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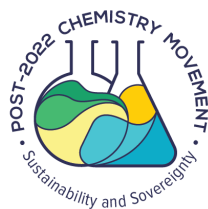
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Amino Acid-Based Deep Eutectic Solvents in Biomass Processing - Recent Advances

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The use of non-conventional solvent systems, such as deep eutectic solvents (DES), for biomass processing is a growing interest. DES are formed by two or more components, usually solids at room temperature, which can interact with each other via hydrogen bonding, from a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), resulting in a liquid phase. The most studied HBA in the literature is choline chloride with several HBD and their use have been extensively reviewed. However, other abundant and natural HBA can be successfully applied on the preparation of different DES, e.g., amino acids. These amino acid-based DES have been used in biomass pretreatment, providing the fractionation of the main macromolecular components by lignin solubilization. In addition, amino acid-based DES can be applied in biomass chemical conversion to obtaining platform chemicals such as furanic derivatives. Bearing this in mind, this review focuses on exploring the use of amino acid-based DES on biomass processing, from pretreatment to chemical conversion.

Keywords: deep eutectic solvent, amino acids, biomass, pretreatment, chemical conversion

1. Introduction

The integral use of renewable feedstocks is a pivotal role to achieve truly environmentally friendly processes. One alternative that has been explored in recent years is the use of non-conventional solvents in biorefinery applications, such as ionic liquids¹ and deep eutectic solvents (DES).² In view of their unique properties, DES have been emerged as a promising alternative for pretreatment and chemical conversion of biomass. DES are formed by two or more components, usually solids at room temperature, which can interact with each other via hydrogen bonding, resulting in a liquid phase.^{3,4} This interaction comes from the presence of hydrogen bonding acceptor (HBA) and hydrogen bonding donor (HBD) species in the system. When both components come from natural sources, the system is commonly called NADES, which stands for natural deep eutectic solvents.⁵ Like ionic liquids (IL), the DES have low vapor pressure, non-flammability, and polarity according to their components. In comparison to IL, the DES have some advantages such as the use of low cost and less toxic starting materials, and non-laborious synthetic procedures since they are

prepared simply by the combination of readily accessible and abundant chemicals.⁴

The application of deep eutectic solvents has covered several areas, from natural products extraction, electrochemistry, nanoparticles synthesis to biodiesel purification.⁶ These systems have also been investigated as a green alternative for biomass pretreatment and chemical conversion in view of their ability to solubilize very polar compounds, such as carbohydrates.⁷

The literature indicates that choline chloride (ChCl) is the most studied HBA, which can form eutectic mixtures with a wide range of HBD, for instance urea, alcohols, carboxylic acids, carbohydrates and many other compounds (Figure 1).⁸ Choline cation can be found mostly in higher plants and its biosynthesis involves an enzymatic decarboxylation of serine to ethanolamine followed by three parallel, interconnected and successive enzymatic *N*-methylations.⁹ Nonetheless, choline chloride is synthesized in industry by reacting hydrogen chloride, ethylene oxide, and trimethylamine, producing insignificant industrial residue. Interestingly, choline chloride is considered a provitamin in Europe serving as food supplement for animals.⁴ Besides choline chloride, other HBA can provide different DES that have great potential for biorefinery applications, such as amino acids, due to their low cost, low toxicity and natural abundance.

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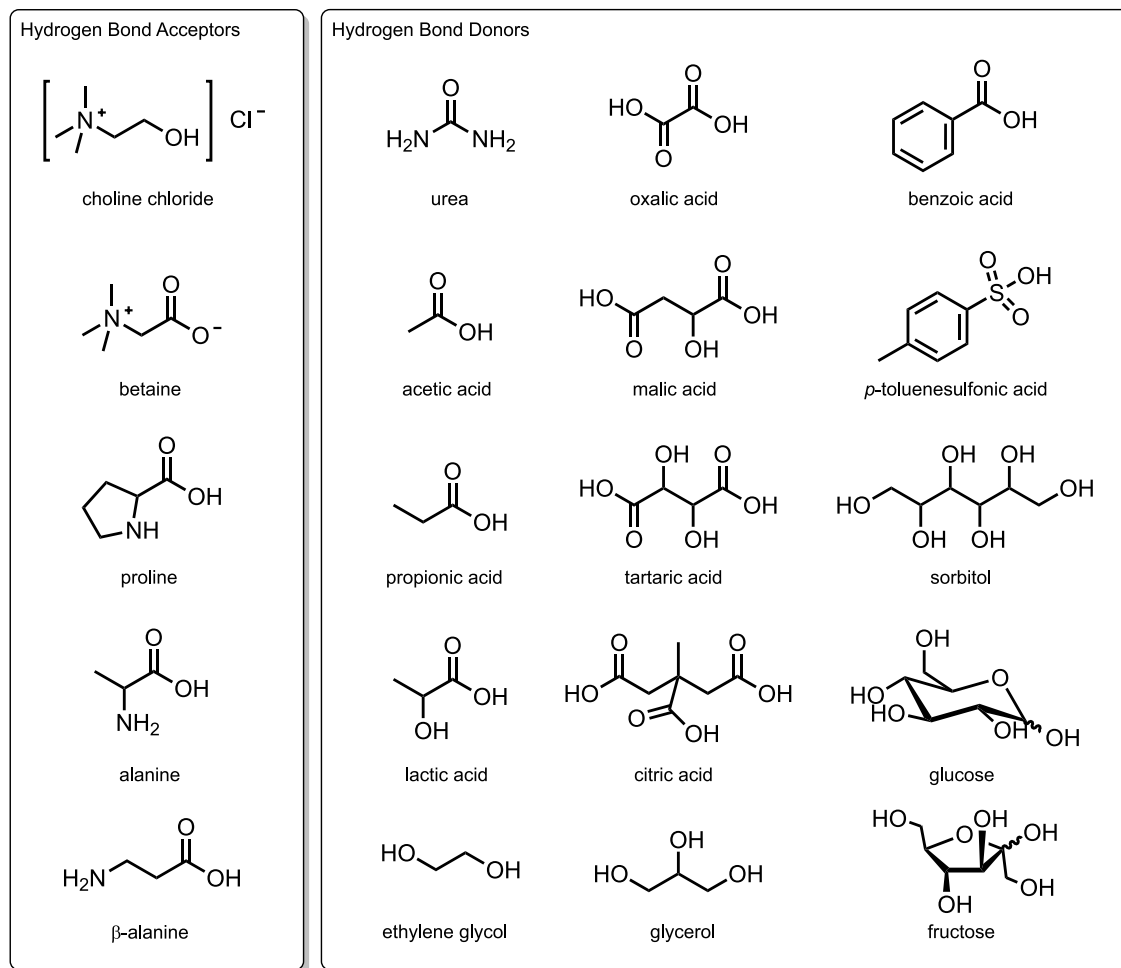


Figure 1. Chemical structure of different compounds with the ability to form deep eutectic solvents.

2. Amino Acid-Based DES

Amino acids have promising characteristics for DES preparation, like low toxicity and low cost. Thus, it is not surprising that several amino acids have been used for DES preparation, such as proline, alanine, glycine, and others. Due to its structural similarity to choline, glycine betaine is the most important amino acid derivative used as HBA. Although glycine betaine is commonly reported only as betaine, it should be mentioned that any fully *N*-methylated amino acid is considered a betaine compound (e.g., proline betaine, alanine betaine, β-alanine betaine, etc.). Glycine betaine can be vastly found in food, especially in sugar beet. In addition, the anhydrous zwitterion is an approved drug for the treatment of homocysteinemia.^{10,11}

When two different solids are mixed together, the intrinsic net of hydrogen bonding between HBA and HBD species to form an eutectic mixture occurs only in specific molar proportions of the components, as shown in Figure 2. The decrease of the melting point of the whole

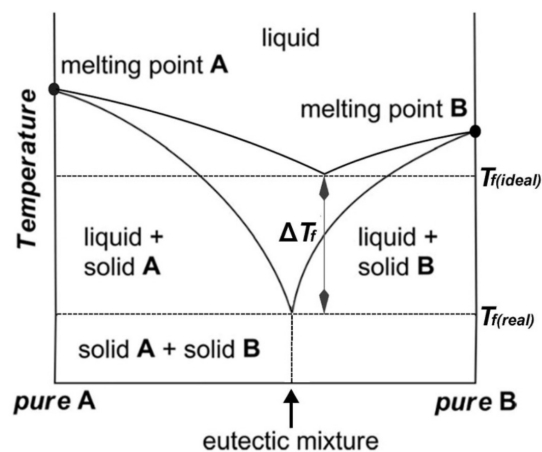


Figure 2. A binary phase diagram for eutectic mixture formation (figure from reference 12 with CC-BY attribution).

system is more abrupt than expected due to stabilization via hydrogen bonding.¹²

Table 1 brings a full description of chemical compositions of non-metal and non-choline amino acid-based DES and their respective HBA:HBD molar ratios available in the

Table 1. Non-metal and non-choline amino acid-based DES binary mixtures recently reported in the literature

HBA	HBD	HBA:HBD ^a	Reference	HBA	HBD	HBA:HBD ^a	Reference
Alanine	lactic acid	1:1; 1:9	13-17	Betaine (anhydrous)	phytic acid sodium	6:1	18
	malic acid	1:1	13,17		benzoic acid	2:3	30
	oxalic acid (anhydrous)	1:1	13		salicylic acid	2:3	30
	oxalic acid (dihydrate)	1:2	13		<i>o</i> -chlorobenzoic acid	2:3	30
					<i>m</i> -chlorobenzoic acid	2:3	30
β-Alanine	malic acid	3:2; 1:1	18		<i>p</i> -chlorobenzoic acid	2:3	30
	citric acid (anhydrous)	1:1	18		2-furoic acid	1:2	30
					phenylacetic acid	1:2	30
Proline	lactic acid	1:1; 1:2; 1:3; 3:10; 1:4	13,18-20		mandelic acid	1:1	30
	malic acid	3:1; 2:1; 1:1; 1:2; 1:3	13,18,21,22		glycolic acid	1:2	30
	oxalic acid (anhydrous)	1:1; 2:3; 1:2	13,21,23		citric acid (monohydrate)	2:3	30
	oxalic acid (dihydrate)	1:1	13		xylitol	2:1; 1:1; 1:2	35
	acetic acid	1:2	19		erythritol	2:1; 1:1; 1:2	35
	propionic acid	1:2	19	glycerol	1:2; 1:3; 1:4; 1:6; 1:8	37,38	
	propanedioic acid	1:2	23,24	propylene glycol	1:3; 1:4; 1:6; 1:8	37	
	glutaric acid	1:2	23	propionic acid	1:2	39	
	glutamic acid	2:1; 1:1	21	acetic acid	1:3	39	
	tartaric acid	1:1	21	urea	1:2	40	
	citric acid (anhydrous)	3:1; 2:1; 1:1	18,21,22	ethylene glycol	1:2	40	
	glycolic acid	1:1; 1:2; 1:3	19	glycine	1:2	40	
	ethylene glycol	1:2	25	lactic acid	1:1	40	
	methanesulfonic acid	1:2	25	glycerol	2:1; 1:1; 2:3; 1:2; 1:3; 1:6; 1:7	41-43	
	<i>p</i> -toluenesulfonic acid	2:1; 1:2	23,25	water	1:2	43,44	
	glucose	5:3; 1:1	18,21	lactic acid	1:9	13,16,45	
	fructose	1:1	21	malic acid	1:1	13	
	sucrose	4:1; 3:1; 2:1; 1:1	18	oxalic acid (dihydrate)	1:1; 1:2; 1:3	13	
	sorbitol	1:1	18	lactic acid	1:5; 1:6; 1:7; 1:8; 1:9	13	
	malonic acid	1:1	18	malic acid	1:1; 1:2	13	
	phytic acid sodium	6:1	18	oxalic acid (dihydrate)	1:1	13	
Betaine (anhydrous)	lactic acid	1:1; 1:2; 1:5	13,15-17, 19,20,22, 26-29	Lysine	ethylene glycol	1:6	25
	malic acid	1:1	13,17,18,22	Glutamic acid	glycerol	1:8	25
	oxalic acid (dihydrate)	1:1; 1:2	13,30	Ornithine	tartaric acid	1:1	21
	acetic acid	1:2	19		malic acid	1:1	21
	propionic acid	1:2	19		citric acid (anhydrous)	1:1	21
	lysine	1:1	31	tartaric acid	1:1	21	
	arginine	1:1	31	oxalic acid (anhydrous)	1:1	21	
	histidine	1:1	31	malic acid	1:1	21	
	levulinic acid	2:1; 1:2	22,32	citric acid (anhydrous)	1:1	21	
	glycerol	2:1; 1:1; 1:2; 1:3	33-35	glycerol	1:4; 1:5; 1:6; 1:7; 1:8	46	
	ethylene glycol	2:1; 1:1; 1:2	35	tartaric acid	1:1	21	
	formic acid	1:10	36	malic acid	1:1	21	
	glucose	5:2	18	citric acid (anhydrous)	1:1	21	
	sucrose	4:1; 2:1; 1:1	18	malic acid	3:2; 1:1	18	
	trehalose	4:1	18	glucose	5:4	18	
	sorbitol	3:1	18	glucose	1:1	18	
	tartaric acid	2:1	18	sucrose	2:1	18	
	mannose	5:2	18	urea	1:4	47	
	citric acid (anhydrous)	1:1	18,22	^a HBA:HBD ratios are expressed in molar ratio. DES: deep eutectic solvent; HBA: hydrogen bond acceptor; HBD: hydrogen bond donor.			

literature up to date. This review focuses on the binary eutectic mixtures based exclusively on amino acid acting as HBA. Nevertheless, we highlight some ternary mixtures found in the literature in fewer examples.

Betaine-based DES is normally described as a high viscosity liquid system, which makes them difficult to manipulate. One alternative to circumvent this issue is adding water as third component to decrease viscosity. Aroso *et al.*⁴⁸ reported two DES following this strategy, betaine/tartaric acid/water, and betaine/citric acid/water, both DES formed with equimolar proportions of the three components. According to the authors, DES viscosity decreases significantly with the increase of temperature and water content for deep eutectic solvents obtained from choline chloride and betaine. The strong H-bond interactions between the DES components are gradually decreased when in the presence of water,⁴⁹ which can account for the “plasticizer-like” effect of water on DES preparations.

Castro *et al.*⁵⁰ reported other two DES using water as third component, betaine/lactic acid/water (1:2:2) and betaine/malic acid/water (2:1:3). More examples are presented in Table 2, which also shows that, besides water, other compounds can be added as third component in DES composition providing liquids with different physicochemical properties compared to binary mixtures.

As described in Table 2, ternary mixtures can be prepared using carboxylic acids, polyols, sugars, amino acids, and others. In binary mixtures, there are a clearer description of the HBA and HBD role of the components in the system. On the other hand, ternary mixtures have a more complex hydrogen bond network, and in a different arrangement compared to binary ones, which results in an unclear distinction. Nevertheless, more than three components can be applied in DES preparations, for example, Castro *et al.*⁵⁰ reported a quaternary mixture composed by malic acid:betaine:proline:water (1:1:1:2).

3. Biomass Pretreatment Mediated by Amino Acid-Based DES

Biomass pretreatment is a key step for biotechnology procedures, due to the disruption of the strong chemical association of the main macromolecular components, cellulose, hemicelluloses, and lignin, making cellulose more accessible to enzymes.⁵⁵ As described earlier, one of the most relevant characteristics of DES is the solubilization of polar compounds. When applied to raw biomass, the main effect of DES pretreatment is the separation of holocellulose (cellulose and hemicelluloses) from lignin, which means biomass delignification (Figure 3).

Table 2. Non-metal and non-choline amino acid-based DES ternary mixtures recently reported in literature

Mixture	Molar ratio	Reference
Betaine:proline:glucose	1:1:1	18
Betaine:proline:sucrose	5:2:2; 1:1:1	18
Betaine:urea:water	1:2:1	33,51
Betaine:urea:glycerol	1:2:3	52
Betaine:methylurea:water	1:2:1	51
Betaine:glycerol:water	1:1:2	51
Betaine:glycerol:propionic acid	1:1:1	37
Betaine:ethylene glycol:water	1:2:1	51
Betaine:ethylene glycol:lactic acid	1:1:1	52
Betaine:ethylene glycol:glycerol	1:2:2	52
Betaine:glycerol:citric acid	1:2:1	52
Betaine:propylene glycol:glycerol	1:1:1; 1:2:2	37
Betaine:propylene glycol:propionic acid	1:2:2	37
Betaine:oxalic acid:water	1:1:1	33
Betaine:oxalic acid:glucose	1:1:1	18
Betaine:malic acid:water	2:1:3; 1:1:1	33,50
Betaine:malic acid:proline	1:1:1	18
Betaine:malic acid:glucose	1:1:1	18
Betaine:malic acid:inositol	1:1:1	18
Betaine:lactic acid:water	1:2:2	50
Betaine:citric acid:water	1:1:1	33,48
Betaine:tartaric acid:water	1:1:1	48
Betaine:glucose:water	1:3:1	51
Betaine:sorbitol:water	1:1:1; 1:1:2	33,51
Betaine:inositol:raffinose	9:1:1	18
Betaine:propanediol:lactic acid	1:3:1	52
Alanine:malic acid:lactic acid	1:1:3	52
Alanine:lactic acid:citric acid	1:3:1	52
β -Alanine:malic acid:water	1:1:3	53
β -Alanine:citric acid:water	1:1:3	53
Proline:lactic acid:citric acid	1:3:1	52
Proline:glycerol:citric acid	1:3:1; 1:4:1	52
Proline:malic acid:lactic acid	2:1:4	52
Glycine:malic acid:glycerol	1:1:2	52
Arginine:citric acid:water	1:1:4; 1:1:5; 1:1:6; 1:1:7	54
Histidine:lactic acid:water	1:9:5	50

It is described in the literature that DES can provide a good lignin solubilization.^{19,56} In addition, the nature of HBA/HBD interaction can induce a mild acid-base catalytic environment that is able to cleave the aryl-ether linkages, resulting in a lignin depolymerization process.⁵⁷ As amino acid-based DES have Bronsted acidity in the HBA fraction, the hemicelluloses can also be extracted due to the cleavage of the acid-labile glycosidic linkages, according to the pretreatment conditions.

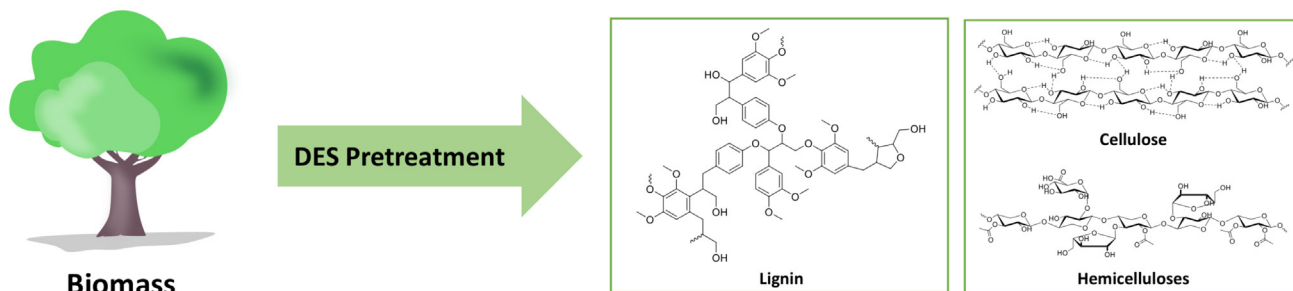


Figure 3. Representation of DES pretreatment-lignin separation from holocellulose.

Lactic acid is one of the most important HBD present in amino acid-based DES for pretreatment of different lignocellulosic materials. Jablonsky *et al.*¹⁶ reported a mild delignification of wheat straw using lactic acid as HBD and glycine, betaine, and alanine as HBA. The DES alanine:lactic acid (1:9) provided 24% of lignin removal at 60 °C for 24 h, whereas the other DES, betaine:lactic acid (1:2) and glycine:lactic acid (1:9), failed to provide any lignin removal.

One way to improve the delignification process is increase temperature. Li *et al.*⁴⁵ described a delignification method using glycine:lactic acid (1:9) at 120 °C for 12 h achieving 58% of lignin removal from poplar wood. Wang *et al.*²⁷ applied a betaine:lactic acid (1:2) DES on *moso* bamboo pretreatment, achieving 54% of delignification at 140 °C for 6 h, affording lignin oligomers with number averaged molar mass (M_n) and weight averaged molar mass (M_w) of 885 and 4410 Da, respectively. Despite of having moderate lignin removal, the polydispersity of recovered lignin is pretty high ($PDI = M_w/M_n = 4.98$), which characterizes a heterogeneous material. Song *et al.*²⁸ reported a pretreatment procedure for corn stover and willow using a betaine:lactic acid (1:2) DES. The authors achieved a lignin removal of 79 and 53% for corn stover and willow, respectively, at 140 °C for 3 h. The recovered lignin after DES pretreatment provided materials with a M_n of 1020 Da (corn stover) and of 1130 Da (willow) with a polydispersity around 3.2.

Another example for the use of betaine:lactic acid (1:2) was described by Guo *et al.*²⁹ using a xylose residue from corncob processing as feedstock. The authors achieved a very good 82% delignification yield at 120 °C for 2 h, recovering a lignin with an excellent polydispersity of 1.10. Compared to the other feedstocks described above, the xylose residue is a processed biomass, which justify the high delignification yield in relatively short pretreatment times.

Besides lactic acid, other organic acids can be applied in pretreatment acting as HBD, such as levulinic acid, an important platform chemical obtained from carbohydrates

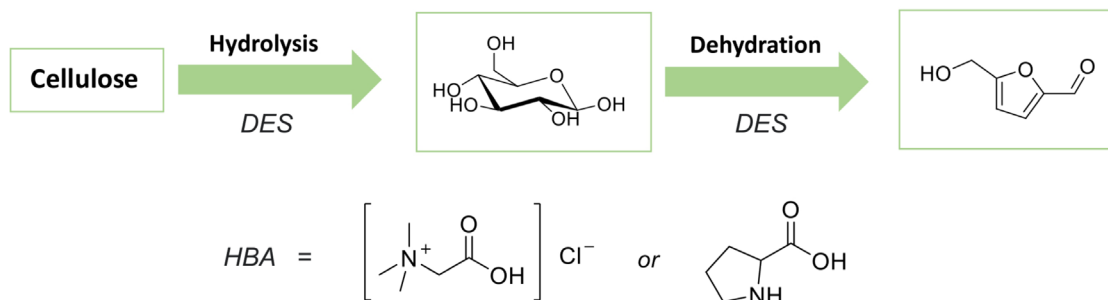
dehydration.⁵⁸ Ling *et al.*³² reported a pretreatment method using betaine:levulinic acid (1:2) DES for *moso* bamboo delignification, however only 13% of lignin removal was reached at 120 °C for 2 h. Although levulinic acid is a bio-based, non-toxic chemical for DES preparation, the previous example indicates that it has low efficiency for delignification compared to lactic acid.

Liang *et al.*³¹ described a method for corncob fractionation mediated by fully amino acid-based DES solution having betaine as HBA and lysine, arginine, and histidine as HBD, in an equimolar ratio, with water content ranging from 65 to 93 wt.%. They reached 48 and 49% for xylan and lignin removal, respectively, for betaine:lysine 87 wt.% aqueous solution; 42 and 57% for xylan and lignin removal, respectively, for betaine:arginine 82 wt.% aqueous solution. The betaine:histidine 93 wt.% aqueous solution did not provide good performance for both xylan and lignin, compared to the other DES evaluated. The authors also explored the DES pretreated materials in enzymatic hydrolysis, which resulted in a glucose equivalent two-fold higher than the untreated corncob owing to the better access of the enzymes to the remaining macromolecular component-cellulose. Indeed, detailed characterization showed that the enhancement of cellulose digestibility derived mainly from xylan and lignin removal.

4. Chemical Conversion Mediated by Amino Acid-Based DES

Most of the amino acid-based DES has Bronsted acidity from the HBA and/or HBD composition which can play a bifunctional solvent/catalyst role according to the DES composition. As far as biorefinery applications are concerned, Bronsted acidic DES can be applied in cellulose hydrolysis to produce reducing sugars as well as sugar dehydration to furanic compounds, as described in Scheme 1.⁵⁹ Betaine derivatives and proline are the most used HBA in chemical conversion mediated by DES.

Ren *et al.*²⁵ has shown that a mixture of proline and ethylene glycol (1:2) with $FeCl_3 \cdot 6H_2O$ as additive could



Scheme 1. Chemical pathway of cellulose conversion to furanic compounds.

hydrolyze a cotton linter pulp in 86% cellulose conversion furnishing total reducing sugars in 67% yield. This high conversion and yield were obtained only when a Lewis acid was introduced as additive. Indeed, the DES without any additive lead to 21% of cellulose conversion and total reducing sugars were achieved in only 15% yield. This example highlights that, in some cases, the association of Lewis and Bronsted acids is detrimental for achieving good hydrolysis levels.

In terms of furanic derivatives production, betaine-based DES is the only one that has contributed to 5-(hydroxymethyl)-furfural (HMF) production, according to the literature. Vigier *et al.*⁴³ reported the application of betaine hydrochloride (BHC) in fructose and inulin dehydration. The deep eutectic solvent composed by $\text{ChCl/BHC/H}_2\text{O}$ (10/0.5/2) exhibited the best performance in HMF production: 84 and 52% from fructose and inulin, respectively, at 110 °C under conventional heating for 1 h.

Delbecq *et al.*³⁶ reported a DES composed by betaine as HBA and formic acid as HBD, the latter also acting as a catalyst, in a traditional water/methyl isobutyl ketone (MIBK) biphasic system for HMF production from different carbohydrates under microwave irradiation (Figure 4). The authors prepared HMF in 82% yield from fructose (160 °C, 60 min), 55% yield from glucose (190 °C, 60 min), 45%

yield from starch (190 °C, 60 min) and in 26% yield from microcrystalline cellulose (200 °C, 80 min). As can be seen, the HMF yield decreased according to the complexity of the substrate used for the dehydration process.

The biphasic system is an excellent alternative for optimizing HMF yields by avoiding side reactions, such as rehydration to levulinic and formic acids, and condensation reactions to form a dark insoluble solid called humins.⁶⁰ In addition, the *in situ* extraction is a one-pot purification step during the reaction, resulting in a furan-rich organic phase and an aqueous DES phase that can be recycled.

Another example of the combined use of a Lewis-Bronsted catalytic system was presented by Feng *et al.*⁶¹ by the association of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and betaine derivatives for the sugar dehydration in a water/MIBK biphasic system. This approach avoids over exposure of the product HMF to the acidic conditions minimizing the formation of humins, an insoluble polymeric material. The authors achieved 65% HMF yield from glucose (170 °C, 30 min) and around 35% from microcrystalline cellulose (170 °C, 30 min). Additionally, although it is more challenging, the use of raw biomass was also evaluated for HMF production in the same study. The use of corn stover, rice straw, bamboo powder and wheat straw afforded HMF in 40-52% yield. According to the proposed mechanism presented in Scheme 2, both the anion (X^-) and cation ($(\text{CH}_3)_3\text{NCH}_2\text{COOH}^+$) played a key role in the process and had a synergistic effect on the HMF yield. The anion participates in hydrogen bonding with the hydroxyl group of the carbohydrate, whereas H^+ dissociates from the cation to catalyze the formation of HMF.

Gomes and Pastre⁶² reported the application of DES based in betaine hydrochloride as HBA, carboxylic acids as HBD and water as third component in equimolar quantities as solvent/catalyst system for fructose-based carbohydrate dehydration under microwave irradiation. The authors achieved HMF in 94% yield from fructose (140 °C, 11 min) and in 72% yield from sucrose (160 °C, 11 min) in a DES system composed by BHC/malic acid/ H_2O (1:1:1) as reaction media and ethyl acetate as extraction solvent.

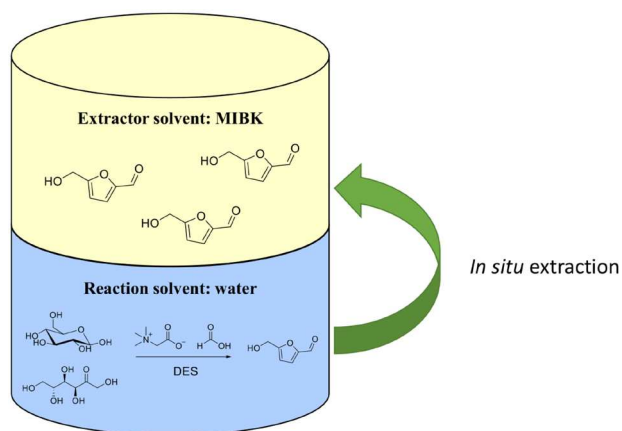
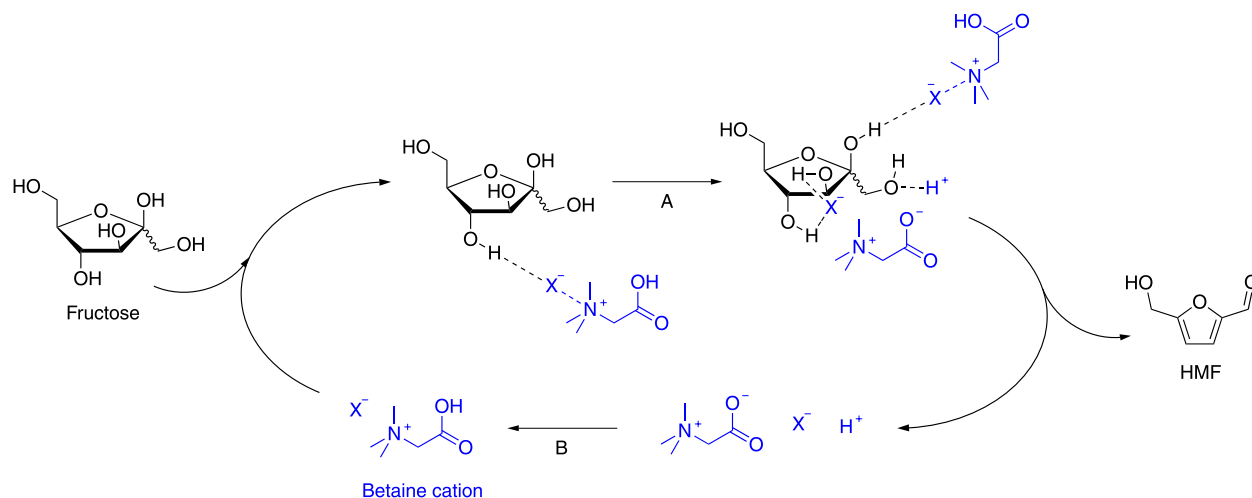


Figure 4. Representation of water/MIBK biphasic system for HMF production using betaine:formic acid (1:10) developed by Delbecq *et al.*³⁶



Scheme 2. Anion and cation effect on the fructose dehydration to HMF (adapted from reference 61).

However, these DES with natural carboxylic acids (citric, malic, tartaric acids) as HBD lead to DES degradation at the reaction conditions, hampering the recycling of the system. Indeed, thermal gravimetric mass spectrometry (TG-MS) analyses showed that decarboxylation reactions above 140 °C account for the loss of the acidity of the media.

The examples described above were related to furanic derivatives production. However, betaine-based system may also be applied on furanic derivatives upgrading, such as oxidation reactions. Araji *et al.*⁶³ described a method for furfural oxidation to maleic and fumaric acids using betaine hydrochloride/water system and hydrogen peroxide as the oxidant agent. In a BHC/water molar ratio of 1:9 with 10 equiv. of H₂O₂, the authors reported full furfural conversion giving maleic acid and fumaric acid in 44 and 4% yields, respectively, at 90 °C for 30 min. Despite the low yields, this work highlights the potential for the preparation of high added-value compounds like bulk chemicals and commodities entirely from renewable resources using NADES as alternative solvent.

5. Conclusion

In summary, in this review we presented some recent advances of amino acid-based DES for biorefinery applications. Compared to conventional methods for biomass processing, including pretreatment and chemical conversion, deep eutectic solvents present some advantages like the easy preparation by simple mixing, the use of low-cost materials (in many cases, obtained from natural resources) low toxicity and good solubilization of lignocellulosic biomass. On top of that, it is considered a green method for platform chemicals production, which makes them relevant for industrial applications. However,

factors such as DES composition and physicochemical properties must be considered in order to achieve good yield, selectivity, recyclability by avoiding DES degradation and good mass and heat transfer by tailoring viscosity, which are all key elements that need to be considered for a large-scale production of chemicals. Looking at the biorefinery scenario, so far, deep eutectic solvents proved to be a promising methodology for carbohydrates valorization towards the preparation of high added-value compounds, mainly furanic derivatives such as HMF and furfural. The examples highlighted herein may inspire the application of amino acid-based DES in other relevant transformations with greater performance and lower environmental impact when compared to conventional organic solvents.

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