phyllostachys pubescens*) of up to 94.39 % lignin removal were reported with

527   ChCl/Lactic acid pretreatment (Liu et al., 2019). In addition, most studies also reported lignin

528   removal in the range of 40-50 % depending on the type of biomass and green solvents used.

529   ChCl/Oxalic acid also demonstrated the highest delignification efficiency in several biomass

530   samples but the applicability could be restricted due to its toxicity and caustic properties (Kohli et

531   al., 2020). In this sense, ChCl/Lactic acid and ChCl/Malic acid are more preferable although they

532   have lower delignification efficiency compared to oxalic acid based green solvents. As discussed

533   herein, choline chloride is indeed a potential starting material which requires further exploration

534   to unleash its full potential in terms of understanding the way it interacts with HBDs in the

535   formation of DESs/LTTMs.

536   **5. Challenges and future prospects**

537   Advances in lignocellulosic biomass pretreatment techniques are continuously developed and

538   improvised to improve the yield of certain substrates in the lignocellulosic biomass. Considering

539   the recent emphasis on green chemistry, there will be a large room for advancements in green

540   solvents for the pretreatment of lignocellulosic biomass considering the near-infinite possible

541   combinations of DESs/LTTMs with different pairs of HBA and HBA.

542   Although active researches were devoted to the application of DESs/LTTMs, comprehensive

543   studies and characterisation of the physicochemical properties of DESs/LTTMs are still scarce. A

544   gap exists in fully understanding DESs/LTTMs, which can be attributed to the ambiguity in the

545   building principles, incomprehensive knowledge on the mechanisms of formation, as well as the

546   intermolecular interactions within the solvent. After all, the pivotal key to explore deeper into

547   DESs/LTTMs lies upon its fundamental, where its physicochemical properties play a significant

548   role in modulating the species reactivity and behaviour of the DESs/LTTMs (Savi et al., 2019).

549   The future advances in this field could outseen the possibilities of developing green solvents

550   with extraordinary performances in lignocellulosic biomass pretreatment through in-depth studies

551   on the physicochemical properties of DESs/LTTMs with advanced design methodologies in

552   formulating a task-specific DESs/LTTMs. Apart from that, the application and recycling of

553   solvents are limited by their thermal instability and susceptibility to contaminants, which could

554   interfere with interactions between HBAs and HBDs (Tang et al., 2017). Hence, on-going studies

555   into the development of stable and recyclable DESs/LTTMs systems are needed.

556   Recent studies also underscored the concern associated with cytotoxic profiles of existing

557   green solvents despite their low toxicity nature, especially for use in pharmaceuticals and

558   therapeutic mediums which requires an essentially safe margin of toxic levels (Hayyan et al.,

559   2016). Consequently, emerging trends of synthesis of solvents from natural sources to create

560   natural deep eutectic solvents (NADES) (Mitar et al., 2019) and those certified safe for therapeutic

561   means as in therapeutic deep eutectic solvents (THEDES) (Dwamena, 2019) could be outseen as

562   the future prospects of green solvents.

563   **6. Conclusions**

564   Pretreatment process plays a significance role in disrupting the recalcitrant structure of

565   lignocellulosic biomass to obtain the enzyme accessible substrates. DESs/LTTMs came up as the

566   most promising alternative among other pretreatment technologies and solvents with their

567   versatility and a highly tunable nature by just varying the composition of its constituents. The

568   immense interest in ChCl sparked an exponential growth on the studies of ChCl-based solvents

569   whereby most of them was applied in lignocellulosic biomass pretreatment. More detailed

570 information on green solvents development associated with existing research gaps can contribute

571 to the field of biomass-to-energy conversion in the future.

572 **CRediT authorship contribution statement**

573 **Chung Loong Yiin: Conceptualization, Writing – original draft, Writing – review & editing,**

574 **Visualization, Supervision, Funding acquisition. Kok Liang Yap: Writing – original draft,**

575 **Writing – review & editing.** Andrian Zi En Ku**: Writing – original draft, Writing – review &**

576 **editing.** Bridgid Lai Fui Chin**: Writing – review & editing.** Serene Sow Mun Lock**: Writing –**

577 **review & editing.** Kin Wai Cheah**: Writing – review & editing.** Adrian Chun Minh Loy**: Writing**

578 **– review & editing.** Yi Herng Chan**: Writing – review & editing.**

583 **References**

584 [1] Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel

585   solvent properties of choline chloride/urea mixtures. *Chemical Communications*, *1*, 70–71.

586 [2] Abood, H. M. A., Abbott, A. P., Ballantyne, A. D., & Ryder, K. S. (2011). Do all ionic liquids

587   need organic cations? Characterisation of [AlCl2·nAmide]+ AlCl4- and comparison with

588   imidazolium based systems. *Chemical Communications*, *47*(12), 3523–3525.

589 [3] Abranches, D. O., Martins, M. A. R., Silva, L. P., Schaeffer, N., Pinho, S. P., & Coutinho, J.

590   A. P. (2019). Phenolic hydrogen bond donors in the formation of non-ionic deep eutectic

591   solvents: The quest for type V des. *Chemical Communications*, *55*(69), 10253–10256.

592   [4] Aguilar-Reynosa, A., Romaní, A., Ma. Rodríguez-Jasso, R., Aguilar, C. N., Garrote, G., &

593   Ruiz, H. A. (2017). Microwave heating processing as alternative of pretreatment in second-

594   generation biorefinery: An overview. *Energy Conversion and Management*, *136*, 50–65.

595   [5] Alañón, M. E., Ivanović, M., Gómez-Caravaca, A. M., Arráez-Román, D., & Segura-

596   Carretero, A. (2020). Choline chloride derivative-based deep eutectic liquids as novel green

597   alternative solvents for extraction of phenolic compounds from olive leaf. *Arabian Journal of*

598   *Chemistry*, *13*(1), 1685–1701.

599   [6] Alhadid, A., Mokrushina, L., & Minceva, M. (2020). Design of deep eutectic systems: A

600   simple approach for preselecting eutectic mixture constituents. *Molecules*, *25*(5), 1077.

601   [7] Alkhatib, I. I. I., Ferreira, M. L., Alba, C. G., Bahamon, D., Llovell, F., Pereiro, A. B., Araújo,

602   J. M. M., Abu-Zahra, M. R. M., & Vega, L. F. (2020). Screening of Ionic Liquids and Deep

603   Eutectic Solvents for Physical CO2Absorption by Soft-SAFT Using Key Performance

604   Indicators. *Journal of Chemical and Engineering Data*, *65*(12), 5844–5861.

605   [8] Agu, O. S., G. Tabil, L., Meda, V., & Dumonceaux and Edmund Mupondwav, T. (2019).

606   Pretreatment of Crop Residues by Application of Microwave Heating and Alkaline Solution

607   for Biofuel Processing: A Review. In *Renewable Resources and Biorefineries*. IntechOpen.

608   [9] Amin, F. R., Khalid, H., Zhang, H., Rahman, S., Zhang, R., Liu, G., & Chen, C. (2017).

609   Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express*, *7*(1),

610   72.

611   [10]   An, S., Li, W., Xue, F., Li, X., Xia, Y., Liu, Q., Chen, L., Jameel, H., & Chang, H. min.

612   (2020). Effect of removing hemicellulose and lignin synchronously under mild conditions on

613   enzymatic hydrolysis of corn stover. *Fuel Processing Technology*, *204*, 106407.

614   [11]   Anwar, Z., Gulfraz, M., & Irshad, M. (2014). Agro-industrial lignocellulosic biomass a key

615   to unlock the future bio-energy: A brief review. *Journal of Radiation Research and Applied*

616   *Sciences*, *7*(2), 163–173.

617 [12]   Azmin, S. N. H. M., Yunus, N. A., Mustaffa, A. A., Alwi, S. R. W., & Chua, L. S. (2015).

618   Computer-Aided Approach for Designing Solvents Blend for Herbal Phytochemical

619   Extraction. In *Computer Aided Chemical Engineering* (Vol. 37, pp. 1427–1432). Elsevier B.V.

620 [13]   Baaqel, H., Díaz, I., Tulus, V., Chachuat, B., Guillén-Gosálbez, G., & Hallett, J. P. (2020).

621   Role of life-cycle externalities in the valuation of protic ionic liquids-a case study in biomass

622   pretreatment solvents. *Green Chemistry*, *22*(10), 3132–3140.

623 [14]   Bai, X., Wang, G., Yu, Y., Wang, D., & Wang, Z. (2018). Changes in the physicochemical

624   structure and pyrolysis characteristics of wheat straw after rod-milling pretreatment.

625   *Bioresource Technology*, *250*, 770–776.

626 [15]   Baruah, J., Nath, B. K., Sharma, R., Kumar, S., Deka, R. C., Baruah, D. C., & Kalita, E.

627   (2018). Recent trends in the pretreatment of lignocellulosic biomass for value-added products.

628   *Frontiers in Energy Research*, *6*, 141.

629 [16]   Behera, S., Arora, R., Nandhagopal, N., & Kumar, S. (2014). Importance of chemical

630   pretreatment for bioconversion of lignocellulosic biomass. *Renewable and Sustainable Energy*

631   *Reviews*, *36*, 91–106.

632 [17]   Bergez-Lacoste, M., Thiebaud-Roux, S., De Caro, P., Fabre, J.-F., Gerbaud, V., &

633   Mouloungui, Z. (2014). From chemical platform molecules to new biosolvents: Design

634   engineering as a substitution methodology. *Biofuels, Bioproducts and Biorefining*, *8*(3), 438–

635   451.

636 [18]   Bernasconi, R., Panzeri, G., Accogli, A., Liberale, F., Nobili, L., & Magagnin, L. (2017).

637   Electrodeposition from Deep Eutectic Solvents. In *Progress and Developments in Ionic*

638   *Liquids* (pp. 235–262). InTech Open.

639   [19]   Bharathiraja, B., Jayamuthunagai, J., Chakravarthy, M., & Kumar, R. P. (2018).

640   Bioprocessing of Biofuels for Green and Clean Environment. In V. Sivasubramanian (Ed.),

641   *Bioprocess Engineering for a Green Environment* (pp. 237–249). CRC Press.

642   [20]   Bhatia, S. K., Kim, S. H., Yoon, J. J., & Yang, Y. H. (2017). Current status and strategies

643   for second generation biofuel production using microbial systems. *Energy Conversion and*

644   *Management*, *148*, 1142–1156.

645   [21]   Bhutto, A. W., Qureshi, K., Harijan, K., Abro, R., Abbas, T., Bazmi, A. A., Karim, S., &

646   Yu, G. (2017). Insight into progress in pre-treatment of lignocellulosic biomass. *Energy*, *122*,

647   724–745.

648   [22]   Bolado-Rodríguez, S., Toquero, C., Martín-Juárez, J., Travaini, R., & García-Encina, P. A.

649   (2016). Effect of thermal, acid, alkaline and alkaline-peroxide pretreatments on the

650   biochemical methane potential and kinetics of the anaerobic digestion of wheat straw and

651   sugarcane bagasse. *Bioresource Technology*, *201*, 182–190.

652   [23]   Borand, M. N., & Karaosmanoğlu, F. (2018). Effects of organosolv pretreatment

653   conditions for lignocellulosic biomass in biorefinery applications: A review. *Journal of*

654   *Renewable and Sustainable Energy*, *10*(3), 033104.

655   [24]   Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K. B., & Ramakrishnan, S.

656   (2011). Chemical and physicochemical pretreatment of lignocellulosic biomass: A review.

657   *Enzyme Research*, *2011*(1), 1–17.

658   [25]   Capolupo, L., & Faraco, V. (2016). Green methods of lignocellulose pretreatment for

659   biorefinery development. *Applied Microbiology and Biotechnology*, *100*(22), 9451–9467.

660   [26]   Chen, H.-Z., & Liu, Z.-H. (2015). Steam explosion and its combinatorial pretreatment

661   refining technology of plant biomass to bio-based products. *Biotechnology Journal*, *10*(6),

662   866–885.

663   [27]   Chen, H., Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., & Han, S. (2017). A

664   review on the pretreatment of lignocellulose for high-value chemicals. *Fuel Processing*

665   *Technology*, *160*, 196–206.

666   [28]   Chen, Y., Yu, D., Chen, W., Fu, L., & Mu, T. (2019). Water absorption by deep eutectic

667   solvents. *Physical Chemistry Chemical Physics*, *21*(5), 2601–2610.

668   [29]   Cicci, A., Sed, G., & Bravi, M. (2017). Potential of choline chloride - Based Natural Deep

669   eutectic solvents (NaDES) in the extraction of microalgal metabolites. *Chemical Engineering*

670   *Transactions*, *57*, 61–66.

671   [30]   Dahadha, S., Amin, Z., Bazyar Lakeh, A. A., & Elbeshbishy, E. (2017). Evaluation of

672   Different Pretreatment Processes of Lignocellulosic Biomass for Enhanced Biomethane

673   Production. *Energy and Fuels*, *31*(10), 10335–10347.

674   [31]   Dai, Y., van Spronsen, J., Witkamp, G. J., Verpoorte, R., & Choi, Y. H. (2013). Natural

675   deep eutectic solvents as new potential media for green technology. *Analytica Chimica Acta*,

676   *766*, 61–68.

677   [32]   Das, S., Mondal, A., & Balasubramanian, S. (2017). Recent advances in modeling green

678   solvents. *Current Opinion in Green and Sustainable Chemistry*, *5*, 37–43.

679   [33]   Deng, X., Duan, X., Gong, L., & Deng, D. (2020). Ammonia Solubility, Density, and

680   Viscosity of Choline Chloride-Dihydric Alcohol Deep Eutectic Solvents. *Journal of Chemical*

681   *and Engineering Data*, *65*(10), 4845–4854.

682   [34]   Duan, M., Luo, M., Yang, Z., Xiong, Y., Shi, P., Fang, S., & Qin, S. (2020). Application

683   of choline-based deep eutectic solvent for the extraction of crude-oil contaminated soils.

684   *Environmental Technology*, 1–6.

[35]   Duque, A., Manzanares, P., & Ballesteros, M. (2017). Extrusion as a pretreatment for lignocellulosic biomass: Fundamentals and applications. *Renewable Energy*, *114*, 1427–1441.

[36]   Durand, E., Lecomte, J., & Villeneuve, P. (2015). Are emerging deep eutectic solvents (DES) relevant for lipase-catalyzed lipophilizations? *OCL - Oilseeds and Fats, Crops and Lipids*, *22*(4), D408.

[37]   Dwamena, A. K. (2019). Recent Advances in Hydrophobic Deep Eutectic Solvents for Extraction. *Separations*, *6*(1), 9.

[38]   El-Naggar, N. E. A., Deraz, S., & Khalil, A. (2014). Bioethanol production from lignocellulosic feedstocks based on enzymatic hydrolysis: Current status and recent developments. *Biotechnology*, *13*(1), 1–21.

[39]   Emami, S., & Shayanfar, A. (2020). Deep eutectic solvents for pharmaceutical formulation and drug delivery applications. *Pharmaceutical Development and Technology*, *25*(7), 779–796.

[40]   Ezgi Ünlü, A., & Takaç, S. (2020). Use of Deep Eutectic Solvents in the Treatment of Agro-Industrial Lignocellulosic Wastes for Bioactive Compounds. In *Agroecosystems – Very Complex Environmental Systems*. IntechOpen.

[41]   Francisco, M., Van Den Bruinhorst, A., & Kroon, M. C. (2012). New natural and renewable low transition temperature mixtures (LTTMs): Screening as solvents for lignocellulosic biomass processing. *Green Chemistry*, *14*(8), 2153–2157.

[42]   Francisco, M., Van Den Bruinhorst, A., & Kroon, M. C. (2013). Low-transition-temperature mixtures (LTTMs): A new generation of designer solvents. *Angewandte Chemie - International Edition*, *52*(11), 3074–3085.

707   [43]   Fu, S. F., Wang, F., Yuan, X. Z., Yang, Z. M., Luo, S. J., Wang, C. S., & Guo, R. B. (2015).

708   The thermophilic (55 °C) microaerobic pretreatment of corn straw for anaerobic digestion.

709   *Bioresource Technology*, *175*, 203–208.

710   [44]   Fukaya, Y., Iizuka, Y., Sekikawa, K., & Ohno, H. (2007). Bio ionic liquids: Room

711   temperature ionic liquids composed wholly of biomaterials. *Green Chemistry*, *9*(11), 1155–

712   1157.

713   [45]   Gao, W., Lei, Z., Tabil, L. G., & Zhao, R. (2020). Biological Pretreatment by Solid-State

714   Fermentation of Oat Straw to Enhance Physical Quality of Pellets. *Journal of Chemistry*, *2020*.

715   [46]   Haraźna, K., Walas, K., Urbańska, P., Witko, T., Snoch, W., Siemek, A., Jachimska, B.,

716   Krzan, M., Napruszewska, B. D., Witko, M., Bednarz, S., & Guzik, M. (2019).

717   Polyhydroxyalkanoate-derived hydrogen-bond donors for the synthesis of new deep eutectic

718   solvents. *Green Chemistry*, *21*(11), 3116–3126.

719   [47]   Hayyan, M., Mbous, Y. P., Looi, C. Y., Wong, W. F., Hayyan, A., Salleh, Z., & Mohd-Ali,

720   O. (2016). Natural deep eutectic solvents: cytotoxic profile. *SpringerPlus*, *5*(1), 913.

721   [48]   Husanu, E., Mero, A., Rivera, J. G., Mezzetta, A., Ruiz, J. C., D'andrea, F., Pomelli, C. S.,

722   & Guazzelli, L. (2020). Exploiting Deep Eutectic Solvents and Ionic Liquids for the

723   Valorization of Chestnut Shell Waste. *ACS Sustainable Chemistry and Engineering*, *8*(50),

724   18386–18399.

725   [49]   Hussin, M. S. A., Varanusupakul, P., Shahabuddin, S., Boon, Y. H., & Mohamad, S.

726   (2020). Synthesis and characterization of green menthol-based low transition temperature

727   mixture with tunable thermophysical properties as hydrophobic low viscosity solvent. *Journal*

728   *of Molecular Liquids*, *308*, 113015.

729   [50]   Jędrzejczyk, M., Soszka, E., Czapnik, M., Ruppert, A. M., & Grams, J. (2019). Physical

730   and chemical pretreatment of lignocellulosic biomass. In A. Basile & F. Dalena (Eds.), *Second*

731   *and Third Generation of Feedstocks* (pp. 143–196). Elsevier.

732   [51]   Kalhor, P., & Ghandi, K. (2019). Deep eutectic solvents for pretreatment, extraction, and

733   catalysis of biomass and food waste. *Molecules*, *24*(22), 1–37.

734   [52]   Kalita, E., Nath, B. K., Deb, P., Agan, F., Islam, M. R., & Saikia, K. (2015). High quality

735   fluorescent cellulose nanofibers from endemic rice husk: Isolation and characterization.

736   *Carbohydrate Polymers*, *122*, 308–313.

737   [53]   Kandanelli, R., Thulluri, C., Mangala, R., Rao, P. V. C., Gandham, S., & Velankar, H. R.

738   (2018). A novel ternary combination of deep eutectic solvent-alcohol (DES-OL) system for

739   synergistic and efficient delignification of biomass. *Bioresource Technology*, *265*, 573–576.

740   [54]   Kim, J. S., Lee, Y. Y., & Kim, T. H. (2016). A review on alkaline pretreatment technology

741   for bioconversion of lignocellulosic biomass. *Bioresource Technology*, *199*, 42–48.

742   [55]   Kohli, K., Katuwal, S., Biswas, A., & Sharma, B. K. (2020). Effective delignification of

743   lignocellulosic biomass by microwave assisted deep eutectic solvents. *Bioresource*

744   *Technology*, *303*, 122897.

745   [56]   Kottaras, P., Koulianos, M., & Makris, D. (2017). Low-Transition Temperature Mixtures

746   (LTTMs) Made of Bioorganic Molecules: Enhanced Extraction of Antioxidant Phenolics from

747   Industrial Cereal Solid Wastes. *Recycling*, *2*(1), 3.

748   [57]   Kovács, A., Neyts, E. C., Cornet, I., Wijnants, M., & Billen, P. (2020). Modeling the

749   Physicochemical Properties of Natural Deep Eutectic Solvents. *ChemSusChem*, *13*(15), 3789–

750   3804.

751   [58]   Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment

752   of lignocellulosic feedstocks: a review. *Bioresources and Bioprocessing*, *4*(1), 7.

753 [59] Kumar, A., Anushree, Kumar, J., Bhaskar, T., 2020. Utilization of lignin: A sustainable

754   and eco-friendly approach. *Journal of the Energy Institute,* 93, 235-271.

755 [60] Li, H., Qu, Y., Yang, Y., Chang, S., & Xu, J. (2016). Microwave irradiation - A green and

756   efficient way to pretreat biomass. *Bioresource Technology*, *199*, 34–41.

757 [61] Li, X., Sun, C., Zhou, B., & He, Y. (2015). Determination of Hemicellulose, Cellulose and

758   Lignin in Moso Bamboo by Near Infrared Spectroscopy. *Scientific Reports*, *5*(1), 17210.

759 [62] Liu, Q., Yuan, T., Fu, Q. jin, Bai, Y. yuan, Peng, F., & Yao, C. L. (2019). Choline chloride-

760   lactic acid deep eutectic solvent for delignification and nanocellulose production of moso

761   bamboo. *Cellulose*, *26*(18), 9447–9462.

762 [63] Liu, X., Fu, N., Zhang, Q., Cai, S., Wang, Q., Han, D., & Tang, B. (2019). Green Tailoring

763   with Water of Choline Chloride Deep Eutectic Solvents for the Extraction of Polyphenols from

764   Palm Samples. *Journal of Chromatographic Science*, *57*(3), 272–278.

765 [64] Liyakathali, N. A. M., Muley, P. D., Aita, G., & Boldor, D. (2016). Effect of frequency

766   and reaction time in focused ultrasonic pretreatment of energy cane bagasse for bioethanol

767   production. *Bioresource Technology*, *200*, 262–271.

768 [65] Louis, A. C. F., & Venkatachalam, S. (2020). Energy efficient process for valorization of

769   corn cob as a source for nanocrystalline cellulose and hemicellulose production. *International

770   Journal of Biological Macromolecules*, *163*, 260–269.

771 [66] Luo, J., Fang, Z., & Smith, R. L. (2014). Ultrasound-enhanced conversion of biomass to

772   biofuels. *Progress in Energy and Combustion Science*, *41*(1), 56–93.

773 [67] Mainberger, S., Kindlein, M., Bezold, F., Elts, E., Minceva, M., & Briesen, H. (2017).

774   Deep eutectic solvent formation: a structural view using molecular dynamics simulations with

775   classical force fields. *Molecular Physics*, *115*(9–12), 1309–1321.

776 [68] Mallakpour, S., & Dinari, M. (2012). Ionic liquids as green solvents: Progress and

777 prospects. In *Green Solvents II: Properties and Applications of Ionic Liquids* (pp. 1–32).

778 Springer Netherlands.

779 [69] Mansor, A. M., Lim, J. S., Ani, F. N., Hashim, H., & Ho, W. S. (2019). Characteristics of

780 cellulose, hemicellulose and lignin of MD2 pineapple biomass. *Chemical Engineering*

781 *Transactions*, *72*, 79–84.

782 [70] Marcus, Y. (2019). Applications of Deep Eutectic Solvents. In *Deep Eutectic Solvents* (pp.

783 111–151). Springer International Publishing.

784 [71] Maurya, D. P., Singla, A., & Negi, S. (2015). An overview of key pretreatment processes

785 for biological conversion of lignocellulosic biomass to bioethanol. *3 Biotech*, *5*, 597–609.

786 [72] Mitar, A., Panić, M., Kardum, J. P., Halambek, J., Sander, A., Kučan, K. Z., Redovniković,

787 I. R., & Radošević, K. (2019). Physicochemical Properties, Cytotoxicity, and Antioxidative

788 Activity of Natural Deep Eutectic Solvents Containing Organic Acid. *Chemical and*

789 *Biochemical Engineering Quarterly*, *33*(1), 1–18.

790 [73] Mood, S. H., Hossein Golfeshan, A., Tabatabaei, M., Salehi Jouzani, G., Najafi, G. H.,

791 Gholami, M., & Ardjmand, M. (2013). Lignocellulosic biomass to bioethanol, a

792 comprehensive review with a focus on pretreatment. *Renewable and Sustainable Energy*

793 *Reviews*, *27*, 77–93.

794 [74] Nauman Aftab, M., Iqbal, I., Riaz, F., Karadag, A., & Tabatabaei, M. (2019). Different

795 Pretreatment Methods of Lignocellulosic Biomass for Use in Biofuel Production. In *Biomass*

796 *for Bioenergy - Recent Trends and Future Challenges*. IntechOpen.

797 [75] Noshadi, I., Walker, B. W., Portillo-Lara, R., Sani, E. S., Gomes, N., Aziziyan, M. R., &

798 Annabi, N. (2017). Engineering Biodegradable and Biocompatible Bio-ionic Liquid

Conjugated Hydrogels with Tunable Conductivity and Mechanical Properties. *Scientific Reports*, *7*(1), 1–18.

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

[77]   Peña-Lucio, E. M., Londoño-Hernández, L., Ascacio-Valdes, J. A., Chavéz-González, M. L., Bankole, O. E., & Aguilar, C. N. (2020). Use of coffee pulp and sorghum mixtures in the production of n-demethylases by solid-state fermentation. *Bioresource Technology*, *305*, 123112.

[78]   Pielhop, T., Amgarten, J., Von Rohr, P. R., & Studer, M. H. (2016). Steam explosion pretreatment of softwood: The effect of the explosive decompression on enzymatic digestibility. *Biotechnology for Biofuels*, *9*(1), 152.

[79]   Rajendran, K., Drielak, E., Sudarshan Varma, V., Muthusamy, S., & Kumar, G. (2018). Updates on the pretreatment of lignocellulosic feedstocks for bioenergy production–a review. *Biomass Conversion and Biorefinery*, *8*(2), 471–483.

[80]   Ratnasingam, J., Ramasamy, G., Tau Wai, L., Senin, A. L., & Muttiah, N. (2015). The Prospects of Rubberwood Biomass Energy Production in Malaysia. *BioResources*, *10*(2), 2526–2548.

[81]   Ratti, R. (2014). Ionic Liquids: Synthesis and Applications in Catalysis. *Advances in Chemistry*, *2014*, 1–16.

[82]   Ravindran, R., & Jaiswal, A. K. (2016). A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: Challenges and opportunities. *Bioresource Technology*, *199*, 92–102.

822   [83]   Reddy, K. O., Maheswari, C. U., Dhlamini, M. S., Mothudi, B. M., Kommula, V. P.,

823   Zhang, J., Zhang, J., & Rajulu, A. V. (2018). Extraction and characterization of cellulose single

824   fibers from native african napier grass. *Carbohydrate Polymers*, *188*, 85–91.

825   [84]   Reis, R. S., Tienne, L. G. P., Souza, D. de H. S., Marques, M. de F. V., & Monteiro, S. N.

826   (2020). Characterization of coffee parchment and innovative steam explosion treatment to

827   obtain microfibrillated cellulose as potential composite reinforcement. *Journal of Materials*

828   *Research and Technology*, *9*(4), 9412–9421.

829   [85]   Rodriguez-Donis, I., Thiebaud-Roux, S., Lavoine, S., & Gerbaud, V. (2018). Computer-

830   aided product design of alternative solvents based on phase equilibrium synergism in mixtures.

831   *Comptes Rendus Chimie*, *21*(6), 606–621.

832   [86]   Saha, S. K., Dey, S., & Chakraborty, R. (2019). Effect of choline chloride-oxalic acid based

833   deep eutectic solvent on the ultrasonic assisted extraction of polyphenols from Aegle

834   marmelos. *Journal of Molecular Liquids*, *287*, 110956.

835   [87]   Samarov, A. A., Smirnov, M. A., Sokolova, M. P., & Toikka, A. M. (2018). Liquid-Liquid

836   Equilibrium Data for the System N-Octane + Toluene + DES at 293.15 and 313.15 K and

837   Atmospheric Pressure. *Theoretical Foundations of Chemical Engineering*, *52*(2), 258–263.

838   [88]   Santos, J., Ouadi, M., Jahangiri, H., & Hornung, A. (2020). Valorisation of lignocellulosic

839   biomass investigating different pyrolysis temperatures. *Journal of the Energy Institute*, *93*(5),

840   1960–1969.

841   [89]   Savi, L. K., Dias, M. C. G. C., Carpine, D., Waszczynskyj, N., Ribani, R. H., & Haminiuk,

842   C. W. I. (2019). Natural deep eutectic solvents (NADES) based on citric acid and sucrose as a

843   potential green technology: a comprehensive study of water inclusion and its effect on thermal,

844   physical and rheological properties. *International Journal of Food Science and Technology*,

845   *54*(3), 898–907.

846   [90]   Scholl, A. L., Menegol, D., Pitarelo, A. P., Fontana, R. C., Filho, A. Z., Ramos, L. P.,

847   Dillon, A. J. P., & Camassola, M. (2015). Elephant grass pretreated by steam explosion for

848   inducing secretion of cellulases and xylanases by Penicillium echinulatum S1M29 solid-state

849   cultivation. *Industrial Crops and Products*, *77*, 97–107.

850   [91]   Shirkavand, E., Baroutian, S., Gapes, D. J., & Young, B. R. (2016). Combination of fungal

851   and physicochemical processes for lignocellulosic biomass pretreatment - A review.

852   *Renewable and Sustainable Energy Reviews*, *54*, 217–234.

853   [92]   Silva, J. M., Pereira, C. V., Mano, F., Silva, E., Castro, V. I. B., Sá-Nogueira, I., Reis, R.

854   L., Paiva, A., Matias, A. A., & Duarte, A. R. C. (2019). Therapeutic Role of Deep Eutectic

855   Solvents Based on Menthol and Saturated Fatty Acids on Wound Healing. *ACS Applied Bio*

856   *Materials*, *2*(10), 4346–4355.

857   [93]   Sindhu, R., Binod, P., & Pandey, A. (2016). Biological pretreatment of lignocellulosic

858   biomass - An overview. *Bioresource Technology*, *199*, 76–82.

859   [94]   Singh, J., Suhag, M., & Dhaka, A. (2015). Augmented digestion of lignocellulose by steam

860   explosion, acid and alkaline pretreatment methods: A review. *Carbohydrate Polymers*, *117*,

861   624–631.

862   [95]   Smith, E. L., Abbott, A. P., & Ryder, K. S. (2014). Deep Eutectic Solvents (DESs) and

863   Their Applications. *Chemical Reviews*, *114*(21), 11060–11082.

864   [96]   Sun, S., Sun, S., Cao, X., & Sun, R. (2016). The role of pretreatment in improving the

865   enzymatic hydrolysis of lignocellulosic materials. *Bioresource Technology*, *199*, 49–58.

866   [97]   Tang, X., Zuo, M., Li, Z., Liu, H., Xiong, C., Zeng, X., Sun, Y., Hu, L., Liu, S., Lei, T., &

867   Lin, L. (2017). Green Processing of Lignocellulosic Biomass and Its Derivatives in Deep

868   Eutectic Solvents. *ChemSusChem*, *10*(13), 2696–2706.

869   [98]   Taylor, M., Alabdrabalameer, H., & Skoulou, V. (2019). Choosing Physical,

870   Physicochemical and Chemical Methods of Pre-Treating Lignocellulosic Wastes to Repurpose

871   into Solid Fuels. *Sustainability*, *11*(13), 3604.

872   [99]   Van Osch, D. J. G. P., Zubeir, L. F., Van Den Bruinhorst, A., Rocha, M. A. A., & Kroon,

873   M. C. (2015). Hydrophobic deep eutectic solvents as water-immiscible extractants. *Green*

874   *Chemistry*, *17*(9), 4518–4521.

875   [100]   Verardi, A., Blasi, A., Marino, T., Molino, A., & Calabrò, V. (2018). Effect of steam-

876   pretreatment combined with hydrogen peroxide on lignocellulosic agricultural wastes for

877   bioethanol production: Analysis of derived sugars and other by-products. *Journal of Energy*

878   *Chemistry*, *27*(2), 535–543.

879   [101]   Wagner, A., Lackner, N., Mutschlechner, M., Prem, E., Markt, R., & Illmer, P. (2018).

880   Biological Pretreatment Strategies for Second-Generation Lignocellulosic Resources to

881   Enhance Biogas Production. *Energies*, *11*(7), 1797.

882   [102]   Wang, D., & Tang, R. C. (2018). Dissolution of wool in the choline chloride/oxalic acid

883   deep eutectic solvent. *Materials Letters*, *231*, 217–220.

884   [103]   Wang, D., Yang, X. H., Tang, R. C., & Yao, F. (2018). Extraction of keratin from rabbit

885   hair by a deep eutectic solvent and its characterization. *Polymers*, *10*(9).

886   [104]   Welton, T. (2015). Solvents and sustainable chemistry. *Proceedings of the Royal Society*

887   *A: Mathematical, Physical and Engineering Sciences*, *471*(2183).

888   [105]   Wu, H., Shen, M., Chen, X., Yu, G., Abdeltawab, A. A., & Yakout, S. M. (2019). New

889   absorbents for hydrogen sulfide: Deep eutectic solvents of tetrabutylammonium

890   bromide/carboxylic acids and choline chloride/carboxylic acids. *Separation and Purification*

891   *Technology*, *224*, 281–289.

892   [106]   Xu, G. C., Ding, J. C., Han, R. Z., Dong, J. J., & Ni, Y. (2016). Enhancing cellulose

893   accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation.

894   *Bioresource Technology*, *203*, 364–369.

895   [107]   Yiin, C. L., Ho, S., Yusup, S., Quitain, A. T., Chan, Y. H., Loy, A. C. M., & Gwee, Y. L.

896   (2019). Recovery of cellulose fibers from oil palm empty fruit bunch for pulp and paper using

897   green delignification approach. *Bioresource Technology*, *290*.

898   [108]   Yiin, C. L., Quitain, A. T., Yusup, S., Uemura, Y., Sasaki, M., & Kida, T. (2018).

899   Sustainable green pretreatment approach to biomass-to-energy conversion using natural hydro-

900   low-transition-temperature mixtures. *Bioresource Technology*, *261*, 361–369.

901   [109]   Yoo, C. G., Pu, Y., & Ragauskas, A. J. (2017). Ionic liquids: Promising green solvents for

902   lignocellulosic biomass utilization. *Current Opinion in Green and Sustainable Chemistry*, *5*,

903   5–11.

904   [110]   Yue, J., Zhu, Z., Yi, J., Lan, Y., Chen, B., & Rao, J. (2020). Structure and functionality of

905   oat protein extracted by choline chloride–dihydric alcohol deep eutectic solvent and its water

906   binary mixtures. *Food Hydrocolloids*, *112*, 106330.

907   [111]   Zabed, H., Sahu, J. N., Boyce, A. N., & Faruq, G. (2016). Fuel ethanol production from

908   lignocellulosic biomass: An overview on feedstocks and technological approaches. *Renewable*

909   *and Sustainable Energy Reviews*, *66*, 751–774.

910   [112]   Zdanowicz, M., Wilpiszewska, K., & Spychaj, T. (2018). Deep eutectic solvents for

911   polysaccharides processing. A review. *Carbohydrate Polymers*, *200*, 361–380.

912   [113]   Zhang, K., Pei, Z., & Wang, D. (2016). Organic solvent pretreatment of lignocellulosic

913   biomass for biofuels and biochemicals: A review. *Bioresource Technology*, *199*, 21–33.

914   [114]   Zhang, Q., Tan, X., Wang, W., Yu, Q., Chen, X., Miao, C., Guo, Y., Zhang, Y., Zhuang,

915   X., Sun, Y., Kong, X., & Yuan, Z. (2020). A Novel Recyclable Alkaline Biphasic 2-

916   Phenoxyethanol/Water System for Rice Straw Biorefinery under Mild Conditions. *ACS*

917   *Sustainable Chemistry and Engineering*, *8*(20), 7649–7655.

918   [115]   Zhao, Wei, Yang, R., Zhang, Y., & Wu, L. (2012). Sustainable and practical utilization of

919   feather keratin by an innovative physicochemical pretreatment: High density steam flash-

920   explosion. *Green Chemistry*, *14*(12), 3352–3360.

921   [116]   Zhao, Wenfeng, Chi, X., Li, H., He, J., Long, J., Xu, Y., & Yang, S. (2019). Eco-friendly

922   acetylcholine-carboxylate bio-ionic liquids for controllable: N-methylation and N-formylation

923   using ambient CO2 at low temperatures. *Green Chemistry*, *21*(3), 567–577.

924   [117]   Zhekenov, T., Toksanbayev, N., Kazakbayeva, Z., Shah, D., & Mjalli, F. S. (2017).

925   Formation of type III Deep Eutectic Solvents and effect of water on their intermolecular

926   interactions. *Fluid Phase Equilibria*, *441*, 43–48.

927   [118]   Zhou, T., McBride, K., Linke, S., Song, Z., & Sundmacher, K. (2020). Computer-aided

928   solvent selection and design for efficient chemical processes. *Current Opinion in Chemical*

929   *Engineering*, *27*, 35–44.

930   [119]   Zhuang, X., Wang, W., Yu, Q., Qi, W., Wang, Q., Tan, X., Zhou, G., & Yuan, Z. (2016).

931   Liquid hot water pretreatment of lignocellulosic biomass for bioethanol production

932   accompanying with high valuable products. *Bioresource Technology*, *199*, 68–75.

933   [120]   Zoghlami, A., & Paës, G. (2019). Lignocellulosic Biomass: Understanding Recalcitrance

934   and Predicting Hydrolysis. *Frontiers in Chemistry*, *7*, 874.

Table 1. Composition of selected lignocellulosic biomass wastes.

Lignocellulosic Materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Bamboo	45.0	24.0	20.0	(Li et al., 2015)
Coffee Parchment	22.0	18.0	53.0	(Reis et al., 2020)
Coffee Pulp	33.0	29.0	26.0	(Peña-Lucio et al., 2020)
Corn Cob	45.0	33.0	14.0	(Louis & Venkatachalam, 2020)
Corn Straw	45.4	22.7	10.8	(Fu et al., 2015)
Corn Stover	34.0	23.0	21.0	(An et al., 2020)
Elephant Grass	36.0	24.0	28.0	(Scholl et al., 2015)
MD2 Pineapple	30.0 – 42.0	32.0 - 37.0	32.0 – 37.0	(Mansor et al., 2019)
Napier Grass	47.0	31.0	22.0	(Reddy et al., 2018)
Newspaper	55.0	40.0	30.0	(Anwar et al., 2014)
Oat hulls	35.0 – 45.0	32.0 – 35.0	17.0 – 20.0	(Santos et al., 2020)
Oil Palm Empty Fruit Bunch	65.0	33.5	30.5	(Yiin et al., 2019)
Poplar	49.9	28.7	19.2	(Zabed et al., 2016)
Rice Husk	37.1	29.4	24.1	(Kalita et al., 2015)
Rice Straw	42.0	25.0	24.0	(Zhang et al., 2020)
Sugarcane Bagasse	40.0 – 50.0	20.0 – 30.0	20.0 – 25.0	(Santos et al., 2020)
Wheat Straw	35.0	22.3	15.6	(Bolado-Rodríguez et al., 2016)

Table 2. Comparative summary of different pretreatment methods.

Pretreatment Methods	Solvents Used	Advantages	Disadvantages	Reference
Physical pretreatment				
Milling	—	• High surface contact and pore volume of biomass • No formation of toxic and inhibitory compounds	• High energy demand • High cost of mechanical equipment	(Bai et al., 2018; Baruah et al., 2018)
Microwave irradiation	Sodium chlorite; Hydrogen peroxide	• Short process time • Easy operation • Highly selective • Less inhibitors produced • Faster heat transfer • Eco-friendly	• Poor distribution of microwave power • Uneven heating • Low penetrating radiation	(Baruah et al., 2018; Louis & Venkatachalam, 2020; Agu et al., 2019)
Extrusion	—	• Short residence time • Rapid mixing • High shear • Continuous operation • Moderate barrel temperature • Easy scale-up • No formation of inhibitors • Adaptable to process modifications	• High energy demand • Partial hemicellulose degradation • Incomplete destruction of the lignin-carbohydrate matrix in certain materials	(Capolupo & Faraco, 2016; Mood et al., 2013)
Ultrasonication	—	• High enzymatic digestibility • Effective sugar production • Reduction in the duration of biomass hydrolysis • Promotes the disruption of lignocellulosic biomass	• High energy demand • Not suitable for high-scale applications	(Luo et al., 2014)

		Chemical Pretreatment		
Concentrated acid pretreatment	Sulphuric acid; p-Toluenesulfonic acid	• Enhance the enzymatic hydrolysis of cellulose and hemicelluloses • High sugar conversion rate • Complete removal of crystalline structure of cellulose	• Toxicity • Equipment corrosion • High cost of operation and maintenance • Acid recovery • Formation of fermentation inhibitors	(An et al., 2020; Baruah et al., 2018; Zabed et al., 2016)
Dilute acid pretreatment	Dilute sulphuric acid	• Economical • Eco-friendly • Improved digestibility • Lesser inhibitors produced	• Little lignin removal • Requires neutralisation of the pretreated slurry	(An et al., 2020; Zabed et al., 2016)
Ozonolysis	Ethanol	• Increased biodegradability of cellulose fibrils • Strong oxidant • Low amounts of inhibitors produced	• Highly flammable, reactive, corrosive • High energy demand • High generation costs	(Mood et al., 2013; Zabed et al., 2016)
Alkaline pretreatment	Sodium hydroxide; Potassium hydroxide; Calcium hydroxide; Ammonia	• Reduction in crystallinity • Decrease in degree of polymerisation • Increase of surface area and porosity • Low operating temperature • Complex reactors are not needed	• Long residence time from hours to days • Neutralisation of the pretreated slurry	(Behera et al., 2014; Gao et al., 2020; Mood et al., 2013)
Organosolv pretreatment	Ethanol; Methanol; Glycol; Glycerol; Formic acid; Acetic acid; Acetone; Phenol; Dioxane	• Easy recovery • Lignin obtained from the pretreatment as value-added by-products	• Costly • High energy demand • Risky due to high pressure • Highly flammable and volatile • Formation of inhibitors	(Borand & Karaosmanoğlu, 2018; Gao et al., 2020; Zhang et al., 2016)
		Biological Pretreatment		

Pretreatment with micro-organisms	Potato dextrose agar	• Low cost of operation • Low energy demand • No chemicals requirement • Environmentally friendly and sustainable	• Long residence time • Low efficiency • Large space required • Constant supervision of micro-organisms growth	(Bhatia et al., 2017; Maurya et al., 2015; Peña-Lucio et al., 2020; Sindhu et al., 2016)
		Physicochemical Pretreatment		
Steam explosion	Ethanol; Toluene; Sulphuric acid; Potassium hydroxide; Sodium hydroxide	• Low capital costs • Minimum environmental effect • Limited use of chemicals • Low energy demand • High sugar recovery	• Formation of inhibitors at harsh conditions	(Gao et al., 2020; Pielhop et al., 2016; Reis et al., 2020; Verardi et al., 2018)
Ammonia fiber explosion (AFEX)	Liquid ammonia	• Removal of hemicellulose and lignin • Reduction in cellulose crystallinity • No inhibitors formed	• High operating cost • Non-environmentally friendly • Highly volatile • Lignocellulosic biomass with low lignin content is preferable • High energy demand	(Baruah et al., 2018; Gao et al., 2020)
Supercritical CO_2 explosion	Supercritical CO_2	• Increased accessibility of cellulose fibers to enzymatic hydrolysis • Non-flammability • Non-toxicity • Easy recovery	• High equipment costs • Unsuitable for lignocellulosic biomass with no moisture content	(Baruah et al., 2018; Bharathiraja et al., 2018; Capolupo & Faraco, 2016)
Liquid hot water (LHW)	Water	• Removal of lignin • Increased accessible surface area • No formation of toxic materials • Minimal inhibitors formed	• High water demand • High energy demand	(Bhutto et al., 2017; Zhuang et al., 2016)

		• No catalysts or chemicals requirement		
		Green Solvents Pretreatment		
Deep eutectic solvents (DESs)	Choline chloride/Glycerol; Choline chloride/Lactic acid	• Disintegration of complex structure • Highly biodegradable and sustainable • Less costly • Easily prepared • Low energy demand	• Hygroscopicity properties of DESs • Highly viscous	(Chen & Mu, 2019; Zdanowicz et al., 2018)
Ionic liquids (ILs)	Imidazolium-based ($[(C_3N_2)X_n]^+$); Ammonium-based $[NX_4]^+$	• Dissolution of hemicelluloses and lignin • Increased porosity and amorphous structure of cellulose • Easily recovered and recycled • High thermal stability • Conducted at moderate condition • Non-volatile and non-toxic	• Expensive • Not suitable for large-scale applications chi	(Baruah et al., 2018; Chen et al., 2017; Mood et al., 2013)
Low-transition-temperature-mixtures (LTTMs)	L-lactic acid-Glycine / L-lactic acid-Choline chloride / L-lactic acid-L-alanine	• Higher extraction yields • Highly biodegradable and sustainable • Economical • Non-toxic • Non-flammable • Easily prepared	• Thermal stability is not based on the thermal stability of starting materials	(Francisco et al., 2013; Kottaras et al., 2017)

Table 3. Classification of eutectics based on the nature of the complexing agent and

their respective general formulas (Abranches et al., 2019; Kalhor & Ghandi, 2019;

Smith et al., 2014)

Type	General Formula	Terms
I	$Cat^+X^-zMCl_x$	M = Zn, Sn, Fe, Al, Ga, In
II	$Cat^+X^-zMCl_x \cdot yH2O$	M = Cr, Co, Cu, Ni, Fe
III	Cat^+X^-zRZ	Z = $CONH_2$, COOH, OH
IV	$MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}^-$	M = Al, Zn; and Z = $CONH_2$, OH
V	*Non-ionic DESs	Composed only of molecular substances

Type V DES: Recently proposed and not well established (Abranches et al., 2019)

Table 4. Applications of ChCl-based solvents in lignocellulosic biomass pretreatment.

DESs/LTTMs	Application	Key Findings	Reference
ChCl/Urea 1:2	Pretreatment of rice straw biomass for the isolation of holocellulose, α-cellulose, and acid-insoluble lignin (AIL)	Attained highest dissolution capacity for AIL at 22.87%, followed by 16.71 % of hemicellulose and amorphous cellulose, and 9.60% of α-cellulose. ChCl/Urea also demonstrated higher dissolution selectivity on lignin.	(Pan et al., 2017)
ChCl/Oxalic acid dihydrate 1:1	Pretreatment and delignification of Poplar wood lignocellulosic biomass to extract lignin oligomers	The LTTMs coupled with Microwave-Assisted Extraction (MAE), successfully extracted lignin oligomers of high purity (about 96 %) from the sample.	(Liu et al., 2017)
ChCl/L-Malic acid/Water 2:4:2 ChCl/Malic acid (cactus)/Water 2:4:2	Delignification of oil palm biomass residues	Cactus malic acid can attain a considerable performance in lignin removal compared to L-malic acid, with lignin removal at 41.94 % by using ChCl/L-Malic acid/Water while its cactus malic acid variant attained 37.22 % delignification.	(Yiin et al., 2017)
ChCl/Lactic acid 1:9	Delignification of tortoise-shell bamboo (*Phyllostachys pubescens*) for the recovery of cellulose nanofibers	Most of the lignin was efficiently removed (up to 94.39 %) after pre-treatment with ChCl/Lactic acid at 120 °C over a duration of 3 h with a solid-to-solvent ratio of 0.04 (w/w), and 91 % recovery of cellulose was recorded.	(Liu et al., 2019)
ChCl/Lactic acid 1:10 to 1:250	Delignification of Gum tree (*Eucalyptus globulus*) chips	ChCl/Lactic acid was found to have a slightly lower lignin solubility compared to pure lactic	(Smink et al., 2019)

	biomass with small amount of HBA	acid, however, a surge in the bond fission rate of *β-O*-4 linkages of the lignin was observed.	
ChCl/Formic acid 1:2	Pretreatment of lignin to produce lignin with tailor-made properties	The regenerated lignin samples were reported to be 44-75 % implying that delignification occurred to a certain extent.	(Hong et al., 2020)
ChCl/Lactic acid; ChCl/Oxalic acid; ChCl/Malic acid; ChCl/Urea	Pretreatment and delignification of Asplund pulp from Norway spruce (*Picea abies*)	Around 50 % lignin removal was equally achieved by using ChCl/Lactic acid, ChCl/Oxalic acid and ChCl/Urea DESs while ChCl/Malic acid achieved significantly less effective delignification.	(Fiskari et al., 2020)
ChCl/Acetic acid 1:2; ChCl/Formic acid 1:2; ChCl/Glycerol 1:2; ChCl/Lactic acid 1:2; ChCl/Malic acid 1:1; ChCl/Oxalic acid 1:1	Pretreatment and delignification of miscanthus and birchwood for lignin extraction	ChCl/Oxalic acid demonstrated the highest delignification efficiency for both the miscanthus and birchwood samples. ChCl/Glycerol DES was reported to produce the lowest amount of recovered lignin.	(Kohli et al., 2020)
ChCl/Oxalic acid 1:2; ChCl/Urea 1:2	Pre-treatment and delignification of lignocellulosic bamboo (*Bambusa bambos*) stem	The delignification using ChCl/Oxalic acid exhibited a higher lignin dissolution in *Bambusa bambos* stem with 25.4 % maximum lignin dissolution as opposed to ChCl/Urea that attained 19.4 % lignin dissolution at 120 °C for 10 h.	(Ramesh et al., 2020)
ChCl/Urea 2:1; ChCl/Citric acid 2:1; ChCl/Oxalic acid 2:1; ChCl/Glycerol 2:1	Dissolution of microcrystalline cellulose	The highest dissolution effect was demonstrated by ChCl/Oxalic acid 2:1, followed by ChCl/Citric acid 2:1, ChCl/Urea 2:1, and ChCl/Glycerol 2:1, in descending order of cellulose solubility.	(Zhang et al., 2020)

ChChl/Ethylene glycol 1:2 ChCl/Glycerol 1:2; ChCl/Lactic acid 1:2; ChCl/Oxalic acid 1:1; ChCl/Urea 1:2	Pre-treatment for the separation of lignin and hemicellulose in dried bagasse biomass samples	The solubility of lignin in ChCl/Oxalic acid was the highest (47.85 %) but the bagasse was carbonized after pretreatment. ChCl/Lactic acid was more suitable for cellulose separation while ChCl/Ethylene glycol, ChCl/Glycerol and ChCl/Urea had selectivity towards lignin separation.	(Li et al., 2021)
ChCl/Glycerol/ FeCl$_3$·6H$_2$O 62:124:1	Pre-treatment and delignification of corn stover biomass	Delignification up to 48.35 % and xylan removal of 59.15 % from corn stover samples by using lewis acid catalyzed ChCl/Glycerol DES which was lower than direct pretreatment by using individual ChCl and glycerol solutions. However, the recyclability of ChCl/Glycerol DES was significantly higher than both ChCl and glycerol aqueous solution pretreatment.	(Zhu et al., 2021)

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: