

## 1 **Deep Eutectic Solvents – ideal solution for clean air or hidden danger?**

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21 **Abstract:** The industrial sector is one of the fastest-growing sources of greenhouse gases, due  
22 to its excessive energy consumption to meet the rapidly growing demand for energy-intensive  
23 products. The use of deep eutectic solvents (DESs) has been studied extensively in order to  
24 cope with these harmful gases, but their usage can be an issue in respect to ecological reasons.  
25 Do deep eutectic solvents harm the atmosphere? Yes, these solvents can be harmful if their  
26 constituents (HBA and HBD) that are volatile and toxic in nature. A number of scientific re-  
27 ports present their application without care on cross-contamination of treated media. Herein, we  
28 highlight the ecotoxicity behavior of DESs as treatment materials for three major toxic gas  
29 treatment methods, including carbon dioxide (CO<sub>2</sub>) capture, biogas treatment and air purifica-  
30 tion. Special attention is given to the health consequences of HBDs due to their toxicity and  
31 emission outside of the treatment system into the environment. The physicochemical charac-  
32 teristics of DESs are evaluated and addressed in comparison to the benchmark solvents.  
33 Emission of DESs can be predicted based on simulation software like COSMO-RS or Molec-  
34 ular Dynamics (MD). Furthermore, we suggest some simple protocols to estimate this issue and  
35 thus make aware researchers to think about it when experimenting with DES for different  
36 applications.

37 **Keywords:** Carbon Capture; waste gases treatment; flue gases treatment; biogas purification;  
38 fuels combustion; absorption; ammonia; hydrogen sulfide; BTEX; VOC.



## 40 1. Introduction

41 Green chemistry is concerned with the use and production routes of chemicals that are  
42 eco-friendlier. It motivates scientists either to minimize the use of toxic chemicals or to use  
43 alternative media, reaction conditions, and sources of energy [1-3]. The use of eco-friendly  
44 solvents and safer chemicals is one of the 12 principles of green chemistry. Among the most  
45 challenging issues facing researchers today are environmental issues and the energy crisis.  
46 Using sustainable components as part of this efficiency improvement will also alleviate envi-  
47 ronmental issues [4]. Global population growth and improved quality of life have led to an  
48 increase in energy demand, which is primarily derived from fossil fuels. In comparison with  
49 other fossil fuels, natural gas has the least adverse environmental effects. As a result of tech-  
50 nological advancements, it has become more economic to extract natural gas from substandard  
51 reservoirs. Sub-quality natural gas contains impurities, such as CO<sub>2</sub>, that must be eliminated  
52 since they are corrosive and reduce heating value [5, 6]. The removal of CO<sub>2</sub>, ammonia and  
53 hydrogen sulfide present in biogas is essential for sustainability, resulting in higher energy  
54 consumption of these processes. The traditional methods for CO<sub>2</sub> capture from flue gases have  
55 involved the use of aqueous amine solutions as chemical solvents for the absorption of CO<sub>2</sub>.  
56 These solutions include 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA)  
57 and monoethanolamine (MEA) [7-12]. In addition to being cheap, fast reacting, selective, and  
58 absorbing, they have a number of other desirable properties [13]. However, they are toxic,  
59 partially degradable, produce corrosive byproducts, require a lot of energy, and are expensive to  
60 acquire, so they are not eco-friendly. As a result, in recent years, the use of ecologically friendly  
61 solvents has gained a high attention [14]. In this regard, Ionic liquids (ILs) are a type of green  
62 solvent that have been used in a wide range of chemical techniques and processes [15, 16]. The  
63 majority of ILs are time-consuming and costly to synthesize. Furthermore, most of ILs have  
64 revealed to be highly polluting leading to negative effects on various living beings [15-18]. As a



65 consequence, there is a need to replace ILs with more eco-friendly solvents. Deep eutectic  
66 solvents (DESs) are now regarded as one of the most promising IL replacement options. Un-  
67 doubtedly, various studies have demonstrated that DESs present several similarities to IL [19],  
68 but less expensive, easy to synthesize, and more environment benign than IL [14, 20, 21].  
69 However, some concerns are already raised regarding their potential toxicity [22]. A typical  
70 DES is made by combining low-cost components (with hydrogen-bond formation properties) to  
71 create a eutectic mixture with a melting point much lower than either of its individual com-  
72 ponents [19, 20, 23, 24]. Mostly, DES is made by combining a salt with a hydrogen-bond donor  
73 (HBD) molecule in various molar ratios [19]. Absorption plays a significant role in the core  
74 mechanism of operation of DES-based technologies for gas processing. The ability of deep  
75 eutectic solvents (DESs) to absorb toxic gases has significant potential [25]. DESs contain two  
76 or more constituents linked together through hydrogen bonds between the hydrogen-bond  
77 acceptor (HBA) and the hydrogen-bond donor (HBD),  $\pi$  -  $\pi$  interaction or halogen bonds  
78 [26-28]. As an example, choline chloride (ChCl)/urea mixture, with a melting point value of 12  
79 °C (in a 1:2 molar ratio), is in liquid state at room temperature, in which its melting point is  
80 much lower than the melting points of its constituents, e.g., the melting points of ChCl and urea  
81 are 302 and 133 °C, respectively [14, 19]. As for their applications, DESs have been proposed  
82 in several approaches including stationary phases for chromatography [29], absorption [30],  
83 analytical chemistry [31, 32], extraction [33-36], synthesis of materials [37-40], electrochem-  
84 istry [19, 41, 42], drug discovery [43-45], lubrication [46], biotransformation [47], nanotech-  
85 nology [48], among others. Natural deep eutectic solvents (NADES) are those that obtain DESs  
86 from natural sources, such as amino acids, sugars, urea, and organic acids [49]. However, risk  
87 evaluations for all current and prospective chemicals are a top priority for the European Union's  
88 REACH (Registration, Evaluation, and Authorization of Chemicals) regulation, as well as other  
89 global organizations [50]. According to characteristic of ideal solvent as given by EU's REACH



90 regulation the solvent must have low toxicity, low volatility, low flammability but DESs meets  
91 all other parameters but only few drawbacks are more viscosity and toxic in nature. Therefore,  
92 it is very important to focus on the environment since the extensive use of DESs and their  
93 entrance into the industry could be a serious conservational problem, having a devastating  
94 impact on environments and, eventually on humankind. As a result, the impact of DESs on  
95 ecological systems should be investigated.

96 In general, DESs are often named as non-volatile, giving them the advantages of no loss and  
97 zero emission into the air. In contrast to the various papers on the stability of ionic liquids [40,  
98 51], volatilization of DESs is rarely mentioned. However, such generalization about DESs, in  
99 many cases, can cause serious methodological issues in case of their studies or applications. In  
100 particular, DESs are studied as sorptive media for waste gases treatment. Several applications  
101 regarding CO<sub>2</sub> capture, treatment of hydrogen or biogas as well as air purification were recently  
102 published. Interestingly, some of these chemical compounds used for synthesis of DESs own a  
103 volatile or semi-volatile character. It is obvious that under dynamic conditions gas-liquid  
104 equilibrium will cause partial evaporation of these compounds. In most of the papers, this  
105 aspect of the study is omitted, thus published developments are out-off purpose for real sce-  
106 nario. This review timely highlights this aspect, summarizing the current state of the art in this  
107 field, as well as providing suggestions for future research in terms of good research practice.

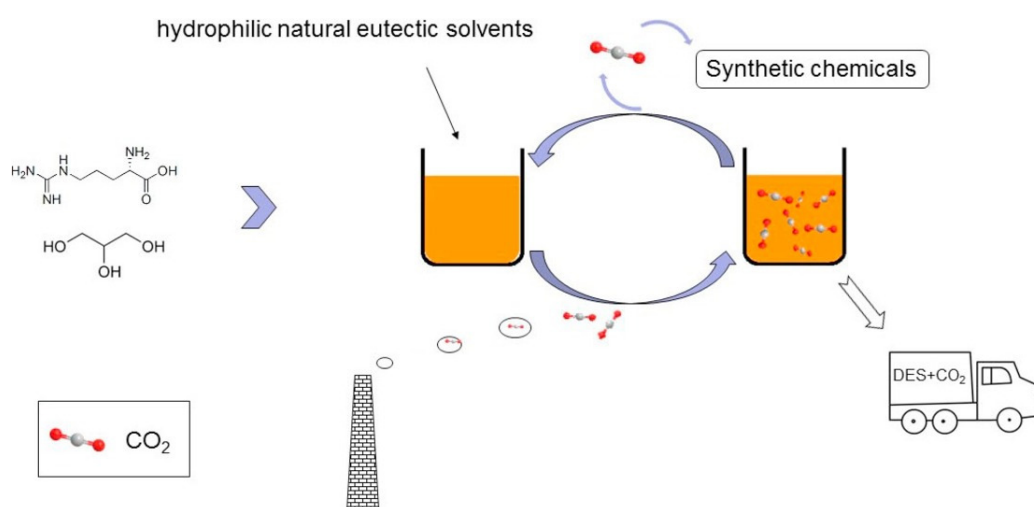
## 108 **2. Unaddressed concerns about DESs volatility in separation and purification of gaseous** 109 **streams**

### 110 2.1. CO<sub>2</sub> absorption

111 DESs have been explored in recent investigations for CO<sub>2</sub> capture due to their promising fea-  
112 tures, as shown in (Fig.1). We focused on HBDs that are generally organic and nonionic in  
113 nature, particularly those that are volatile and can cause serious health problems even at low

114 concentrations. Many studies claim that DESs are environmentally friendly, but the issue re-  
115 mains unclear because their precursors often are volatile, and after use, they may evaporate in  
116 the surrounding environment, bringing serious respiratory problems as well as odorous nui-  
117 sance. In addition, some of them can corrode technical equipment of the process installation and  
118 change their physical appearance. Phenol, for instance, is often used as HBD in DESs, which is  
119 known to be very corrosive to metals including Al, Cu and Al-Cu alloys [52].

120



121

122 Fig. 1. DES with hydrophilic and natural bases for green CO<sub>2</sub> capture. "Reprinted from [53]

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124 Phenol is easily absorbed into human body through a number of pathways (inhalation, skin  
125 contact and ingestion) and quickly spreads throughout the organism. The vapors of phenol are  
126 corrosive and toxic to the eyes, skin, and respiratory tract and it is also extremely toxic to  
127 neurons, if introduced to the bloodstream, it can cause immediate death by disrupting the neural  
128 transmission system.

129 We consider a few studies that used phenol as HBD. As DESs are formed by weak interactions  
130 (hydrogen bonds), it maintains the toxicity even after formation of DESs. Wang et al. reported  
131 two DESs tetrabutylphosphonium bromide - Phenol (TBPB-PhOH) (1:4) and tetrabu-

132    tylphosphonium bromide - diethylene glycol (TBPB-DEG) (1:4), which revealed an out-  
133    standing result for CO<sub>2</sub> absorption [54]. Unfortunately, their HBD components are volatile in  
134    nature. Diethylene glycol is a low volatile organic compound that can cause liver damage,  
135    respiratory failure, and seizures. Li et al. synthesized ChCl/ mono ethanolamine (MEA) based  
136    DESs with good CO<sub>2</sub> absorption and reusability [55], although the HBD is relatively volatile  
137    and a corrosive chemical that can cause respiratory issues. Shukla et al. developed  
138    1-methylimidazolium chloride and ethylene diamine (HmimCl: EDA) with a molar ratio (1:2)  
139    [56], which contains the HBD component EDA that irritates the nose and throat. Organic  
140    amines are known as odorous compounds, thus their emission at even very low rates will cause  
141    issues with air quality around the emitting facility. According to Liu et al., acetylcholine chlo-  
142    ride and guaiacol (ACC/guaiacol) with a molar ratio (1:3) [57], their HBD part guaiacol, can  
143    induce respiratory tract irritation, skin irritation, and eye discomfort. Table (1) summarizes the  
144    toxicity of these HBDs. None of these studies addressed the aspect of DES components' vola-  
145    tility or loss of the DES during the operation.

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**Table 1.** Compilation of the toxicity of precursors of DESs used for CO<sub>2</sub> Absorption.

Type of DESs	M.P (°C)	Mole Ratio	T (K) of treatment process	Ref (Application)	Problematic compound	Volatility	Toxicity	Ref (Toxicity)
TBPB:PhOH	HBA= 104 °C HBD=40.5 °C DES= not reported	1:4	343.15 K	[54]	Phenol	Volatile (b.p = 181.7 °C)	Irritation to the skin, eyes, nose, throat, Neurotoxin	[58]
TBPB:DEG	HBA=104 °C HBD=-6.5 °C DES= not reported	1:4	343.15 K		Diethylene glycol	Low volatile (b.p = 244 °C)	Liver toxicity, respiratory failure, and seizures.	[59]
ChCl:MEA	HBA=302 °C HBD=10.3 °C DES= 4.54 °C	1:5	343.15	[55]	Mono ethanamine	Volatile (b.p =170 °C)	Corrosive chemical, breathing problems	[60]
HmimCl:EDA	HBA= RTIL* HBD=8 °C DES= not reported	1:2	353.15	[56]	Ethylene diamine	Volatile (bp= 116 °C)	Irritate the nose and throat	[61]
ACC:guaiacol	HBA=146-150 °C HBD=26-29 °C DES= not reported	1:3	353	[57]	Guaiacol	Volatile (b.p = 205 °C)	Causes respiratory tract irritation, Skin irritation, Eyes irritation.	[62]

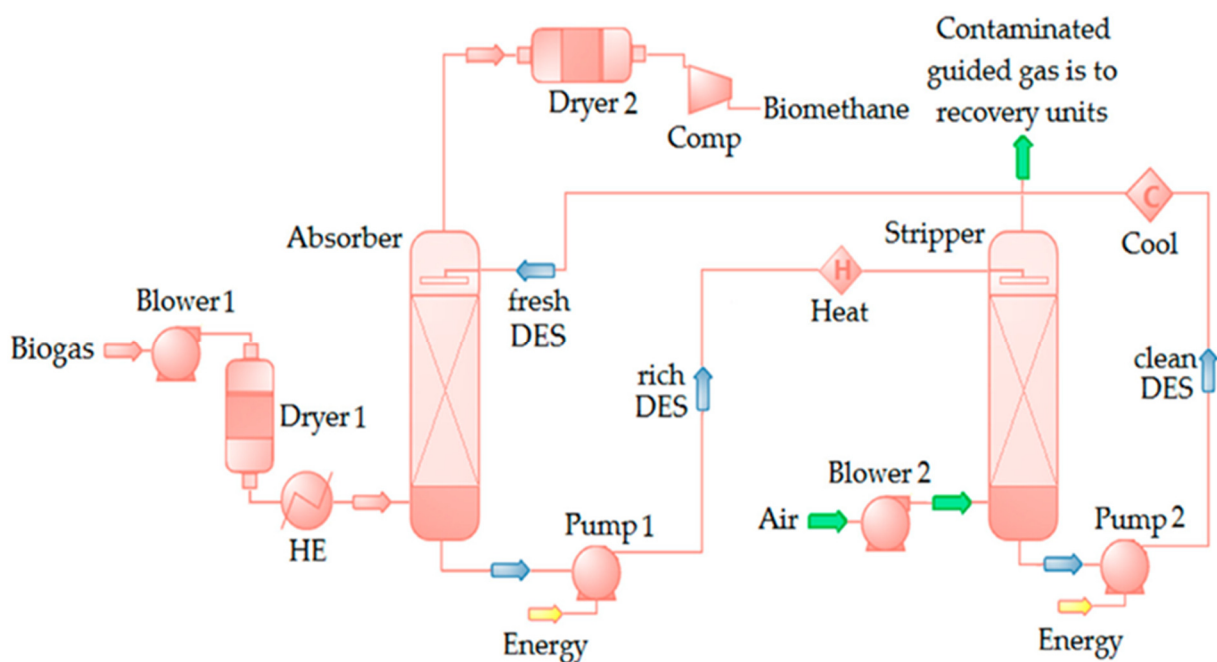


	reported							
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148 \*RTIL – ROOM TEMPERATURE IONIC LIQUID

149 2.2. Biogas treatment

150 Biogas is produced under anaerobic conditions using specified bacteria and waste materials as  
151 feedstock, such as wastewater treatment sludge or dumpsites, as represented in (Fig.2).  
152 Biogas, which is composed of carbon dioxide (25–50%) and methane (50–75%) and other toxic  
153 substances, such as ammonia, hydrogen sulfide, linear hydrocarbons (HC), aromatic  
154 hydrocarbons (benzene, ethylbenzene, toluene, and xylenes (BTEX), halogen compounds, and  
155 siloxanes, must be removed from biogas before it can be converted into energy [63-65].  
156 Besides, to remove these toxic contaminants from the biogas, scientists are experimenting with  
157 a variety of strategies, including absorption, adsorption, membrane technologies, cooling, and  
158 processes utilizing various types of catalysts [66-68].



159

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Fig.2. Scheme for the biogas upgrading technology [69, 70].

161 Here, we report few studies that have used DESs for biogas treatment, but their precursor,  
 162 mainly HBD, have serious environmental issues. For example, Słupek et al. reported ChCl  
 163 DEG based DESs for purification of biogas from toluene in which they used diethylene glycol  
 164 (as HBD) [71]. This latter compound has low volatility, but is recognized to cause liver toxicity,  
 165 respiratory failure, and seizures. In a more recent study, Słupek et al. reported [72] several  
 166 DESs for theoretical and economic evaluation of low-cost DES for effective biogas upgrading  
 167 to bio-methane. Selected DESs were formed using HBD volatile compounds, such as Butyric  
 168 Acid, Ethylene glycol, Phenol, Methacrylic acid. All of these chemicals cause serious health  
 169 issues especially breathing problems. Particularly, Butyric Acid has corrosive nature but also  
 170 causes skin, nose, eyes, and lungs irritation. Ethylene glycol, for instance, causes irritation of  
 171 mucous membranes and the upper respiratory tract, while Methacrylic acid is a highly corrosive  
 172 chemical and contact with it can severely irritate and burn the skin and eyes with possible eye  
 173 damage, nose irritation, coughing, and shortness of breath. The volatility of these HBDs is  
 174 significant, as their boiling point values are: Methacrylic acid (b.p = 161 °C) > Butyric Acid  
 175 (b.p = 163.5 °C) > Phenol (b.p = 181.7 °C) > Ethylene glycol (b.p = 197 °C) > diethylene glycol  
 176 (b.p = 244 °C). A compilation of volatility and toxicity of these HBDs is given in Table (2).

177 **Table 2.** Comparison of toxicity of DESs precursors used for Biogas treatment.

Type of DESs	M.P (°C)	Mole Ratio	T (K) of treatment process	Ref (Application)	Problematic compound	Volatility	Toxicity	Ref (Toxicity)
Ch:DEG	HBA=302 °C HBD= 6.5 °C DES= 17.8	1:2	353.15	[71]	diethylene glycol	Low volatile (b.p = 244 °C)	Liver toxicity, respiratory failure, and seizures.	[59]

	°C							
TEABr:Bu	HBA=286 °C HBD= -5.1 °C DES= not reported	(1:2)	293.15		Butyric Acid	Volatile (b.p = 163.5 °C)	Corrosive, Skin irritation, irritate Nose, Eyes, lungs	[73]
TBACl:EG	HBA= 41-44 °C HBD= -12.9 °C DES= not reported	1:3	293.15		Ethylene glycol	Volatile (b.p = 197 °C)	Irritation of mu- cous membranes and the upper respiratory tract.	[74]
TBABr:Ph	HBA=286 °C HBD=40.5 °C DES=not reported	1:2	293.15	[72]	Phenol	Volatile (b.p= 181.7 °C )	irritation to the skin, eyes, nose, throat, Neuro- toxin	[58]
ChCl:MthA	HBA=302 °C HBD= 14 to 15 °C DES= not reported	(1:2)	293.15		Methacrylic acid	Volatile (b.p = 161 °C)	Highly corrosive chemical and contact can se- verely irritate and burn the skin and eyes with possi- ble eye damage. Nose irritation, coughing, short- ness, of breath	[75]

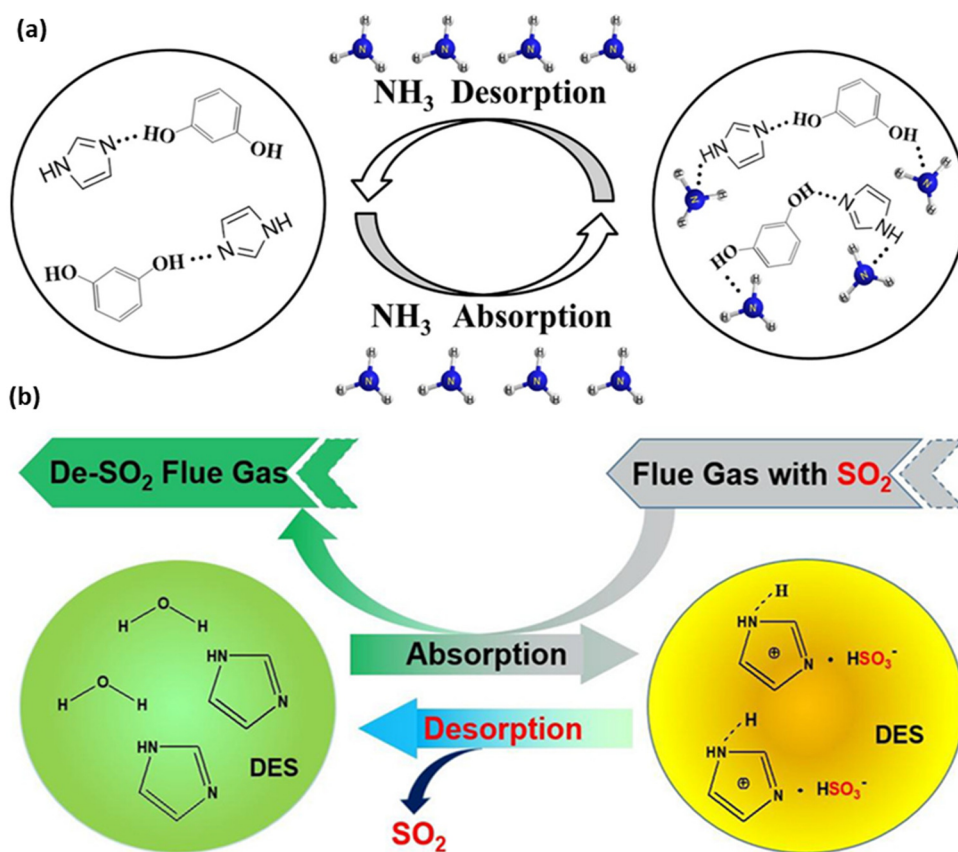


178 According to figure 2, the recovery of absorbent takes place via stripping operation. To mini-  
179 mize the DES emission at the stripping stage it must be operated, at the lowest possible tem-  
180 perature and proper overpressure. Such solutions are known from different processes. For  
181 example, it is possible to separately strip-out ammonia and hydrogen sulfide from sour  
182 wastewater (according to Chevron WWT process) [76]. Same trapped impurities of biogas  
183 could be selectively stripped-out from DES. This aspect demands proper studies and modelling  
184 in future papers.

### 185 **2.3 Air treatment**

186 There are a number of toxic gases in waste air streams, including CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>S, and  
187 Ammonia (NH<sub>3</sub>), as shown in (Fig.3). Due to their harmful effects on the environment and  
188 human health, many countries restrict the release of certain gases into the atmosphere.  
189 Mitigation of greenhouse gas emissions is a major global challenge, considering their  
190 significant role in driving global warming and climate change.

191



192

193 Fig.3. (a) DESs used for removal of NH<sub>3</sub>. "Reprinted from [77] Copyright (2021), with per-  
 194 mission from Elsevier." (b) DESs used for removal of SO<sub>2</sub> "Adapted with permission from  
 195 [78]. Copyright (2020) American Chemical Society".

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197 To some extent, the commercial processes for capturing these gases have a number of draw-  
 198 backs, including the use of volatile solvents, the generation of hazardous byproducts, and a high  
 199 energy expenditure [79]. Scrubbing with water or acids (mostly sulphuric acid, phosphoric  
 200 acid, and organic acids) is widely used in numerous areas, but it has faced significant difficul-  
 201 ties [80-82]. Due to the high vapour pressure and strong interaction between acid and NH<sub>3</sub>, the  
 202 absorbent recycling process consumes an enormous amount of energy. Additionally, it is  
 203 challenging to avoid equipment corrosion while significant wastewater is generated during the  
 204 method [77]. Over the last few decades, limestone has been used to control the emission of SO<sub>2</sub>

205 [83]; unfortunately, large amounts of waste  $\text{CaSO}_4$  and wastewater are generated during the  
206 process, and this waste prevents usable  $\text{SO}_2$  from being recovered [84].

207 Presently, the use of DESs for the capture of toxic gases has received a lot of attention. Here, we  
208 report several studies that used DESs as a “green” approach for air treatment but their precursor,  
209 such as phenol, Resorcinol, Glycerol, Ethyl alcohol and Malonic acid, display serious health  
210 issues due to their volatile nature. Jiang et al. reported the application of ethylamine hydro-  
211 chloride  $\text{Et}_3\text{N}/\text{phenol}$  with a molar ratio (1:2) for  $\text{NH}_3$  capture [85]. Luo et al. synthesized  
212 Imidazole (Im)/resorcinol (Res) Im/Res based DESs (1:1) for capture of  $\text{NH}_3$  [77]. Resorcinol,  
213 used as HBD, is a semi-volatile compound with an aromatic odour and a sweetish bitter taste, so  
214 it is clear it will be emitted into the treated air, causing its pollution. According to the New  
215 Jersey Department of Health, breathing resorcinol can result in irritation to the throat and lungs,  
216 as well as cause drowsiness, tiredness, headache, and a blue colour to the skin and lips, a con-  
217 dition known as methemoglobinemia. It is known that exposure on resorcinol at very high  
218 levels can cause troubles with breathing, collapse and even death [86] (Table 3).

219

220



221 **Table 3.** Comparison of toxicity of DES components used for Air treatment.

Type of DESs	M.P (°C)	Mole Ratio	T (K) of treatment process	Ref (Applica-tion)	Problematic compound	Volatility	Toxicity	Ref (Toxicity)
EaCl:phenol	HBA=110.0 to 115.0 °C HBD=40.5 °C DES= not re-ported	1:2	293.2	[85]	Phenol	Volatile (b.p = 181.7 °C)	irritation to the skin, eyes, nose, throat, Neurotox-in	[58]
Im:Res	HBA=89 to 91 °C HBD= 110 °C DES= not re-ported	1:1	353.15	[77]	Resorcinol	Semi Volatile (b.p = 277°C)	Exposure to very high levels can cause trouble breathing, col-lapse and even death	[86]
ChCl:glycerol	HBA=302 °C HBD= 17.8 °C DES= 17.8 °C	1: 1	343.15	[25]	Glycerol	Semi-volatile (b.p =290 °C)	May cause irrita-tion to skin, eyes, and respiratory tract and affects kidney	[87]
BA:P4444Cl	HBA= HBD= 122 °C DES= not re-ported	1:2	303.15	[88]	Benzoic acid	Semi-volatile (b.p = 249.2 °C)	eye damage, irritation of throat, nose, skin, coughing, and shortness of breath	[89]



ChCl:MA	HBA=302 °C HBD= 135 to 137 °C DES= -50 °C	1:1	343	[90]	Malonic acid	volatile (b.p = 140°C)	Corrosive, Irritant	[91]
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223 Yang et al. synthesized ChCl–glycerol (1:1) DESs which showed excellent efficiency for SO<sub>2</sub>  
 224 absorption [25], but their HBD precursor glycerol is semi-volatile according to U.S. EPA  
 225 Reference Method 24 (M24), which calculates volatility by converting weight percent loss at  
 226 the end of 60 min at 110 °C in a forced draft oven into VOC content [92]. It may cause irritation  
 227 to skin, eyes, and respiratory tract and affects kidney. Zhang Lvhong et al. synthesized tetra  
 228 butyl phosphine chloride (P4444Cl) benzoic acid (BA) BA/P4444Cl based DESs with a molar  
 229 ratio (1:2), which can reversibly and efficiently absorb nitric oxide (NO) [88], but their HBD  
 230 part is benzoic acid which is semi volatile in nature. Health effects that can occur immediately  
 231 or shortly after benzoic acid exposure include eye damage, irritation of throat, nose, skin,  
 232 coughing, and shortness of breath. Sun et al. prepared ChCl:MA (Malonic acid) (1:1) DESs for  
 233 SO<sub>2</sub> absorption [90] but its precursor Malonic acid owns serious environmental concerns such  
 234 as corrosive, and irritant in nature.

235 The thermophysical properties of these toxic HBDs are very important to evaluate their  
 236 harmful effects in environments. For instance, the n-octanol-water partition coefficient, often  
 237 known as log P, is a measure of the distribution between hydrophobic and hydrophilic envi-  
 238 ronments. It is calculated by taking the ratio of a chemical's solubility in n-octanol and its  
 239 solubility in water. A higher Log P value indicates that the chemical is more hydrophobic (has a  
 240 greater affinity for the octanol phase), whereas a lower Log P value suggests that the chemical  
 241 is more hydrophilic (has a higher affinity for the water phase). The density ( $\rho$ ) of a solvent is  
 242 another significant parameter. On the other hand, the significance of this parameter is relatively  
 243 minor in the absorption process. DES density values can influence the process of DES regen-





244 eration. Deep eutectic solvents, whose densities range greatly from common solvents, such as  
 245 water, can be regenerated through extraction [93]. In table 4 detailed characteristics of these  
 246 toxic HBDs are mentioned.

247 Table 4. Thermophysical properties of HBDs.

Compound	Log P (partition coefficient between n-octanol and water)	CAS number	Density	flash point	limit of exposition
Phenol	2.3	108-95-2	1.07 g/cm <sup>3</sup> at 20°C	79°C (174°F)	0.5 ppm an 8-hour TWA
Malonic acid	-1.45	141-82-2	1.6 g/cm <sup>3</sup> at 10°C - 25°C	171°C (340°F)	0.1 mg/m <sup>3</sup> as an 8-hour TWA.
Mono ethan- olamine	-1.45	111-42-2	1.02 g/cm <sup>3</sup> at 20 °C	85°C (185 °F).	0.1 mg/m <sup>3</sup> as an 8-hour TWA
Ethylene di- amine	0.45	105-57-7	0.945 g/cm <sup>3</sup> at 20 °C	34°C (93.2 °F)	0.5 ppm as an 8-hour TWA

Guaiacol	2.7	124-80-9	1.09 g/cm <sup>3</sup> at 20 °C	82°C (179°F)	0.1 mg/m <sup>3</sup> as an 8-hour TWA
Ethylene glycol	-1.45	111-46-6	1.11 g/cm <sup>3</sup> at 20 °C	124°C (255.2°F)	5 mg/m <sup>3</sup> as an 8-hour TWA.
Butyric Acid	-1.25	107-92-6	1.037 g/cm <sup>3</sup> at 25°C	72°C (161.6 °F)	0.5 ppm over an 8-hour TWA
Ethylene glycol	-1.45	107-21-1	1.09 g/cm <sup>3</sup> at 25°C	111-121°C (231.8-249.8 °F)	25 ppm over an 8-hour TWA
Methacrylic acid	-1.45	108-46-3	1.09 g/cm <sup>3</sup> at 25°C	170°F (77°C)	25 ppm as an 8-hour (TWA)
Resorcinol	2.3	108-46-3	1.27 g/cm <sup>3</sup> at 20°C	260.6 °F (127°C)	0.1 mg/m <sup>3</sup> as an 8-hour



					TWA
Glycerol	-1.7	56-81-5	1.261 g/cm <sup>3</sup> at 25°C	350 °F (177 °C).	TLV of 5 mg/m <sup>3</sup> for glycerol vapor.
benzoic acid	2.9	65-85-0	1.32 g/cm <sup>3</sup> at 20 °C	249.8 °F (121°C)	5 mg/m <sup>3</sup> as 8-hour TWA

248 \*ppm (parts per million), \*TWA (time-weighted average), \*TLV (Threshold Limit Value)

249

250 Flash point means the minimum temperature at which volatile combustible vapors ignite in air  
251 when exposed to a flame. According to the (table 4) the flash point values of these HBDs are  
252 higher than n-hexane (-22°C or -9°F) and aromatic solvents such as benzene, toluene, and  
253 xylene flash point values (< -17.78°C or < 0°F), (4°C or 39.2°F) and (32°C or 89.6°F) respec-  
254 tively. The limit of exposition, also known as the permissible exposure limit (PEL), is a legis-  
255 lative limit on the permissible air concentration of a substance. According to the Occupational  
256 Safety and Health Administration (OSHA), the permissible limit of hexane is 500 ppm aver-  
257 aged over an 8-hour work shift [94], Benzene has a limit of 1 ppm averaged over an 8-hour  
258 work shift and a maximum of 5 ppm during any 15-minute work period [95], Toluene has an  
259 average concentration of 200 ppm over an 8-hour work shift; 300 ppm cannot be exceeded  
260 during any 15-minute period. [96], and xylene has 100 ppm averaged over an 8-hour work shift

261 [97]. So, these benchmark solvents have much higher exposure limits as compared to HBDs but  
262 still they cause a lot of problem. Thus, high awareness should be dedicated to processes based on  
263 DESs based on volatile HBD components.

264 n-Hexane is a highly toxic solvent that can cause nausea, headaches, vomiting, and dizziness.

265 It can cause coma and death at greater concentrations. Also it irritates the skin and eyes [94].

266 In comparison, aromatic solvents such as benzene, toluene, and xylene are likewise extremely

267 hazardous, with acute inhalation exposure causing depression of the central nervous system,

268 nausea, vomiting, and dizziness. In addition, they influence the respiratory, central and pe-

269 ripheral nervous, gastrointestinal, cardiovascular, renal, hepatic, cutaneous, and hematological

270 systems [95-97]. Deep eutectic solvents (DESs) are potentially competitive substitutes for

271 benchmark solvents (such as n-hexane, aromatic, etc.) due to lower toxicity of some possible

272 components. In order to assist in the implementation of the European strategy for a

273 non-hazardous environment. There are several alternatives to n-hexane, aromatics and DES

274 for the extraction of natural products, including solvent-free extraction, water, NADESs,

275 bio-based solvents, supercritical fluids or liquefied gases.

276 Minimization of DES emission into the environment, beside selection of proper DES, could be

277 obtained by “at the end of the pipe (absorber)” solutions such as trapping of DES vapors on

278 adsorbent (like activated carbon), absorption in proper solvent (in case of hydrophilic com-

279 pounds water could be used) or thermal/catalytic incineration. Compounds that are highly

280 volatile, or evaporate more than 95% by weight in ambient conditions after 6 months (by def-

281 inition named VOCs), are completely available to form ozone at rates proportional to their



282 individual reactivity rates. The most challenging category of compounds to categorize is the  
283 semi-volatile category, which includes substances that evaporate between 5% and 95% by  
284 weight in 6 months when exposed to room temperature and relative humidity [92].

285

### 286 **3. Outlook and Future Challenges**

287 DESs are an interesting class of alternative solvents due to their advantages in terms of sim-  
288 plicity in synthesis and inexpensive, and they can be tailored to meet the needs of a specific  
289 method. These characteristics make DESs an ideal replacement for both ILs and typical organic  
290 solvents. This opens up exciting new possibilities for the development of truly eco-friendly  
291 solvent systems that meet the criteria for sustainable and green chemistry. DESs as solvents  
292 have versatile uses, such as catalysts, lubricants, additives, metal processing materials, syn-  
293 thetic materials, and energy materials, while considered environmentally friendly, benign, and  
294 non-toxic compounds. In this review, relevant findings revealed that their eco-friendly char-  
295 acter is not entirely true and that such broad presumptions should be overlooked. Therefore, it is  
296 necessary to investigate ecotoxicological aspects due to their volatile and toxic precursors. We  
297 highlighted the toxicity and volatility of compounds used for DES synthesis and subsequently  
298 used for carbon capture, biogas treatment, and air treatment.

299 Risk assessment regarding the emission of DES components can be easily done under labora-  
300 tory conditions. Here, we suggest some examples of protocols useful to control these issues –  
301 they relate to control of weight loss of DES, condensation as well as headspace-gas chroma-  
302 tography technique.

#### 303 *3.1. Weight loss of DESs*

304 Weight loss of DESs is the key parameter for evaluation of their evaporation when applied as  
305 sorptive medium for gases treatment. Simple control of DES mass before and after the treat-  
306 ment process should allow for estimating the loss. However, in this case, it should be consid-



307 ered that the absorbed pollutant will increase the mass of the absorbent. This latter aspect can be  
308 adjusted based on the mass balance of the absorption process.

### 309 *3.2. Condensation*

310 In the case of gases treatment focused on the removal of low molecular impurities, such as  
311 hydrogen sulfide or CO<sub>2</sub> absorption, outlet gas could be subjected to a low-temperature con-  
312 densation zone, where volatilized DES components could be effectively trapped and quantified.

### 313 *3.4. Headspace technique coupled with gas chromatography*

314 Headspace analysis, both under static or dynamic conditions, would be used to monitor the  
315 volatility of the DES components. In the first option, a specific amount of DES would be  
316 equilibrated in elevated conditions in a hermetic vial. Herein, a small portion of gas-phase  
317 (typically between 0.2-05 mL) would be sampled and analyzed by gas chromatography (GC) to  
318 inspect the concentration of the DES components in the gas phase. In the second option, volatile  
319 components emitted from DES would be continuously trapped on the solid sorbent, followed by  
320 thermal desorption of analytes into the GC. This protocol was already proved to be effective to  
321 detect phenol (a one of popular HBDs used for DES formation) in water matrix, which exhibits  
322 same interactions with phenol (hydrogen bonding) as most of HBAs [98]. Typically, a flame  
323 ionization detector or mass spectrometer would be used. However, in the case of DES com-  
324 ponents, more selective and sensitive detectors, such as electron capture detector (ECD, for  
325 halogen-containing compounds), flame photometric detector (FPD, for sulfur or phosphorous  
326 compounds) as well as nitrogen – phosphorous detector (NPD) would be used. Headspace  
327 analysis coupled with GC was used in several applications to evaluate the emission from many  
328 types of samples [98-103]. Such dedicated studies focused on the emission of DES components  
329 seem to be a good idea in near future. It is clear that high demand on such protocols and reports  
330 in relation to DESs currently exists.

### 331 *3.4 Prediction of DES volatility by software*



332 Deep eutectic solvents (DESs) are increasingly used in many industries due to their unique  
333 properties, such as volatility, viscosity and enhanced solubility. The prediction of their vola-  
334 tility is essential for many chemical processes, such as distillation and evaporation. To predict  
335 the volatility of DESs, several software programs and computer simulations have been devel-  
336 oped. These programs and simulations use different methods to calculate the vapor pressure of  
337 the DES, and the accuracy of the results vary depending on the method used. With further  
338 research and development, these methods may become more accurate and reliable. These  
339 programs use mathematical equations to calculate the vapor pressure of a given DES. COS-  
340 MO-RS is the one of the best softwares to predict the volatility of deep eutectic solvents by  
341 calculating their vapor pressure.

#### 342 *3.4.1 COSMO-RS*

343 COSMO-RS is a powerful computational method that can be used to predict the volatility of  
344 deep eutectic solvents. It utilizes an advanced thermodynamic model to create a reliable pre-  
345 diction of the activity coefficients of the different components in the solution. It then combines  
346 this data with experimentally determined vapor pressures to accurately predict the vapor  
347 pressures of the solution. The resulting vapor pressures can then be used to predict the volatility  
348 of the DES. One of the primary goals of COSMO-RS is to determine the structure-property  
349 relationship of the DES structure [104-106].

350 COSMO-RS is a highly accurate and cost-effective method for predicting the volatility of  
351 DESs. It is capable of producing results that are comparable to experimental measurements and  
352 can save time, money, and materials when compared to traditional laboratory testing.

#### 353 *3.4.2 Simulating DESs*

354 Another approach to predicting the volatility of DESs is to use computer simulations. Molec-  
355 ular dynamics (MD) simulates the motion of certain groupings of elements by solving the  
356 classical equations of motion, providing information on the atomic-scale system dynamics



357 [107]. It is used for validating the best-performing force field by obtaining agreement between  
358 simulated densities, volume expansion coefficients, heat capacities, and diffusion coefficients  
359 and actual results [108]. In this approach, the molecular structure of the DES is simulated using  
360 equations of motion to determine the behavior of the DES over time. This can be used to cal-  
361 culate the vapor pressure of the DES.

362 In another work, molecular simulations on multiple DESs revealed very high agreement with  
363 experimental densities and thermodynamic parameters. Anion-HBD interactions were found to  
364 be crucial for all four systems by structural and hydrogen bond studies [109].

#### 365 **4. Conclusions**

366 Due to the nature and diversity of DESs, academic and industrial communities are gaining  
367 attention in these mixtures. It has been shown that DESs can be used for a wide range of pur-  
368 poses, including biocatalysts [110, 111], biotechnology [112, 113], food [114], pharmaceuticals  
369 [115, 116], or as a biofuel [117, 118]. Here, we focused on three major air treatment processes  
370 including carbon capture, biogas, and air treatment. We analyzed specific HBD compounds of  
371 DESs that can cause a serious health concerns in environments. Since such compounds need to  
372 be monitored over their use and further disposal, we also suggested some protocols to cope with  
373 these conditions and thus reduce their impact on the ecological systems.

374 It is clear, that in many studies the authors focused only on the removal effectiveness of target  
375 pollutants. The serious environmental risk related to the emission of DES components into the  
376 atmosphere is totally omitted. In our opinion, studies in this field without proper analysis and  
377 assurance of the DES zero-emission process shouldn't be published, or at least make emphasis  
378 on the potential risk when manipulating such compounds. This is a clear example that science  
379 rather than offering new knowledge for promising solutions to society's concerns affects po-  
380 tentially the existing ecosystems. At this point, we (researchers) must be aware when experi-  
381 menting with the chemical synthesis of new feedstocks and their side effects in applications.





382 As a first step, to make a more green and clean solvent, a detailed database of the eco-and  
383 cytotoxicity aspects of DESs is required, including many outcomes and an appropriate com-  
384 bination of HBA/HBD. Secondly, it is necessary to develop computational predictive methods  
385 that consider the volatility of the components of the DES mixture as well as a variety of possible  
386 prediction scenarios [102]. Finally, the risk of emission should be quantitatively evaluated  
387 when performing experiments. Simple protocols to control DES emission based on headspace  
388 analysis coupled with gas chromatography were herein proposed. It is essential to consider the  
389 thermophysical parameters of DESs, such as their boiling point, vapor pressure, and flash point,  
390 when developing processes that use DESs. The physicochemical characteristics of DESs are  
391 discussed and evaluated in light of comparisons to conventional solvents.

392 Analysis of available literature reveals also additional concerns regarding the term "deep eu-  
393 tectic solvent", that is not taken seriously by most of researchers. Most of researchers use the  
394 DES term, regardless how big depletion of melting point comparing to pure components was  
395 observed. In our opinion, DES term should be reserved for mixtures having significant deple-  
396 tion of melting point, while for other mixtures a term "eutectic mixture" should be used [103].  
397 In some cases, no report was available about the solid-liquid equilibrium of the mixtures dis-  
398 cussed here. The authors didn't study the melting point of formed DES, so it is impossible to  
399 even refer to them as "eutectic" solvents. In future papers, this aspect should be treated seri-  
400 ously, and researchers should measure the melting point of newly obtained DESs for their  
401 studies and on this basis refer to proper nomenclature of obtained mixtures.

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