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Development of Deep Eutectic Solvents for Pretreatment of Sugarcane Bagasse and Corncob

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Research Article

Abstract

Lately, deep eutectic solvent (DESs) being an innovative and green solvent is becoming more popular due to growing environmental concern arising from the uses of conventional organic solvents. In view of this, four deep eutectic solvents based on choline chloride namely DES1 (Choline chloride - Urea), DES2 (Choline chloride - Oxalic acid, DES3 (Choline chloride - Glycerol and DES4 (Choline chloride - Ethylene Glycol were synthesized, characterized and used for pretreatment of sugarcane baggasse and corn cob respectively. The physicochemical and thermal properties of the synthesized DESs, like density, pH, viscosity, refractive index, surface tension, and thermal conductivity were found to be affected by the components and molar ratios of the DESs. The characterization result revealed that the viscosity of the DESs drops drastically as temperature rises. DES3 has the highest viscosity of 499.4 cPs followed by DES2, DES1 and DES4 having 305.72 cPs, 188.50 cPs and 131 cPs respectively. The untreated (raw) corn cob and sugarcane baggasse which contains 20.65 % and 19.06 % lignin were subjected to pretreatment using the synthesized DES1-DES4 under the same conditions in order to remove lignin. Lignin content reduced by 72 % for corncob and 83.26% for sugarcane baggasse compared to conventional solvents having a range of (41-63 %) lignin removal. Regarding lignin removal and holocellulose content, the DESs tested in this study demonstrated their potential for use as biomass pretreatment solvents, with DES1 and DES2 performing better in terms of percentage lignin removal for both sugarcane bagasse and corncob, respectively.

Keywords
Biomass; Choline chloride; Deep eutectic solvents; Environmentally-friendly; Lignin; Pre-treatment

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1. Introduction

Solvents are essential to the development of substances, chemicals, and systems hence, the innovation of low-cost, renewable solvents is highly desired in future biorefineries (Oguche *et al*., 2022). Today's biorefineries still need to pretreat biomass to get rid of lignin and make sugars more accessible to enzymes (Ameri, 2017). Lignocellulosic biomass is the most widely accessible sustainable raw material on the earth (Smink, 2020). Therefore, switching to biomass from fossil fuels like oil, coal, and natural gas can lower the chemical industry's carbondioxide emissions. Lignocellulosic biomass has shown promise. They include Rice husk, corn straw, banana peel, sugarcane bagasse, cassava peels, corn cob, rice straw, and algae. These plant parts are not digestible by humans, which is advantageous because there will be no competition for food. The use of this lignocellulosic feedstock also serves to recycle waste, which is beneficial to the environment (Dimitrios and Loanna, 2015). Lignocellulosic feedstocks consist of lignin, hemicellulose and cellulose networks (Kim *et al*., 2018). Despite being promising, lignocellulosic feedstock presents a significant challenge due to recalcitrance (Karolina *et al*., 2018). As a result, they are resistant to chemical and biological breakdown, making biofuels and lactic acid production difficult. Therefore, a better process for using this biomass feedstock as efficiently as possible are required. Pretreatment causes physical, chemical, and biological changes that disrupt the strong association within the cell wall (Ayşe and Serpil, 2020).

Because different lignocellulosic feedstocks contain varying amounts of lignin, hemicellulose and cellulose, the results vary (Julie *et al.*, 2018).

A good pretreatment method is one that is low in cost, uses little energy, does not denature cellulose and hemicellulose, and does not produce byproducts that inhibit the activity of microorganisms responsible for hydrolysis and fermentation (Karolina *et al*., 2018). Figure 1 represent the role of treatment solvent to increase hydrolysis or conversion of valuable products such as furfural, lactic acid, bioethanol and so on

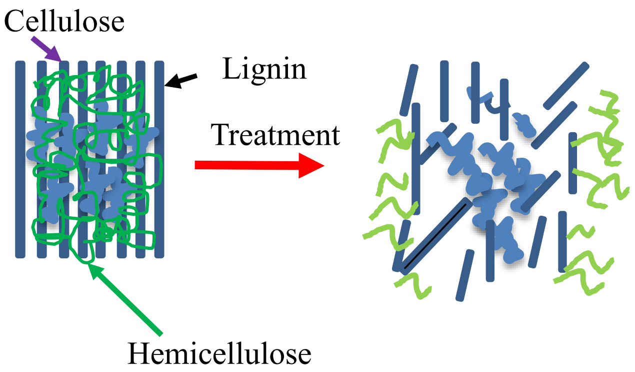


Figure 1: Effect of treatment to release cellulose and hemicellulose from lignocellulosic biomass

Figure 1 shows that pretreatment is a critical step, and it is critical to find pretreatment methods that provide a high yield of products while remaining economical and environmentally friendly.

Because of the chemical composition of lignocellulosic materials, production of biofuels and various valuable chemicals such as lactic acid and furfural will be inefficient if not pretreated.

Pretreatment improves the efficiency and efficacy of various agricultural residue products (Muhammad *et al*., 2019). This is necessary because the cost of producing biofuels and valuable chemicals such as lactic acid is dependent on the most cost-effective pretreatment measure or method, as it is a critical part of the manufacturing process (Rajeev *et al*., 2016). Thus, researchers' current focus is on finding green solvents as an alternative to all solvents (Degam, 2017). As a result, there is a constant need for new and greener alternatives to overcome the drawbacks of traditional solvents like acids, bases, and room temperature ionic liquids (RTILs). As such, Abbott *et al*. (2004) introduced deep eutectic solvents (DESs) as a new type of solvents.

DESs are typically produced through interactions between hydrogen bonds and their constituents.

It is a green solvent formed by two or more components combined at a lower temperature than the individual components at the appropriate molar ratio (Jablonsky *et al*., 2019). These solvents have gained widespread attention and interest in academia since 2004 due to their tunability and green solvent properties, which include biocompatible, non-toxic, recyclable, and biodegradable properties (Van Osch *et al*., 2017). Although, these properties depend solely on ratio of combinations of the components and the type of hydrogen bond donors used. Although, DESs solvents are not costly compared to RTILs, does not require further purification steps after synthesis, are more readily available in synthetic form, extremely pure, recyclable, nontoxic, and biodegradable (Zhang *et al*., 2012, Degam, 2017).

According to Kim *et al*. 2018, there is increasing demand in the use of DESs as suitable alternative solvents to conventional chemicals such as acid, base, and ionic liquids. DESs therefore have the potentials to be used as alternative solvents for biomass delignification (Moura *et al*., 2017, Mirza *et al*., 2015, and López-Salas *et al*., 2014). However, its effectiveness in pretreatment of sugarcane bagasse and corncob has not been tested.

Previously, research on biomass using DESs largely focused on the extraction of components from biomass. (Francisco *et al*., 2012) and biomass solvation (Lu *et al*., 2012). Hence, only a few research on the use of DESs to pretreat biomass have been reported, (Mirza *et al*., 2015, Smink, 2020) and more importantly, there is low efficient performance by acids and bases as a common pretreatment solvents for lignocellulosic biomass., couple with non-environmentally friendly nature, non-recovery, non-recyclable, corrosion problems posed by this solvents hence, there is need to look for an efficient, better and environmentally friendly technology like DESs.

Different kinds of DESs such as Acetoin based DESs for switch grass (Ameri, 2017), Lactic acid based DESs for pretreatment of *Eucalyptus globulus* (Smink, 2020) but only few works have reported using choline chloride based DESs for pretreatment of biomass especially food waste but not for agricultural solid residues like corn cob and sugarcane bagasse. Since the introduction of the DESs phenomena in 2004 by Abbot, choline (2-hydroxyethyl-trimethylammonium) chloride has been the most investigated hydrogen bond acceptor (HBA). Choline chloride is produced on an annual basis per metric ton (MT) as a chicken feed addition and for a variety of several uses. In addition to being affordable and easy to make, it is also nontoxic and biodegradable (Degam, 2017). As a result, even if it is released back into the environment as ChCl or its deep eutectic combination, it presents no harm. Thus, DESs based on choline chloride are able to be applied on a broad scale procedures at a low cost. Therefore, in this current work, four choline chloride was developed and used for delignification of sugarcane baggasse and corncob respectively to investigate their efficiency in the degradation of lignin from these biomass.

2. Materials and Method

Some of the materials and reagents used in this work includes Choline chloride (Sigma Aldrich, 98%), without further purification, urea (Acros Organics, 99.5%), glycerol (Fisher), and ethylene glycol (Sigma Aldrich, 99.8%) were all used. Choline chloride's molar ratio to oxalic acid (CC-OA) was 1:1 while it was 1:2 to urea (CC-U), ethylene glycol (CC-EG), glycerol (CC-G), and urea (CC-U)..DESs was synthesized by heating method where both the hydrogen bond acceptor (HBA) and hydrogen bond donor (HBDs) was mixed at appropriate molar ration at about 80 ^{o}C with 1000 rpm stirring until a homogenous, clear liquid was produced within 30- 60 minutes. The synthesized DESs was carry out in a closed vessel and stored in air tight container to avoid absorption of water. Table 1 shows the various DESs synthesized with their name coded and mole ratio respectively. The physicochemical characterization of the synthesized. DESs carried out in this work includes viscosity, thermal conductivity, density, surface tension, miscibility test, refractive index (RI) and pH measurement. The viscosity, thermal conductivity, density, surface tension of the sythensized DESs were measured at atmospheric pressure from 25 ºC to 60 ºC.

Viscosity and Density were measured using rotating viscometer (Model number of 1909N59, NTVEI intelligent viscometer made in Shanghai, China and a densimeter with model number sigma 702 and serial number of 72296 by Bionic scientific. Each reading was repeated three times with the average value reported. Using a Jenway 4510 conductivity meter, the conductivities of the several DESs under investigation in this paper were measured.

A frequently employed analytical technique for assessing liquid structures is FT-IR spectroscopy.

The ions that make up the materials are usually extremely sensitive to their local potential energy environment through their intramolecular vibrational modes. FTIR analysis of all the synthesized DESs was done using Shimadzu FTIR-8400s model between an intensity ranges of 600 to 4000 cm^{-1} at the department of Chemistry, Ahmadu Bello University (ABU) Zaria. Pretreatment was carried out using the method of Alhafiz *et al*., 2020 in water bath shaker at room temperature (25- 30 ºC). About 10 g of oven dried sugarcane baggasse and corn cob was dissolved in 20 wt. % of each of the synthesized DES1-DES4 with equal volume respectively into 250 ml conical flask and kept for about 45 min. After that, the biomass was filtered and repeatedly rinsed with distilled water until it reached a pH of neutrality and it was subsequently dried in an oven at 50 ºC for 1 hr and later taken to Institute for Agriculture Research (IAR/ABU) Zaria for fiber analysis to determine the % of lignin removal and holocellulose percentage available for conversion based on Association of Official Agricultural Chemists (AOAC) methods as described by Song *et al*., 2019. The analysis was repeated for possible standard deviation and the average values were all reported.

The percentage lignin removal was obtained using equation 1 below according to the method of Chen *et al.*, 2017;

$$\% \text{ Removal of Lignin } (\%) = [1- \frac{a \times w}{a_0 \times w_0} \times 100] \quad (1)$$

Where w = weight of pretreated sample

$W_o =$ Weight of untreated sample

a = amount of lignin (%) in pretreated sample

$a_0 =$ amount of lignin (%)in untreated sample

While the holocellulose content available for bioconversion was determined by simple addition of cellulose and hemicellulose contents after pretreatment respectively. SEM image of the untreated and treated sugarcane baggasse and corn cob was carried out as presented in Plate 1.The morphology were generated at different magnifications ranging from 300 to 3000 using a SEM image machine with the aid of computer program while the data is collected over a selected area of the samples surfaces.

3. Results and Discussion

3.1: Moisture content Determination of the Synthesized DES1 –DES4:

The presence of water in DESs is critical in determining their purity. If not, water molecules would dissolve the DESs' components, preventing them from forming ion pairs (Degam, 2017). The moisture content of all the synthesized DESs was determined and presented in Table 1.

Table 1: Amount of water present in DESs synthesized

DESs	Code-name	Mole ratio	Moisture Content (%)
Choline Chloride: Urea	DES1	1:2	0.612
Choline Chloride:Oxalic acid	DES2	1:1	0.074
Choline Chloride: Glycerol	DES3	1:2	0.115
Choline Chloride :Ethylene glycol	DES4	1:2	0.098

As shown in Table 1, All the DESs sythensized contained very low and insignificant amount of water. Compared to Degam, 2017 that recorded 0.957 % and 0.912 % for DES1 and DES3, the present work recorded a lower percentage of water present in DES1 and DES 3 as 0.612 and 0.115% respectively. This is because, the present work was carried out in air tight condition to avoid absorption of water from the environment DES2 has least amount of water followed by DES4, DES 3 and DES1.This indicate that amount of water present in DES is dependent mainly on the HBD and the molar ratio of the components that formed DESs since all the four DESs used Choline chloride as their HBA for formation of DES. The highest amount of water recorded in DES1 may be due to hygroscopic nature of both the HBA and HBD used hence DES 1 contained 0.612 %, this is because the Urea used as the HBD is very hygroscopic. Degam (2017) stated that even with extreme caution, it is not possible to synthesize DESs with no water present due to the nature of the HBD and HBDs used in their synthesis, which are extremely hygroscopic.

DES1 has a lower viscosity than DES2 and DES3 due to its high-water content. This resulted in high lignin dissolution by DES1 as a result of increased mass transfer, which leads to higher solubility due to lower viscosity. According to Degam (2017), the higher amount of water in DES1 may result in lower surface tension and thus higher lignin solubility because DESs with low surface tension can infiltrate the biomass matrix more easily. Although, the high percentage of lignin degradation reported in DES2 may be attributed to its mole ratio of 1:1, lower freezing temperature and acidic nature of HBD since all the synthesized were in ration of 1:2 except DES2.the higher the ratio, the higher the freezing point hence the lower the mass transfer and consequently reducing dissolution. Also, the higher the molar ratio, the higher the interaction hence the more, the physical properties like surface tension, density and viscosity tends to increase (Castro *et al*., 2018). The amount of water present and ion complex by HBD influence melting and freezing point of DESs (Ameri, 2017). The acidic nature of HBDs also contribute to higher degradation efficiency recorded by DES2. Zhang *et al*. 2020 reported that the melting point of the DESs is influenced by the ratios of the hydrogen bond donor material. DES2 had the best lignin dissolution because of the internal hydrogen link produced by the DES and the high amount of leftover ions that formed a hydrogen bond with the hydroxyl group of the lignin which was also confirmed by Zhang *et al*. 2020.

3.2 Fourier Transform-Infrad-red Spectroscopy (FT-IR) Characterization of the Synthesized DES1 –DES4:

The FT-IR spectra characterization of all the synthesized DES 1 –DES4 was done and presented in Figure 2

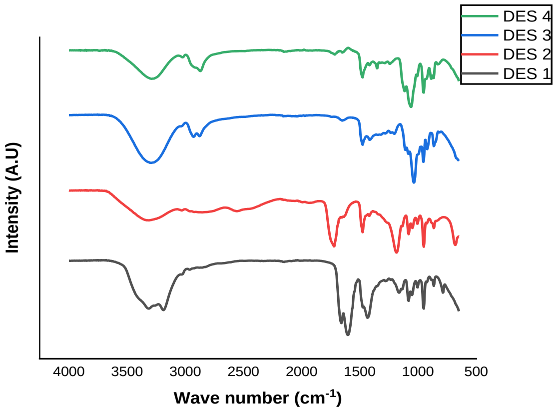


Figure 2: Overlaid FTIR spectra of synthesized DES1 to DES 4.

Figure 2 shows the DESs and each of its distinct components' involved bonds' representative peak shifts and band widening. Because glycerol and ethylene glycol molecules are so similar, the same vibrational bands appear in the DES. Figure 2 depicts four ChCl: EG and three ChCl: Glycerol DES. The bands between 3600 and 3000 confirms the formation of strong hydrogen bond assigned to O-H stretching (shift) vibration which confirmed the formation of DESs. Similar spectra were observed for all of the DESs synthesized. This is due to the identical chemical structure of ChCl as the hydrogen bond donor and the fact that water is present in all DESs, which causes similar peaks to appear in the same area. From DES1 to DE4, the absorption bands at (3000-2885) and (1655, 1035, and 897 cm1) correspond to the asymmetric and symmetric CH-stretching vibrations and the C-C-N+ stretching vibrations in choline chloride, respectively which correspond to the report of Zhang *et al*., 2012 and Degam, 2017.

3.3 Viscosity Determination of the Synthesized DES1 –DES4

Figure 3 indicates the effect of temperature on Viscosities of DES1 to DES4

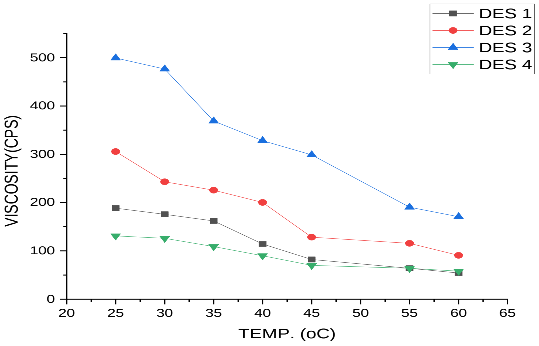


Figure 3: Effect of temperature on Viscosities of the synthesized DESs (DES 1 –DES 4)

Figure 3 depicts the relationship between temperature and the viscosities of each of the produced DESs. From the four DESs synthesized, the results indicated that as temperature increases, the viscosity of DESs decreases. The viscosity for DESs (DES 1 –DES 4) was high at low temperature but decreases rapidly as temperature increase from 35 ^{o}C to 60 ^{o}C. This is due to the mobility of ions in the DESs (DES 1 –DES 4). The internal resistance of the molecules reduces as the temperature rises, enabling the molecules to flow more readily and the liquid to become less viscous. Castro *et al*., 2018 and Arkawazi *et al*., 2020 also obtained similar pattern in their work where viscosity decreased as temperature increases. DES 3 shows highest viscosity is due to capability of coordination of the amide in choline chloride and the formation of self-hydrogen bonds between amides and glycerol compare to other DESs in this research while DES 4 show the lowest viscosity due to lesser number of hydrogen bond that can be formed between the HBA and HBD hence, the differences in viscosities among the sythensized DESs is due to change in HBD that was used in the formation of DESs. It was also reported by Ameri (2017) and Castro *et al*. 2018 that DESs will begin to degrade at temperature above 200 ^{o}C to 324 ^{o}C hence, all the synthesized are very stable and does not degrade for the range of temperature (room temperature) consider for the pretreatment of sugarcane bagasse and corn cob respectively. All the synthesized DES 1 to DES4 have low viscosity except DES3 compared to conventional solvents. Low viscosity lead to high dissolution and solubility of lignin as a result of increase in the mass transfer (Degam, 2017).In this case, DES4 have the lowest viscosity, and however, the nature and ratio of HBDs play a crucial part in the physical properties of DESs. The presence of electrostatic interactions, van der Walls, and hydrogen bonds in the network, may account for DES3 high viscosity (Castro *et al*., 2018). As with conventional solvents and ionic liquids, the internal resistance of a fluid at shear stress and intermolecular interactions are the main factors impacting the reported viscosity values. The order of increasing viscosity among the synthesized DESs is DES4<DES3<DES2<DES1.

3.4 Density Determination of the Synthesized DES1 –DES4

Density values of the four synthesized DESs mixtures within the temperature range from 25 to 60^{o}C were measured using densimeter with model number sigma 702 and serial number of 72296 by Bionic scientific as presented in Figure 4.

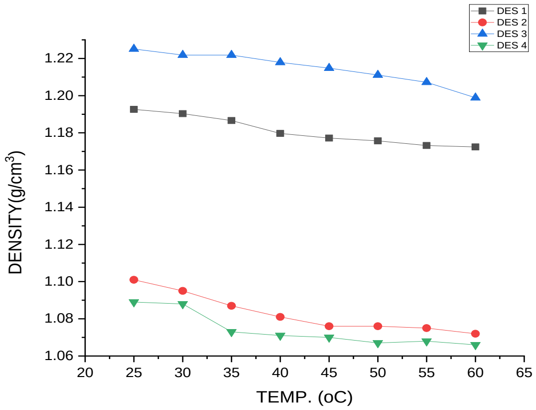


Figure 4: Effect of temperature on Density of the synthesized DESs (DES 1 –DES 4)

As shown in Figure 4, the densities of the four synthesized DES 1 to DES 4 exhibit little variation in densities with respect to increase in temperature respectively. This is mainly due to weakening of the DESs nanostructure thereby promoting the disintegration. As temperature increased, the molecules of the DES 1 to DES4 are been break down hence, they are free to move and mixed properly within the biomass DES 1 has density values of 1.19 g/cm^{3,} DES 2 has 1.098 g/cm^{3}while DES3 and DES4 has 1.225 g/cm^3 and 1.089 g/cm^3 respectively. The density values of all the DESs sythensized is higher in this study than those reported in literature by Crespo *et al.*, 2019 at the same molar ratios, reason being that those reported by Crespo *et al*. (2019) contain higher percentage of water than the ones recorded in this work with the deviations increasing with the HBD in the order EG < Oxalic acid < urea < glycerol. The density results recorded for DES1, DES3 and DES4 as 1.19 g/cm^3, 1.225 g/cm^3 and 1.089 g/cm^3 were in agreement with that of Payam and Ghandi, (2019) who reported 1.25 g/cm^3, 1.12 g/cm^3 and 1.18 g/cm^3 for DES1, DES3 and DES4 respectively at the same compositions.

3.5 Other Physicochemical Determination of the Synthesized DES1 –DES4

Table 2 shows the physicochemical properties (surface tension, refractive index, thermal conductivity and pH of the synthesized DESs was determined and presented in Table 2

Table 2: Physicochemical properties of the synthesized DESs

DESs	Surface Tension (Nm/m)	Refractive Index	Thermal Conductivity ($WK^{-1}m^{-1}$)	pH
DES1	52.26	1.497	0.628	9.4
DES2	57.11	1.463	0.769	2.0
DES3	56.54	1.709	0.931	7.8
DES4	55.43	1.474	0.981	6.6

The physicochemical properties measured in this work are mainly function of the components (HBDs) that are was used in the formation of DESs the molar ratios.

The measured pH obtained in this work for DES1 (9.4) and DES3 (7.8) are similar to that of Degam, (2017) who reported 9.44 and 7.76 respectively for DES1 and DES3. From Table 2, DES2 has the lowest pH of 2 probably due to HBD which is an acid while DES4 has a pH of 6.6. Both DES3 and DES4 have their pH around the neutral region and this result also correspond to that of Degam, (2017). In terms of surface tension, the results showed that DES2 has the highest surface tension of 57.11 Nm/m. The surface tension results obtained in this work for DES1, DES3 and DES4 are 52.26 Nm/m, 56.54 Nm/m and 55.43 Nm/m respectively which are in close range to that of El-hoshoudy *et al.*, (2019) who obtained 52 Nm/m, 55.8 Nm/m and 49 Nm/m respectively for DES 1, DES3 and DES4. Also, this result (DES1) is similar to that of Azhar *et al.*, (2019) in their work, where they recorded lowest surface tension of 55.06 Nm/m for DES1 among the DESs they synthesized which is in close range with this work for DES1. DESs made from choline chloride are more conductive hence, an indication of the presence of anionic species in the DESs which can move independently. Dai *et al.*,2013 reported conductivities of choline chloride based DESs in the range of 0.1 -10 $WK^{-1}m^{-1}$.However, the DESs synthesized in this current work has conductivity ranging from 0.6 -0.98 with DES4 having the highest conductivity of 0.980563 $WK^{-1}m^{-1}$ while DES1 show the lowest conductivity of about 0.628118 $WK^{-1}m^{-1}$. Also, the result of conductivity obtained is also in close range with that of El-hoshoudy *et al.*, 2019 who obtained 0.75 $WK^{-1}m^{-1}$, 1.05 $WK^{-1}m^{-1}$ and 7.61 $WK^{-1}m^{-1}$ for DES1, DES3 and DES4 respectively.

Table 2 also presents experimental data on the reflective indices of the DESs synthesized in this study. The refractive index was measured at room temperature, and it was clear that at low water content, DES3 with a water content of 0.115 has a higher reflective index of 1.709 than DES1 with a water content of 0.612 and a refractive index of 1.497 because of the improved ion packing and increased ion arrangement. Generally, all the synthesized DESs has high refractive indeces as a results of low water content in them. This result is in agreement with Azhar *et al.*, 2019 who obtained 1.4590 in their work. The result of this current work for DES1 (1.497) and DES3 (1.709) are in close range with that of Degam, 2017 who recorded 1.50s69 and 1.4867 for DES1 and DES3 respectively.

3.6 Pretreatment of sugarcane bagasse and corn cob using the synthesized DES1 –DES4

The proximate analysis of the raw materials was carried as presented in Table 3.

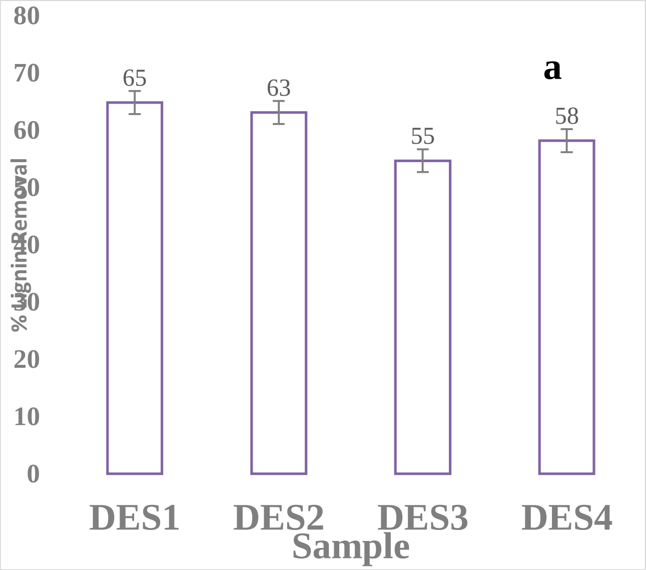
The proximate analysis of 45.86 %, 23.35 % and 20.65 % for corncob are within the range reported in literature by Alhafiz *et al.*, 2020 who obtained a value of 41.8, 31.3 and 21.60 for corncob. Zhang 2016 also recorded a similarresults for untreated corncob with 39.26, 29.05 and 19.60. The small variations in the chemical composition of the untreated materials recorded with that reported in literature may be due to different sources and soil contents been different due to variation in locations where the maize was planted. Similarly in terms of the composition of raw sugarcane bagasse, Rezendel *et al.*, 2014 obtained 50 %, 25 % and 25 % as composition of cellulose, hemicellulose and lignin for their raw sugarcane bagasse which is close to that reported in this work as presented in Table 3 respectively.

Table 3: Proximate analysis of raw sugarcane bagasse and corn cob.

Sample	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Corn cobs	45.86±0.35	23.35 ± 0.30	20.65± 0.35
Sugarcane bagasse	50.09±0.28	24.24 ± 0.22	19.21± 0.21

Percentage lignin degradation was calculated as percentage on the basis of lignin removal after pretreatment using equation 1.

The percentage of lignin removal after pretreatment are shown in Figure 5a and 5b for sugarcane bagasse and corncob respectively while the percentage of holocellulose available for possible conversion into valuable products was also determined and presented in Figure 6a and 6b respectively. The analysis was repeated for possible standard deviation as the average value were used to compute the percentage lignin removal.



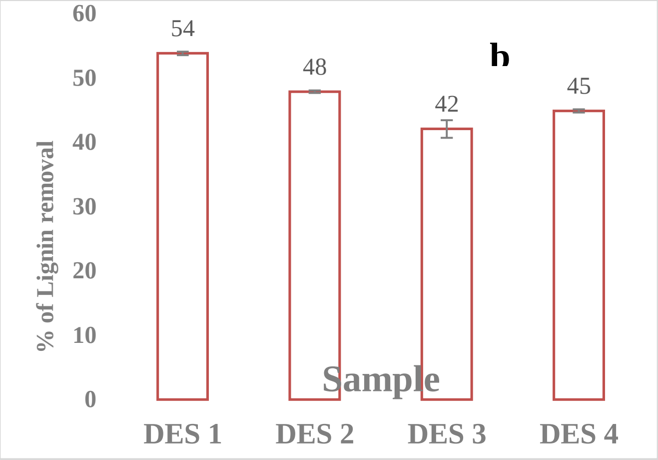


Figure 5: Effect of pretreatment using the synthesized DESs on percentage Lignin removal of **(a)** sugarcane baggasse and **(b)** corncob.

As shown in Figure 5a, DES1 and DES2 show highest percentage removal of lignin with 65% and 63 % respectively while DES3 and DES4 have 55 and 68 percent respectively. The results demonstrate that the synthesized DESs can be used as a suitable solvent for lignin removal from sugarcane baggasse. Similarly, Figure 5b shown the removal of lignin from corncob where DES1 removed more lignin (54%) higher than the remaining DESs synthesized**.** Similar results were obtained for switch grass pretreatment by Degam, 2017 and Ameri, 2017 with 58 % and 40.86 % removal respectively using choline chloride –Acetonitrile and choline chloride –imidazole DESs.

According to Xia *et al.* (2018), the effectiveness of DES 1–DES4 for pretreatment was based on their capacity to break carbon-carbon bonds and alkyl ether bonds in sugarcane bagasse and corn cob structures. The O-H, ether, and H-bonds in lignin are thought to be broken down by DESs, which causes lignin to separate from the lignocellulose complex (Alvarez-Vasco *et al.*, 2016). The presence of hydroxyl O-H groups and alkyl groups in choline chloride and urea, on the other hand, may be attributed to pretreatment enhancement. This is due to the fact that the O-H and alkyl groups formed in choline chloride act as electron donors, with the alkyl group increasing the oxygen electron density in the O-H group on oxalic acid. This strengthens the H-bond between hydrogen and oxygen in DES 1 and DES 2, respectively, resulting in the formation of weaker acids and, as a result, lower acid ionization. This observation is in agreement to that reported by Chen *et al.*, 2018. The O-H group and double bond of HBD (oxalic acid) in DES2 contributed to the higher polarity nature. This might enhanced solvent interaction with lignin through the H-bonding thus functional groups (HBDs) in DES significantly account for lignin dissolution account for high percentage removal of lignin by DES2. Also, to understand the mechanism of DES pretreatment, some physiochemical characterization such as FT-IR, SEM, viscosity, density, conductivity, surface tension etc was carry out on the synthesized DESs for various structure disruption that made the biomass available for hydrolysis and bioconversion. Surface tension, polarity, acidity or alkalinity, conductivity, density, refractive index, solubility, and other properties including viscosity, melting point, freezing point, boiling point, and others could be affected by the structure of HBD and the molar ratio of HBAs / HBDs during DES pretreatment of lignocellulosic biomass (Elhamarnah *et al.*, 2020, Jablonsky *et al.*, 2019). In terms of viscosity, it was observed that high viscosity may impede the fractionation of biomass which may be attributed to DES3 having the lowest percentage of lignin removal since DES3 have the highest viscosity. This was reported by Smink *et al.*, 2020. Density, one of the key physical characteristics of solvents, can provide information on the solution's activity and molecular mobility (Hakkinen and Abbot, 2019).

Conductivity describe the ease with which ions flow in a substance (Ren *et al.*, 2016).In relation to viscosity, Xu *et al.*,2020 reported that it might be easier for DES with reduced density and viscosity to saturate the biomass framework, which was the trend observed in the current work. Figure 6a and 6b show the percentage of holocellulose available for possible conversion into biofuels and valuable chemicals such as lactic acid, furfural**.**

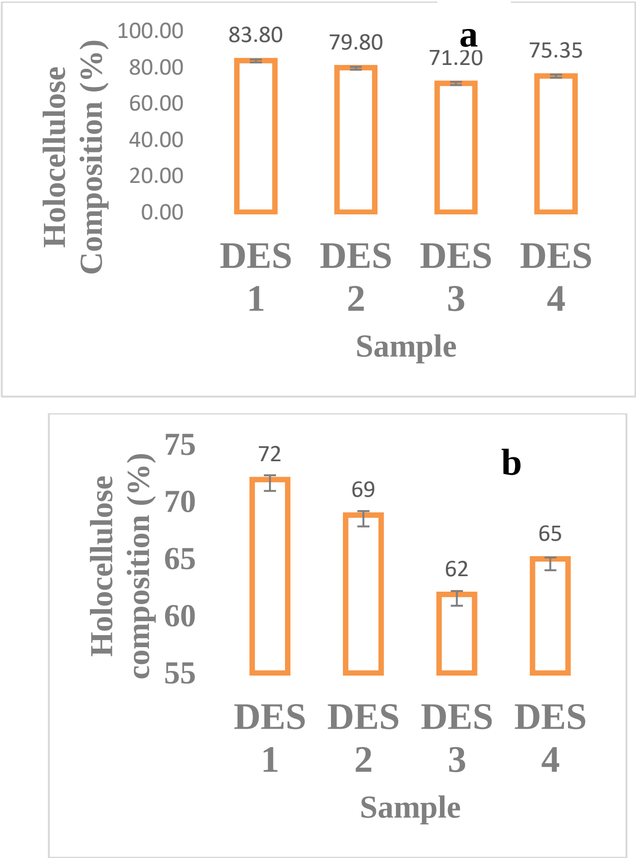


Figure 6: Effect of pretreatment on Holocellulose composition of **(a)** sugarcane baggasse and **(b)** corn cob using the synthesized DESs.

After removal of lignin, the percentages of cellulose and hemicellulose remaining was also determined. DES1 has the highest holocellulose (83.80%) and (72 %) for sugarcane bagasse and corn cob respectively as shown 7. The effect of holocellulose contents on sugarcane bagasse and corn cob after pretreatment increased for all the DESs tested in this work. This is because, hemicellulose in bagasse and corn cob was successfully dissolved by DESs, the -O-4′ ether link between lignin molecules was broken, and the crystallinity of cellulose was also greatly increased. Furthermore, cellulose's hydroxyl groups (-OH) easily form monoesters or cross-linked diesters when carboxyl groups (-COOH) in DESs, particularly DES2, react with them. This prevents cellulose from dissolving during pretreatment. The values obtained is similar to that reported by Ameri, 2017 with 80% success using switch grass.

3.7 FT-IR Spectra of the Untreated and Treated Sugarcane Bagasse and Corn Cob Using the Synthesized DES1 –DES4:

During FT-IR analysis of the untreated and treated sugarcane bagasse and corn cob using the synthesized DES1 –DES4, they undergo several changes. Thus, a comparison of FT-IR spectra of untreated with treated samples was done as shown in Figure 7a and 7b respectively.

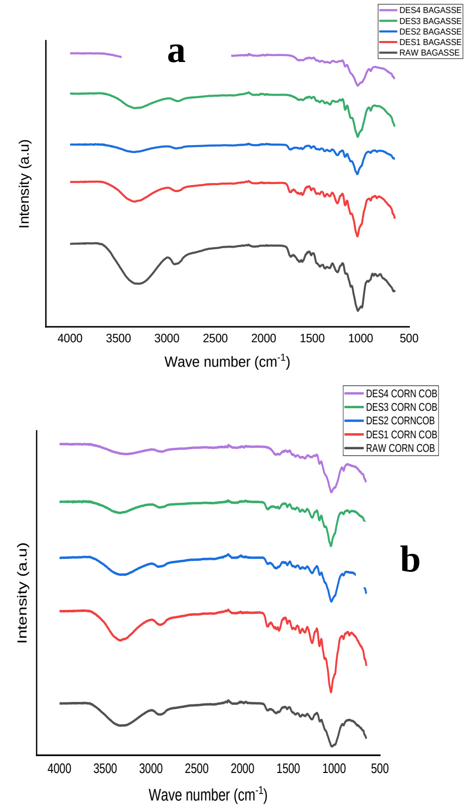


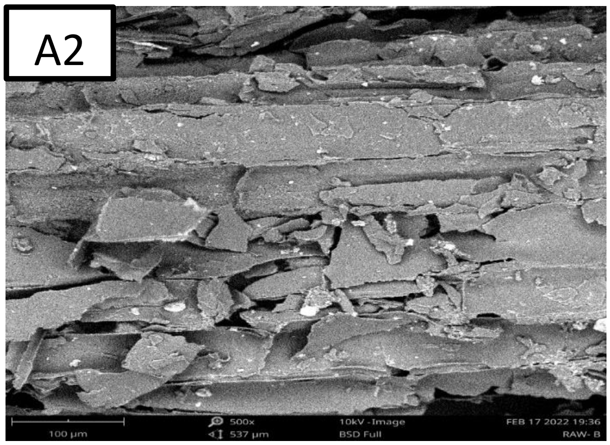
Figure 7: Overlaid of FT-IR spectra for the Untreated and Treated **(a)** Sugarcane bagasse and **(b)** Corn cob.

As depicted in Figure 7a, the (band widening) at 2955- 3651 cm^{-1} for the raw sugarcane bagasse were attributed to O-H stretching in the polysaccharides of sugarcane bagasse. This absorption peak shifted to a lower band of 3000-3362 cm^{-1} after pretreatment, an indication that DESs used as pretreatment solvent have broken the intermolecular H-bonds in the cellulose due to the content of free hydroxyl group that increased after pretreatment. Also, C= H stretching Vibrational peak shows the aromatic ring of lignin decreased from 2920cm^{-1} to 2885cm^{-1}, which indicates that the lignin is removed during pretreatment while the absorption peaks at 1500 to 1600 cm^{-1} almost got disappear after pretreatment, an indication of breakdown of ether links between lignin and hemicellulose. However, C-O stretching vibration at 1048 cm^{-1}coupled with C-O bending of the C-O group of alcohols and aliphatic ester of carbohydrates and C-O-C stretching at 897 cm^{-1} of ß-(1,4)-glycosidic linkages in cellulose remained unchanged after pretreatment signifying the presence of cellulose for bio conversion

Similarly, the FT-IR analysis for raw and treated corn cob (Figure 7b) review the existence of this functional group in untreated and some disappear or decreased due to the effect of pretreatment in the treated corn cob. For example, the O-H group intensity at 3433 cm^{-1} in the Cellulose shifted to lower wavelength of 3355 cm^{-1} confirming that DESs broke the hydrogen bonds between the lignin and hemicelluose to some extent. The effect of pretreatment was further confirmed by the disappearance of C-C vibrational intensity peak at 1755 cm^{-1} in the treated corn cob. This peak's intensity in corncob decreased after DES2 treatment and then disappeared after DES1 treatment.. This is due to breakage of linkage between hemicellulose and lignin. Also, C-H bending peak at 834 cm^{-1} in phenol (syringyl content in lignin) decreased after pretreatment to a peak of 582 cm^{-1} thus, indicating delignification.

3.8 Scanning Electron Microscopy (SEM) Image of the Untreated and Treated Sugarcane bagasse and Corn cob

Plate 1 shows the SEM images of treated and untreated sugarcane bagasse and corn cob A1 (untreated corn cob), A2 (treated corn cob), B1 (untreated sugarcane bagasse) and B2 (treated sugarcane bagasse).The SEM analysis was done using DES1 being that it demonstrated higher pretreatment efficiency compared to other DESs investigated in this work.



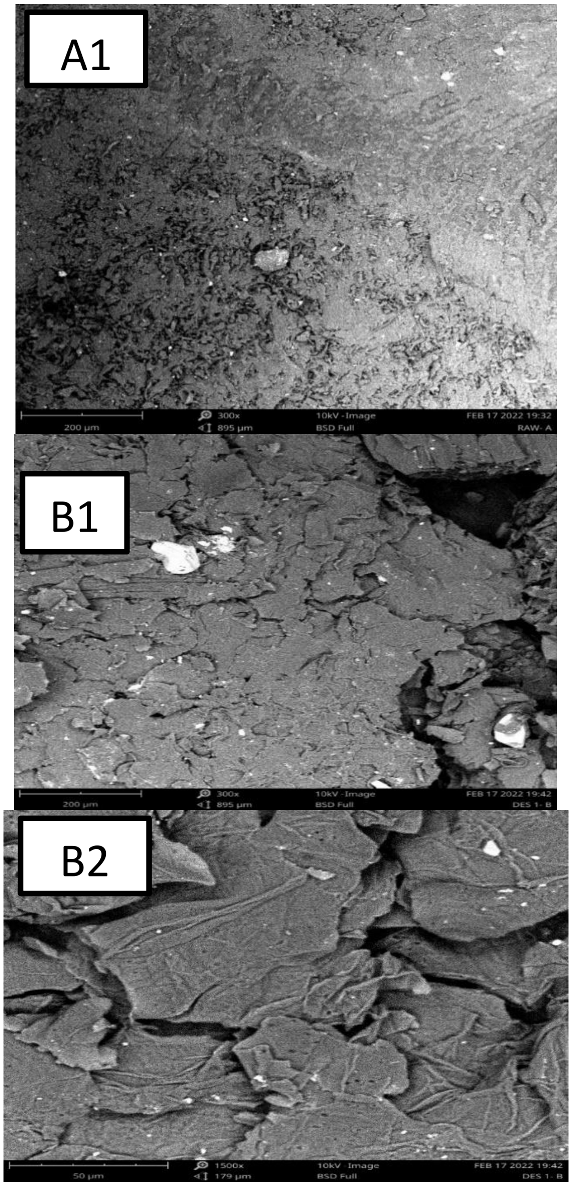


Plate 1: SEM images of treated and untreated sugarcane bagasse and corn cob A1 (untreated Corn cob), A2 (treated Corn cob), B1 (untreated Sugarcane bagasse) and B2 (treated Sugarcane bagasse).

AS shown in plate 1, the SEM images of untreated sample (A1 and B1) indicates a rigid and order symmetrical structure. The treated samples show a loose surface with adjusted particles. There was a disruption in the treated bagasse and corn cob fibers as a result of pretreatment and changes in surfaces area due to lignin breakage, cellulose swelling thereby causing reduction in crystallinity of the treated samples (A2 and B2) respectively. The treated sugarcane bagasse and corn cob fiber surfaces had numerous cracks and pores, and after pretreatment, particularly with DES1, on the surface, there were some holes, and the fiber surface was broken an indication of pretreatment. Although, the fibers may seem to be aggregated, they are very brittle and shown no symmetry as a result of synergistic effect of pretreatment which altered the lignin and expose the cellulose structure. The fiber porosity may be increased due to removal of waxy compounds such as lignin. The treated bagasse show some crack in the treated fiber which confirmed the disruption of lignin with some tiny holes. This observation was also confirmed by report of Chen *et al.*, 2018.

4. Conclusion

In this work, DES1 Choline chloride /Urea (ChCl: U), DES2 Choline chloride /Oxalic acid (ChCl: OA), DES3 Choline chloride /Glycerol (ChCl: G), and DES4 Choline chloride /Ethylene Glycol (ChCl: EG) were synthesized, characterized, and used as treatment solvents for corn cob and, respectively. The effect of viscosity, pH, conductivity, surface tension, density, refractive index, and moisture content were also determined on their abilities for use as potential pretreatment solvent. The different physicochemical properties values of the synthesized DESs resulted in variations in how pretreatment affects bagasse and corn cob. Viscosity generally decreases as temperature increases for all the synthesized with DES 3 having the highest viscosity of 499 CPs. The order of increasing density of the synthesized DESs is the order EG < Oxalic acid < urea < glycerol. FTIR results of the synthesized DESs shows a hydrogen bond interaction and a shift and vibrational peaks recorded in the DESs confirm that DESs was successfully formed. Overall, the experimental findings determined in this study agrees closely with data from the literature, thus the synthesized DESs are consider green and can serve as an alternatives to conventional organic solvents. DES1 and DES2 performed better interms of pretreatment of sugarcane baggasse with percentage removal of lignin to be 65 % and 63% respectively, followed by DES4 with 58 % and DES3 having the least percent (55%) among the synthesized DES1 – DES4. There was a substantial decreased in lignin percentage reduction of 83.26 % and 72 % and a corresponding percentage increased in holocellulose composition by 11.3 % and 4.03% for sugarcane bagasse and corn cob after pretreatment respectively. Furthermore, the DESs tested in this study improved the pretreatment effectiveness of the DESs system, demonstrating their suitability as pretreatment reagents for corn cob and sugarcane bagasse. As a result of its attractive and environmentally friendly properties, it can be utilized as a possible substitute solvent to traditional organic solvents in industry.

References

Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. (2004). Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. Journal of the American Chemical Society, 126 (29), 9142-9147.

Alhafiz, H. A.*, Isa, M. T., Sallau, A. B. and Ameh, A. O. (2020) Delignification Of Corn Cob for the Synthesis of Lactic Acid Journal of the Nigerian Society of Chemical Engineers, 35(1), 2020

Alvarez-Vasco, C.; Ma, R.; Quintero, M.; Guo, M.; Geleynse, S.; Ramasamy, K.K.; Wolcott, M.; Zhang, X. (2018).Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): A source of lignin for valorization. Green Chem, 18, 5133–5141. https://doi.org/10.1039/C6GC01007E

Ameri Maryam al (2017).Deep eutectic solvent pretreatment for enhancing biochemical conversion of switchgrass a thesis presented to the Faculty of the Graduate School at the University of Missouri-Columbia In Partial Fulfillment of the Requirements for the Degree Master of Science

Arkawazi, A.F., A.A. Barzinjy and S.M. Hamad (2020). Physical, thermal and structural properties of 1 choline chloride: 2 urea based ionic liquids. Singapore J. Sci. Res., 10: 417-424.

Ayşe Ezgi Ünlü and Serpil Takaç (2020): Use of Deep Eutectic Solvents in the Treatment of Agro-Industrial Lignocellulosic Wastes DOI: http://dx.doi.org/10.5772/intechopen.92747

Azhar Y M. Al-Murshedi1, Hasan F Alesary and Rajaa Al-Hadrawi1 (2019).Thermophysical properties in deep eutectic solvents with/without water Journal of Physical.: Conference. Series. 1294 052041

Castro Vania I. B., Francisca Mano, Rui L. Reis, Alexandre Paiva, and Ana Rita C. Duarte (2018). Synthesis and Physical and Thermodynamic Properties of Lactic Acid and Malic Acid-Based Natural Deep Eutectic Solvents J. Chem. Eng. Data DOI: 10.1021/acs.jced.7b01037

Chen, Z., Wan, C.,(2017). Ultrafast Fractionation of Lignocellulosic Biomass by Microwave assisted Deep Eutectic Solvent Pretreatment, Bioresource Technology (2017), doi: https://doi.org/10.1016/j.biortech.2017.11.066

Chen, Z.; Bai, X.; Lusi, A.; Wan, C. (2018). High-solid lignocellulose processing enabled by natural deep eutectic solvent for lignin extraction and industrially relevant production of renewable chemicals. ACS Sustain. Chem. Eng. 6, 12205–12216

Crespo Emanuel A., Jo~ao M.L. Costa , Andr_e M. Palma , Belinda Soares , M. Carmen Martín , Jos_e J. Segovia , Pedro J. Carvalho , Jo~ao A.P. Coutinho (2019). Thermodynamic characterization of deep eutectic solvents at high Pressures. journal homepage: www.elsevier.com/locate/fluid Fluid Phase Equilibria 500 (2019) 112249

Dai Yuntao, Jaap van Spronsen, Geert-Jan Witkamp, Robert Verpoorte, Young Hae Choi,(2013). Natural deep eutectic solvents as new potential media for green technology Analytical Chemical Acta 766 (2013) 61– 68

Degam Ganesh (2017) Deep Eutectic Solvents Synthesis, Characterization and Applications in Pretreatment of Lignocellulosic Biomass http://openprairie.sdstate.edu/etd

Dimitrios, K. S., and Ioanna, S. S. (2015). Organosolv Pretreatment as a Major Step of Lignocellulosic Biomass Refining. Proceedings of Biorefinery I: Chemicals and Materials from Thermo-Chemical Biomass Conversion and Related Processes.

https://dc.engconfintl.org/cgi/viewcontent.cgi?article=1013&context=biorefinery_I

Elhamarnah, Y., Qiblawey, H., Nasser, M. S., & Benamor, A. (2020). Thermo-rheological characterization of Malic Acid based Natural Deep Eutectic Solvents. The Science of the total environment, 708, 134848. https://doi.org/10.1016/j.scitotenv.2019.134848

El-hoshoudy, A. N., Soliman, F. S., Mansour, E. M., Zaki, T., &Desouky, S. M. (2019). Experimental and theoretical investigation of quaternary ammonium-based deep eutectic solvent for secondary water flooding. Journal of Molecular Liquids, 294, 111621. https://doi.org/10.1016/j.molliq.2019.111621

Francisco, A. van den Bruinhorst, M.C. Kroon,(2012). New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing, Green Chem. 14 (2012) 2153–2157. doi:10.1039/C2GC35660K

Jablonsky, M., Haz, A. & Majova, V. (2019). Assessing the opportunities for applying deep eutectic solvents for fractionation of beech wood and wheat straw. Cellulose 26, 7675–7684 https://doi.org/10.1007/s10570-019-02629-0

Julie, B., Bikash, K. N., Ritika, S., Sachin, K., Ramesh, C. D., Deben, C., B., & Eeshan, K. (2018). Recent Trends in the Pretreatment of Lignocellulosic Biomass for Value-Added Products. Front. Energy Res. 6:141. doi: 10.3389/fenrg.2018.00141. https://www.frontiersin.org/articles/10.3389/fenrg.2018.00141/full

Karolina, K., Piotr, R., Iwona, H., Rafał, Ł., Marta, G., & Marian, K. (2018). Pretreatment of Lignocellulosic Materials as Substrates for Fermentation Processes. Molecules. doi:10.3390/molecules23112937. https://www.mdpi.com/1420-3049/23/11/2937/pdf

Kim Kwang Ho, Tanmoy Dutta, Jian Sun, Blake Simmons and Seema Singh (2018). Biomass pretreatment using deep eutectic solvents from lignin derived phenols Green Chem., 2018, 20, 809–815 DOI: 10.1039/c7gc03029k.

López-Salas .N, E.O. Jardim, A. Silvestre-Albero, M.C. Gutiérrez, M.L. Ferrer, F. Rodríguez- Reinoso, J. Silvestre-Albero, F. Del Monte, Use of eutectic mixtures for preparation of monolithic carbons with CO2-adsorption and gas-separation capabilities, Langmuir. 30 (2014) 12220–12228. doi:10.1021/la5034146.

Lu Q, W. Liu, L. Yang, Y. Zu, B. Zu, M. Zhu, Y. Zhang, X. Zhang, R. Zhang, Z. Sun, J. Huang, X. Zhang, W. Li, (2012) Investigation of the effects of different organosolv pulping methods on antioxidant capacity and extraction efficiency of lignin, Food Chem. 131 (2012) 313–317. doi:10.1016/j.foodchem.2011.07.116.

Mirza N.R., N.J. Nicholas, Y. Wu, K.A. Mumford, S.E. Kentish, G.W. Stevens, Experiments and Thermodynamic Modeling of the Solubility of Carbon Dioxide in Three Different Deep Eutectic Solvents (DESs), J. Chem. Eng. Data. 60 (2015) 3246–3252. doi:10.1021/acs.jced.5b00492.

Moura.L, T. Moufawad, M. Ferreira, H. Bricout, S. Tilloy, E. Monflier, M.F. Costa Gomes, D. Landy, S. Fourmentin, Deep eutectic solvents as green absorbents of volatile organic pollutants, Environ. Chem. Lett. 15 (2017) 747–753. doi:10.1007/s10311-017-0654-y.

Muhammad, N.A., Irfana, I., Fatima, R., Ahmet, K., & Meisan T. (2019). Different pretreatment methods of lignocellulosic biomass for us in biofuel production. Intechopen. Doi:http://dx.doi.org/10.5772/intechopen.84995.https://www.intechopen.com/books/biomass-for-bioenergy-recent-trends-and-future-challenges/different-pretreatment-methods-of-lignocellulosic-biomass-for-use-in-biofuel-production

Oguche John Enemona, Emeniru Daniel. C, Sorgbara Franklin Lekara, Ameh Alewo Opuada & Adubazi Momohjimoh Onimisi (2022). Emerging applications of deep eutectic solvents in applied sciences; a review. African Scholars Journal of Science Innovation & Tech. Research (JSITR-9) VOL. 24 NO. 9 ISSN: 2878-1894, PP 39-52

Payam Kalhor and Khashayar Ghandi (2019). Deep Eutectic Solvents for Pretreatment, Extraction, and Catalysis of Biomass and Food Waste A Review doi:10.3390/molecules24224012 http//www.mpdci.com.

Rajeev, R., & Amit, K.J. (2016). A comprehensive review on pretreatment strategy for lignocellulosic food industry waste: challenges and opportunities. Bioresource Technology https://www.biofueljournal.com/article_13498_bdaeb53aa8eb3d3798523441a6ca9018.pdf

Ren, H.W., Chen, C.M., Wang, Q.H., Zhao, D.S., Guo, S.H., (2016). The properties of choline chloride-based deep eutectic solvents and their performance in the dissolution of cellulose. BioResources 11 (2), 5435–5451

Rezendel Camila Alves, Marisa Aparecida de Lima, Priscila Maziero, Eduardo Ribeiro deAzevedo, Wanius Garcia and Igor Polikarpov (2014) Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility Biotechnology for Biofuels 2011, 4:54 http://www.biotechnologyforbiofuels.com/content/4/1/54

Smink Dion, Sascha R.A. Kersten, Boelo Schuur (2020).Process development for biomass delignification using deep eutectic solvents. Conceptual design supported by experiments Chemical Engineering Research and Design 1 6 4 86–101 https://doi.org/10.1016/j.cherd.2020.09.018

Song, K., Zhu, X., Zhu, W., & Li, X. (2019). Preparation and characterization of cellulose nanocrystal extracted from Calotropis procera biomass. Bioresources and Bioprocessing, 6(1), 45. Doi: 10.1186/s40643-019-0279-

Van Osch D.J.G.P., L.J.B.M. Kollau, A. Van Den Bruinhorst, S. Asikainen, M.A.A. Rocha, M.C. Kroon,(2017). Ionic liquids and deep eutectic solvents for lignocellulosic biomass fractionation, Phys. Chem. Chem. Phys. 19 (2017) 2636–2665. doi:10.1039/c6cp07499e.

Xia, Q.; Liu, Y.; Meng, J.; Cheng, W.; Chen, W.; Liu, S.; Liu, Y.; Li, J.; Yu, H. (2018). Multiple hydrogen bond coordination in three-constituent deep eutectic solvents enhances lignin fractionation from biomass. Green Chem., 20, 2711–2721 https://doi.org/10.1039/C8GC00900G.

Zhang Heng, Jinyan Lang , Ping Lan , Hongyan Yang , Junliang Lu and Zhe Wang (2020). Study on the Dissolution Mechanism of Cellulose by ChCl-Based Deep Eutectic Solvents Materials 2020, 13, 278; doi:10.3390/ma13020278 www.mdpi.com/journal/materials

Zhang Q, K. De Oliveira Vigier, S. Royer, F. Jérôme (2012). Deep eutectic solvents: syntheses, properties and applications, Chem. Soc. Rev. 41 (2012) 7108–7146. doi:10.1039/C2CS35178A.

Zhang, Z., Xie, Y., He, X., Li, X., Hu, J., & Ruan, Z. (2016). Comparison of high-titer lactic acid fermentation from NaOH- and NH 3 -H 2 O 2 -pretreated corncob by Bacillus coagulans using simultaneous saccharification and fermentation. Nature Publishing Group, (April), 1–10. https://doi.org/10.1038/srep37245