**Biomass Utilization Using Carbohydrate Derived Ionic Liquids.**

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**Abstract**

For over a decade, carbohydrate based ionic liquids (CHILs) are being extensively researched as natural substitutes for traditional ionic liquids. Carbohydrate based ionic liquids are characterized by lower toxicity or high biodegradability, less impact on environment during their synthesis and for their varied applications. These have emerged as an alternate green solvent to VOCs to develop sustainable and eco-friendlier techniques. The present chapter discloses the published papers involving the use of carbohydrate-based ILs for biomass utilization.

**Keywords:** [Carbohydrate](https://www.mdpi.com/search?q=carbohydrate); less toxic; sugar; ionic liquid; biomass; bio-ILs; [biodegradable](https://www.mdpi.com/search?q=biodegradable).

**Introduction**

Excess utilization of conventional fossil fuels along with its adverse effect on the environment led to the emergence of sustainable methodology; ionic liquids (ILs) [1] have remarkably added towards these sustainable developments as they are made of cations (organic) and anions (organic or inorganic), have low vapor pressure, are thermally stable, and non flammable. Due to these properties, they were classified as “green” solvents, and they served as an alternative to the conventional solvents [[2](https://www.mdpi.com/1420-3049/25/14/3285#B2-molecules-25-03285), [3](https://www.mdpi.com/1420-3049/25/14/3285#B3-molecules-25-03285)]. Gabriel and Weiner in 1888 [4] were the first to report ILs. In 1914, the first room temperature IL (RTIL) was synthesized by Walden [5]. The scope of research on ionic liquids and their applications increased further after the reports on ILs tetrafluoroborate and hexafluorophosphate based on imidazolium in 1992 by Wilkes and Zaworotko [6]. Important applications of ILs involves their usage as solvents, additives in synthesis [7-9], cellulose processing [10-11], their usage as electrolytes in batteries and electrochemical synthesis [12-13], for extraction [14-15] etc. However, the inclination towards ILs decreased since reports came regarding the environmental and economic problems during their production and use. Ionic liquids are highy chemically stable and are highly soluble in water, so problems related to their liberation in the environment, where they get accumulated and remain for a longer period of time, led to their further investigations [[16-19](https://www.mdpi.com/1420-3049/25/14/3285#B4-molecules-25-03285)]. But, in the last few decades, Bio Ionic Liquids (Bio-ILs) have turn out to be an alternate green solvent to develop sustainable processes [[20](https://www.mdpi.com/2073-4352/12/12/1776#B6-crystals-12-01776)].

Naturally occuring compounds like carboxylic acids, amino acids, carbohydrates, fatty acids or choline can be used to prepare biomass-derived ILs [21-23]. Theese Bio-ILs exhibited less toxicity and better biocompatibility in comparison to the fossil fuel-derived counterparts and these are reviewed in great detail by Gomes et al. [24] and Hulsbosch et al. [25].

In 2007, carbohydrate based ionic liquids (CHILs) emerged as a category of ionic liquids and from then onwards many progresses have been done, they attracted the expanding organic community and research scientists. Carbohydrates forms a new class of bio-renewable compounds which can be used for facile synthesis of bio-ILs, as they are abundant, renewable and environmental friendly, and are great candidates toward novel applications. The availability of many OH groups on carbohydrates resulted in decreasing the toxicity of the resultant CHILs, promoting carbhydrates as highly potent functionalization agents in terms of “green chemistry” [21]. Apart from that it is known that carbohydrates are intrinsically chiral, promoting their use for the preparation of varied functional materials. Being rich in versatile features like [hydrogen bond](https://encyclopedia.pub/entry/3016) structure, being chiral, with good biodegradability, carbohydrate-based ILs finds a number of applications which includes catalysis [26-30], as solvents [31-32], in synthesis [33] and as herbicides [34].

**Biomass Utilization**

Biomass is natural, renewable organic substance which is obtained from plants and animals [35].   Using various processes, biomass can be easily converted to liquid and gaseous fuels or burned directly to produce heat. Renewable energy production from biomass will definitely help to reduce the world's requirement for fossil fuel.There is emergence of Ionic liquids as novel solvent system and dissolution media for processing biomass to value added products [36-39]. Lignocellulosic biomass being produced through photosynthesis is the most available renewable resources on our globe. Numerous research have been done in the utilization of raw materials from lignocellulosic biomass for sustainable energy production, chemicals and materials for sustainable development [40-41]. Lignocellulosic biomass mostly consists of hemicellulose, cellulose and lignin. Cellulose and hemicellulose are polymers of sugars.

As sugars are easily available, cheaper, renewable, and eco-friendly, much progress has been made in terms of the use of sugars/carbohydrates. Javed et al. [32] used *N*,*N*-diethyl-*N*,*N*-dimethylammonium gluconate for extraction of cellulose from oil palm lignocellulosic biomass. *N*,*N*-diethyl-*N*,*N*-dimethylammonium gluconate can be easily synthesized by gluconic acid mediated neutralization of diethyl dimethyl ammonium hydroxide. Within 30 minutes at a temperature of 25 °C, 52% wt. of cellulose was extracted from the crude biomass, without any pre-treatment on using this sugar-derived IL. The family of carbohydrate-derived IL has flurished very fast from 2003 onwards when Handy et al. [42] synthesized imidazolium IL involving fructose, for the first time, sugars were used as a renewable starting material for the synthesis of ILs. In 2004, the first carbohydrate-derived IL was obtained, where d-glucopyranoside was converted into the corresponding cation [43]. In continuation of these reports, a variety of ILs came up on carbohydrates and their derivatives like glucose, isomannide, xylose [[44-51](https://www.mdpi.com/1420-3049/25/14/3285#B8-molecules-25-03285)].

Hulsbosch group [25] in their perspective, report the syntheses, applications and limitations of bio-ionic liquids prepared from lignin, amino acids, carbohydrates, and other renewable sources. Their group threw lights on the application of these ionic liquids in processing of lignocellulose, as a solvent, organocatalyst and as medium for metal extraction.

Deng et al. [52a] in their study used levulinic acid-derived protic ionic liquids (PILs) [**1**, **2**] (Fig. **1**) as solvents for dissolution of wool keratin fiber and also dissolution of wool keratin and cellulose. Levulinic acid (Lev), is a bio-based platform chemical obtained from carbohydrates [52b]. The solubility was due to keto–enol tautomerism of the ketone group in the levulinate anion, which showed hydrogen bonding forming tendency with cellulose and wool keratin. The properties of Cellulose/wool keratin solution were studied systematically, proving that the viscosities of cellulose/wool keratin solution were highly due to the mass ratio of cellulose to wool keratin, mass concentration, and test temperature. Characterization for the cellulose/wool keratin composite membranes was done by XRD, FTIR, thermo gravimetric analysis and scanning electron microscopy. The cellulose and wool keratin showed high compatibility with the composited membranes with tensile strength (up to 60 Mpa) and an elongation at a break of up to 6%. Apart from that, the prepared membranes being thermally stable have excellent oxygen barrier performance.



**Figure 1**. Levulinic acid-based protic ionic liquids.

Chen and coworkers [53] used levulinic acid (Lev) with a series of organic superbases for the synthesis of protic ILs **3** (PILs) (Fig. **2**). They came up with greener dissolution pretreatment method for increased enzymatic hydrolysis, that can be beneficial in the synthesis of novel solvents for biomass dissolution. Solubility of up to 10 wt % was obtained towards lignocellulose based on corn stover at 140 °C in 40 mins using the PILs. Significant changes in the composition and physical–chemical structures was noted due to dissolution and regeneration of corn stover. These observed changes further led to significantly increased enzymatic hydrolysis of the pretreated sample and yields of 0.8 and 0.49 g/g in a time span of 48 h were obtained for reducing sugar and glucose under optimal conditions. To gain an understanding of the dissolution activation mechanism using various characterization methods, the scientists evaluated the changes in the composition and physicochemical changes in the lignocellulose, during the dissolution and regeneration process, 44.3% of lignin was fractionated and the structure of the fractionated lignin was further characterized and confirmed.



**Figure 2**. DBNH][Lev] PILs

Becherini et al. [54] synthesized two novel levulinate-based protic ionic liquids (Lev PILs) by neutralization reaction between levulinic acid (LA) and amidine superbases (either DBU or DBN). The synthesized PILs were characterized by using various spectroscopic studies and were further studied as cellulose dissolution media. The prepared Bio-ILs demonstrated a dissolving ability (weightcellulose/weightPIL) comparable to the acetate-based PILs. Lev PILs are made up of a larger renewable anion (levulinate vs. acetate). An application of the Lev PILs, namely the levulination of cellulose, was also investigated. The effect of variation in reaction conditions (i.e. temperature, amount of anhydride, amount of co-solvent) on the output of the reaction and on the functionalization degree (up to 1.87) were further studied. γ-Valerolactone, a green solvent prepared from LA, was found as an effective substitute to DMSO when used as co-solvent, and satisfactory functionalization degrees were obtained.

Yue and coworkers [55] synthesized protic ionic liquids (PILs) by solvent free neutralization of 1,5-diazabicyclo [4.3.0]-5-nonene (DBN) with levulinic acid (Lev) derived from biomass, these ILs were found to show good solubility towards silk fibroin under mild reaction conditions. The simultaneous dissolution of silk fibroin and cellulose was also studied, and the interaction was calculated by 13C NMR spectroscopy, they found that the hydrogen bonding forming tendency of [DBNH][Lev] PILs partially arose due to the keto–enol tautomerism of levulinate and helped in the solubility of cellulose and silk fibroin. The researchers carried out dynamic light scattering (DLS) experiments and studied the interaction between cellulose and silk fibroin, they further prepared a number of composite membranes by sol–gel transition making use of ethanol as solvent. Spectroscopic techniques like FTIR, XRD, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and tensile tests were also carried out. They concluded that composited membranes (C50S50) showed best mechanical properties, tensile strength (50 MPa) and oxygen permeability (0.0055 cm3 μm) (m2 day atm)−1, the composited fibre (C80S20) turned up with tensile strength (152 MPa) and an elongation at break of up to 12.8%.

Mezzetta et al. [56] came up with levulinic acid-based imidazolium, ammonium, and phosphonium ionic liquids (ILs) and further characterized them by NMR spectroscopy, FT-IR spectroscopy, TGA, and viscosity measurements. These ILs displayed magnificient dissolution tendency for parent polysaccharide (cellulose). Particularly [EMIM][Lev] dissolved 29 wt% cellulose at 100 °C, which increases under reduced pressure to 38 wt%. Variations in the reaction conditions, which prevent potential side reactions of the imidazolium cation, were also done. The ecotoxicity studies of the prepared ILs and the earlier synthesized protic levulinate ILs was also done on the model organisms.

He group [57] used Levulinic acid for the synthesis of protic ionic liquids for the pretreatment dissolution of lignocellulosic and cellulose biomass for enhancement in [enzymatic hydrolysis](https://www.sciencedirect.com/topics/chemical-engineering/enzymatic-hydrolysis). The DBN (1,5-diaza-bicyclo[4.3.0]non-5-ene) based protic ionic liquids demonstrated highest exhibition at 100 °C in only 1 h, there is 94% yield of glucose. The [DBNH][Lev] protic ionic liquid solvents system can be recycled and reused. The keto–enol tautomerism in the levulinate anion may be responsible for the better performance (Fig **3**).

**Figure 3**. Keto–enol tautomerism in the levulinate anion of [DBNH][Lev] protic ionic liquid.

Socha et al. [58] carried out the synthesis and further evaluation studies of an array of ILs from monomers of lignin and hemicellulose. Reductive amination of the aromatic aldehydes and further reaction with phosphoric acid resulted in three pure ILs in good yields. To compare these ILs to [C2mim][OAc], compositional analysis and yield of sugar from enzymatic hydrolysis of pretreated switchgrass was used. After biomass pretreatment, enzymatic saccharification with ILs, [FurEt2NH][H2PO4] and [*p*-AnisEt2NH][H2PO4] (Fig. **4**) resulted in 90% and 96% of glucose and 70% and 76% of xylose. [FurEt2NH][H2PO4] and [*p*-AnisEt2NH][H2PO4] ILs also showed the highest *β* values, highest basicity, best lignin removal ability. Sugar yields from switchgrass pretreated with these ILs were almost same to yields from switchgrass pretreated with [C2mim][OAc]. Glycome-profiling experiments indicated that the ILs, [FurEt2NH][H2PO4] and [*p*-AnisEt2NH][H2PO4] act on plant cell walls with mechanism different from that of [C2mim][OAc]. Their results showed the effective role of biomass-derived ILs in biomass pretreatment.



**Figure 4.** [FurEt2NH][H2PO4] **5**, [VanEt2NH][H2PO4] **6**, [*p*-AnisEt2NH][H2PO4] **7** and [C2mim][OAc] **8**

Biomass holds a great tendency for the generation of renewable energy and decrease emissions of greenhouse gas [59-65]. There is no doubt that use of biomass is a good alternative to meet energy and product demands along with reducing dependency on [fossil fuel](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/fossil-fuel)s.

**Conclusions**

Carbohydrate-derived ionic liquids (CHILs) are an upcoming category of ionic liquids. Similar to ionic liquids, they have melting points less than 100 °C, but, CHILs are particularly based on carbohydrates and posseess an entire carbohydrate unit. Carbohydrates holds a great potential as the future generation’s ILs, which have decreased toxicity, reduced impact on environment during their synthesis and in their applications. The present chapter aims to cover the recent progress in the applications of ionic liquids (ILs) based on carbohydrate for biomass utilization.

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