CHAPTER 2

LITERATURE REVIEW

The bibliographic survey was conducted to develop the understanding of the research work done in past 10 years on the physicochemical characterization of lignocellulosic biomass and the analytical technique used to assist the properties of biomass for biochemical or/and thermochemical conversion into biofuels. In the second section, the complete literature survey was conducted ILs processing of lignocellulose using imidazolium, cholinium based ionic liquid for the deconstruction of complex biomass cell wall structure for the production of bioethanol and their benefits over conventional pretreatment processes available.

2.1 LIGNOCELLULOSIC BIOMASS AND THEIR PHYSICOCHEMICAL CHARACTERISATION

Lignocellulosic biomass such as agricultural residues, forestry wastes etc. are the most abundant plant material available on earth and are non-competitive to the food-based material, i.e., starch and sucrose.[119] The sun's energy is stored in plants during photosynthesis in the form of carbohydrates, which can be used for the production of biofuel and can reduce the dependency on fossil fuels, mitigate the negative impact on climate change.[105] These lignocellulosic are the sustainable platform for the production of bio-based chemical and energy.[6]

Guha Samar et al. (2010)[120] mentioned that carbohydrates mainly consist of cellulose, hemicellulose, starch and produced by the plant during photosynthesis. Starch is the main constituent of rice, corn, grain, potato; however, lignocellulose consists of cellulose (35-45%), hemicellulose (15-25%) and lignin (15-25%). Both cellulose and starch are a polymer of glucose with same molecular formula but a different arrangement of the molecule. Starch contains D-glucose with 1-4-α (amylose) and 1-6-α-glycosidic bonds (amylopectin) linkage, whereas, cellulose mainly consist of 1-4-β-glycosidic bonds between two glucose units.

Cellulose is composed of glucose monomers linked via. Β-1-4-glycosidic linkage and exist in four polymeric crystalline form, i.e. cellulose I, II, III, IV.[121] Cellulose I and II are most extensively studied. X- ray study showed that cellulose I have two chain packing of cellulose Iα (triclinic) and Iβ (monoclinic).[122] Cellulose Iβ crystalline form is found in all higher plants, bacteria, fungi and algae systems.[123] In the crystalline form in cellulose fibrils, the pyranose rings are in chair conformation and glycosidic bonds are at an equatorial position relative to pyranose rings, with a C-O-C bond angle of 115-117°, which is in lowest energy state and are independent of chain length. Cellulose I comprise strong O3-H---O5 hydrogen bond (E>0.5 kcal/mol), O6 and O2 are involved in hydrogen bonding with H6' and H2 respectively. H6 forms a hydrogen bond between O6 and O5 of the same glucose residue as shown in Figure 2.1. The Figure 2.1 below arrangement of cellulosic chains in the crystalline register in cellulose I and II respectively. It is easy to see that the formation of intra and interchain hydrogen bond formation in the two crystalline forms. Although, cellulose I exist in two distinct crystalline forms cellulose I_{α} and cellulose I_{β}, depending upon the crystal packing, molecular conformation and extent of hydrogen bonding. Cellulose I_{β} predominantly found in all plants and are more stable due to inter/in molecular hydrogen bonding.

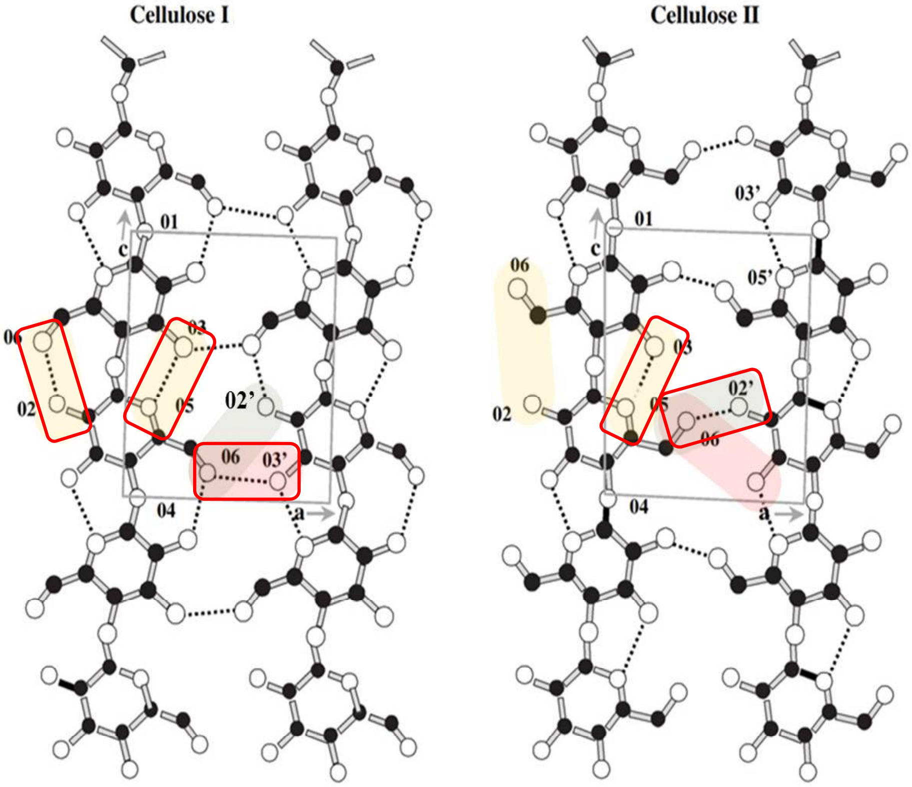


Figure 2.1 Intra/Intermolecular hydrogen bonding in cellulose I and cellulose II chains

Cellulose II has a monoclinic unit cell structure (with a dimension, i.e. α=7.93, β=9.18, γ=10.34 Å with the angle of 117.3°.[122] Cellulose I transform into cellulose II, which possess two intramolecular hydrogen bonds, i.e. O3-H---O5' and O6---H-O2' and interchain hydrogen bonds are along 020 planes of the unit cell, with antiparallel chain arrangement.[124] FT-IR showed that all OH groups are involved in inter/intramolecular hydrogen bonding. It was reported that native and regenerated cellulose structure is similar in many ways, each consisting of parallel array of hydrogen bonding.[121] Cellulose II is thermally more stable polymeric form, produced by mercerization or regeneration after ionic liquid pretreatment. The hydrogen bonding between the centre and corner chains contributes to the high stability of cellulose II as compared to cellulose

I.[125] Ionic liquid treatment of cellulose I help to disrupts these hydrogen bonding.

B. Yang et. al. (2011)[126] investigated that lignocellulosic biomass is a complex heterogeneous mixture and have high recalcitrance towards enzymatic hydrolysis. They showed that enzymatic saccharification involve the formation of polymeric sugars into monomeric sugars, which involves three different type of cellulases and their interactions are highly dependent on characteristics of cellulose in lignocellulosic biomass, hence advanced imaging techniques is helpful to understanding the structural changes before and after pretreatment and is also helpful in deep understanding of cellulose-enzyme interaction. Besides that, cellulose properties in native and pretreated biomass (e.g., size, structure, crystallinity, the degree of polymerization, porosity and specific surface area) were dominant for cellulase adsorption.

Similarly, M. Foston et al. (2012)[127] have shown that LCB is most available, abundant, complex, highly heterogeneous polymer cellulose, hemicellulose, lignin ash, protein, pectins, wax, ash etc. and their chemical composition and architect and arrangement significantly vary depending upon genotypic/ phenotypic, geographical location, climate condition and by environmental growth factors. Cellulose in bonded in a high crystalline matrix in association with hemicellulose and lignin via strong Intra/intermolecular hydrogen bonding, dipole-dipole interaction.[105] Van der Waal forces, covalent bonds etc. which makes biomass highly recalcitrance in nature. Hence, understanding understating the chemistry of basic component of biomass and their arrangement in plant cell wall helps to choose the best suitable method of biomass pretreatment for any bioconversion process.[128-129]

S. Sasmal et al. (2012)[130] conducted a physicochemical characterization study using bonbogori (Ziziphus rugosa)using, moj (Albizia lucida) and nut husk (Areca catheu), which are abundantly available in India (North region) using XRD, TGA, FT-IR, Raman spectroscopy and CHNS/O analysis for proximate and ultimate analysis. They have found areca nut husk fibre have highest crystallinity (63.84%) followed by moj (46.43%) and bonbogori (42.46%). They also determined the higher heating values, which represent the total energy content of any biomass and are helpful for selection of any method for biofuel conversion and were found within the ranged from 17 to 22 MJ/kg and hence tried to find out the reason for biomass recalcitrance.

Oh Sang et al. (2005)[131] have reported that in cellulose chain, for every glucose, three free OH groups are present, which are involved in intra and intermolecular hydrogen bonds between same chains and neighbouring chains, hence, limits its solubilization in conventional organic solvents. The showed that treatment of cellulose with alkali (~10 wt.%), resulted in cellulose transformation. To confirm that have analysed the alkali and CO_2 treated cellulose by FT-IR and XRD. They reported that after treatment cellulose I was converted into cellulose II and confirmed by a shift in FT-IR peak and XRD. The band in FT-IR at 3352 cm^{-1} correspond to OH stretching vibrations, which were dissociated in three peaks in cellulose I, i.e. 3585, 3349, 3195 cm^{-1}) and four bands in cellulose II, which were related to hydrogen bonded OH-group and an intramolecular hydrogen bond at 2-OH---O-6, intramolecular hydrogen bond of 3-OH---O-5 and intermolecular hydrogen bond of 6-O---HO-3' respectively. After cellulose II conversion, a new band appeared around 3115 cm^{-1} corresponding to intermolecular hydrogen bond oh 2-OH---O-2' and intermolecular hydrogen bond of 6-OH---O-2'. They showed that cellulose crystallinity could be calculated using absorbance ratios such as $A_{1431,1419}/A_{897/894}$ and $A_{1263}/A_{1202,1200}$ cm^{-1}. Hydrogen bond intensity (HBI) crystallinity was measured by $A_{4000\text{-}2995}/A_{1337}$ cm^{-1} and A_{1430}/A_{900} cm^{-1}. They have mentioned that in cellulose, I, the bands around 3455-3410, 3375-3450 and 3310-3230 cm^{-1}, corresponds to intramolecular hydrogen bonds (2-OH---O-6 & 3-OH---O-5) and intermolecular hydrogen bonds (6-OH---O-3').[132] They reported that after cellulose II transformation, maximum absorbance of hydrogen bonded stretching was shifted to higher wave number. A new hydrogen bond of 2-OH---O-2' and 6-OH---O2' was formed in cellulose II, along 110 planes. With that, they also reported that band at 1431, 1319 cm^{-1} were assigned for symmetric CH_2 bending and CH_2 wagging.[133-134] Schwanninger, M. et al. (2004)[135] have reported that 2901, 1162, 897 cm^{-1} correspond to C-H stretching and C-O-C stretching for β-1-4-glycosidic linkage.

Colm D. Everard et al. (2012)[136] conducted a spectroscopic study for prediction of gross calorific value for *Miscanthus* using PLS model using visible and NIR spectroscopy and the predicted gross calorific values from PLC model for *Miscanthus* and SRCW were in the range of 13.1–18.6 MJ kg^{-1}, with rms error of cross-validation (RMSECV) of 0.30 MJ kg^{-1} with (R^2) of 0.97 and also developed for *Miscanthus* in the range 13.1–18.3 MJ kg^{-1} (RMSECV, 0.28 MJ kg^{-1}; R^2, 0.96).

Y. Singh et al. (2012)[137] conducted a comprehensive study of characterization of lignocellulosic biomass available in North India for ultimate, proximate and chemical composition analysis, moisture, volatile matter, ash, fixed carbon, total solid, calorific value, X-ray diffraction (XRD thermogravimetric analysis (TGA). They have reported that moisture is an important parameter for energy content was found to be highest in *Typha angustifolia* (13.9%) and lowest in *Eragrostis airoides* (8.2%). High ash content was detrimental for any bioconversion process and the maximum was found in *Arundinella khasiana* (8.12%) and the minimum was in *Eragrostis airoides* (3.6%). TGA also confirms the presence of moisture by a peak below 120 °C indicating the loss of water molecules from the biomass. Cellulose being highly order and crystalline in nature have sharp degradation temperature between 350 to 500 °C. The high amount of carbon represents the high-energy content of biomass and maximum was found *Typha angustifolia* (52.8%) and the minimum was in *Eragrostis airoides* (41.0%). The FT-IR spectra helped to determine the functional group for cellulose and hemicellulose and maximum cellulose was found in *Eragrostis airoides* (43.17%) and minimum was in *Echinochloa stagnina* (24.90%) with a characteristic peak at 3450, 2860, 1668, 1175, 1097, 7872, 625 and 554 cm^{-1} etc. H. Ibrahim et. al. (2013)[138] have investigated the physicochemical properties of some torrefied woods, i.e mixture of hardwoods (oak and birch), eucalyptus, softwoods (pine, spruce) at two temperatures (270 ◦C & 290 ◦C) and two residence times (30 and 60 min). They investigated that in any solid biomass decrease in H/C ratios O/C ratios upon torrefaction is accompanied by loss of OH groups.

L. Burhenne et al. (2013)[139] reported a similar study to understand the pyrolysis behaviour of three biomass; wheat straw and rape straw with different composition in cellulose, hemicellulose and lignin fractions. They showed that lignin degrades above 300 °C with a slow decomposition rate, therefore the biomass with high lignin content needs more energy to decompose.[140] Herbaceous biomass, with higher glucan and xylan content, decomposed faster and produced a larger fraction of gaseous products than woody biomass with a higher lignin content compared with woody biomass.

J. Zhang et al. (2014)[125] analysed the lignocellulosic biomasses by thermogravimetry to understand the interactions between ILs and biomass cell wall components. Thermal decomposition profiles ILs treated (1-butyl-3-methylimidazolium acetate ([C_4mim][OAc], 50–130 °C for 6 h) samples such as Avicel (PH101), xylan from beech wood, alkaline lignin, switchgrass and corn stover were helpful to understand the T_{max} for each component of cellulose, hemicellulose and lignin. Thermogravimetry was also helpful to observe the cellulose I and cellulose II transformation after ionic liquid pretreatment. For example, high-temperature degradation of cellulose showed the cellulose II transformation, which is thermally more stable compared to cellulose II

They have correlated with crystallinity; the untreated cellulose (Avicel PH101) has a cellulose I structure with a crystallinity index (CrI) of 0.72 and pretreatment in [C_4mim][OAc] at different temperature of 50, 90 and 130 °C leads to two peaks on the thermograms for different crystalline form. Cellulose degradation occurs 277 °C for amorphous cellulose and 341 °C for cellulose I. Lignin being polyphenolic degrade over a wide of temperature range from (300–500 °C).

Jiafu Zhang et al. (2014)[141] demonstrated the X-Ray diffraction studies over [C_4mim][OAc] ionic liquid pretreated switchgrass, corn stover and rice husk for determination of cellulose crystallinity and structural transformation during ionic liquid pretreatment at 50 to 130 °C/6 h with a solid loading of 5 wt.%. They reported the crystallinity index of rice husk corn stover and switchgrass were 0.30, 0.28 and 0.37 respectively, which was decreased with temperature from 0.180.17 to, with a shift in cellulose I peak at 200 planes. X-ray diffraction study showed the presence of the peaks at around 12.5° (for cellulose II amorphous form) and absence peak around 15.5° (for cellulose I, crystalline form) and with the formation of XRD peak around 21.5° confirms the cellulose I to cellulose II transformation. A small peak around 12.5° was originated in the X-ray diffraction patterns, which showed the transformation of crystalline structure to amorphous cellulose II structure after ionic liquid pretreatment. The microscopic study showed that reduction in crystallinity was attributed with solubilization of lignin and hemicellulose.

F. H. Isikgor et al. (2015)[6, 142] showed that lignocellulosic biomass is most abundant approximately 90% of the dry matter of plant, bio-renewable biomass on earth, cheap and potential resource for production of energy[143] using biochemical[144] or thermochemical platform[145] and can also be used for production of more than 10,000 valuable chemicals compound and are alternative to fossil resources, which are helpful for reduction of greenhouse gas emission.[146]

Gang Cheng et al. (2015)[111] showed that advanced pretreatment technologies are essential for the effective deconstruction of complex biomass structure for production of monomeric sugars. In this concern, they reported that understanding of the interaction between biomass structure and pretreatment agents were necessary. They have investigated the effect of ionic liquid pretreatment over crystallinity using Scattering techniques such as X-ray a neutron scattering for imaging of ionic liquid pretreated biomass. They have shown that wide and angle neutron scattering (WAS and SAS) techniques for understanding the supramolecular structures of cellulose, lignin before and after IL pretreatment with an in-situ examination of enzyme-biomass interactions to understand the enzyme- cellulose interactions.

Juan F. Saldarriaga et al. (2015)[147] quantified the chemical components and studied the thermal behaviour of biomass using TGA/DTA and correlated with energy content, fixed carbon, kinetics, high heating values and C, O, H analysis. Similarly, Y. Singh et al. (2017)[137] did comprehensive characterization of biomass through proximate and ultimate analysis and showed that highest moisture content was found in Typha angustifolia (13.9 %) below 120 °C with a cellulose degradation ranges between 350-500 °C, with highest carbon higher carbon percentage (52.8 %) resulted in higher heating value (19.6 MJ/kg) due to high cellulose content, hence can be used for biofuel production.

Lishi Yan et. al. (2016)[148] conducted a pretreatment study to understand the behaviour of lignocellulosic biomass and their temperature-dependent cellulose decrystallization mechanism in dilute acid flow through treatment and water treatment processes. They found that disruption of the crystalline structure of cellulose occurred at 270 °C in case of hydrothermal pretreatment and 220 °C for DA (0.05 wt % H_2SO_4) pretreatment. Above this temperature, guaiacyl units of lignin start disintegrating and hemicellulose was degraded to xylose and xylo-oligomers. The enzymatic saccharification was a significant enhancement of cellulose reactivity after water flows through treatment at 270 °C and 220°C for 0.05 wt % H_2SO_4 due to crystallinity reduction and xylose removal.

Demi T. Djajadi et. al. (2017)[149] conducted a study to show the effect of properties, recalcitrance nature and a factor of lignocellulosic biomass for designing of better deconstruction method for 2nd generation biorefinery processes and their correlation with enzymatic digestibility using hydrothermal pretreatment method using Miscanthus, wheat straw etc. They have analysed the physicochemical features of the LCB, chemical composition and characterised the structure with 2D NMR, FT-IR spectroscopy (surface biopolymer composition), the effect of pretreatment and sugar conversion were correlated glucose yield with native and pretreated biomass.

Yengkhom Disco Singh et. al. (2017)[137], have physicochemically characterised five biomass samples (Impereta cylindrica, Eragrostis airoides, Typha angustifolia L., Arundinella khasiana Nees ex Steud, and Echinochloa stagnina (Retz.) P. Beauv) based on the proximate, ultimate, compositional analysis and structural properties. The cellulose content was found the maximum in *Eragrostis airoides* (43.17%) and minimum in *Echinochloa stagnina* (24.90%). Derivative Thermogravimetric (DTG) peak observed below 120 °C indicating the loss of water molecules from the biomass. Cellulose degradation occurred between 350 °C to 500 °C. The maximum carbon content was visible in *Typha angustifolia* (52.95%) and minimum in *Eragrostis airoides* (41.4%). These results demonstrate that the collected lignocellulosic biomass could be a potential candidate for bioethanol production.

2.2 IONIC LIQUID AS A “GREEN SOLVENT’ FOR BIOMASS PROCESSING

Conventional methods of dissolving cellulose are often demanded harsh condition, i.e. either require high temperature/pressure or high doses of acids/or alkali and they often cause serious environmental and climate issues.[31, 150-151] For instance, the formation of inhibitory byproducts during dilute acid[152], steam explosion[67, 153], ammonia and high doses of alkali[154-155] have a drastic effect on sugar recovery from biomass and are not economic.

Hence, the ability to minimise these concern by using some “green” methods for bioprocessing of lignocellulosic biomass is necessary for economic and sustainable developments. Ionic liquids (ILs), in particular is organic salts, which remain liquid below <100 °C, and are mainly composed of organic cations (i.e. pyridinium, imidazolium and quaternary ammonium species) and organic/inorganic anion (i.e., halogen, acetate and some other polyatomic inorganic species) with high viscosity and are able to dissolve cellulose.[10, 117, 156-157]

Cellulose in complex lignocellulosic biomass being highly crystalline are unable to dissolve in common solvents; Ionic liquid as a “Green Solvent” with unique solvation properties can be used for carbohydrates and lignin selectively with certain designed ionic liquids.[119]

Swatloski et al. (2002)[158] showed that ILs, containing 1-butyl-3-methylimidazolium cations ($[C_4mim]^+$) with a different anions, hydrogen-bond acceptors, i.e., Cl^- to large, noncoordinating anions ($[PF_6]^-$) also including [Br], SCN^-, and $[BF_4]^-$ could be used for biomass processing for cellulose solubilization above 100 °C with varying cation alkyl chain substituent from butyl through octyl chain using cellulose dissolving pulp and fibrous cellulose. They have found that high concentrations of chloride ions in ionic liquids can help to interact with inter/intermolecular hydrogen bonding between cellulose chains in cellulose, which results in partial solubilization of cellulose chains in ionic liquids. They also reported that ionic liquid cation, i.e., $[C_6mim][Cl]$ and $[C_8mim][Cl]$ with longer alkyl chain substituted appeared to be less efficient at dissolving cellulose due to steric hindrance and high viscosity. They also reported that the dissolution of cellulose in ILs was decreased with the addition of water, even 1% of water to the ionic liquid promotes the new hydrogen bonds formation in cellulose chains.

Dadi et al. (2006)[159] showed that 1-butyl-3-methylimidazolium chloride IL could disrupt cellulose crystalline lattice after cellulose regeneration, which increases the hydrolysis yield by 50 folds compared untreated avicel. They reported that regenerated avicel have amorphous in nature as determined by XRD, and have greater sites for enzyme adsorption with 13.0mg/mL of reducing sugar release for regenerated avicel compare to untreated (2.6 mg/mL). They explained that this increase in hydrolysis was attributed that imidazolium cation with its electron-rich aromatic π-system has the capability to interacts with cellulose OH group via. Non-bonding or and hence decrease the cellulose inter/intra bonding to reduce the crystallinity and have higher enzymatic efficiency.

Zhang et al. (2010)[160] conducted a ^{13}C and $^{35/37}Cl$-NMR study of native and IL-treated and regenerated cellulose to understand the mechanism for cellulose solubilization in IL ([C_2mim][OAc]) using cellobiose as substrate at a different temperature. They showed that there is a strong hydrogen bonding between the OH of cellobiose, in which hydrogen is strong hydrogen bonding donor and OAc^-, the strong hydrogen bonding acceptor of [C_2mim][OAc], which helps in solubilization of cellulose. This study was further conducted by chemical shift determined by ^1H, and ^{13} C with increase conc. to understand the full mechanism of cellulose solubilisation.

Indira P. Samayam et al. (2010)[161] have pretreated poplar and switchgrass with 1-ethyl-3-methyl imidazolium acetate IL, the pretreated biomass was further hydrolyzed with two commercial enzymes Spezyme CP and Primafast Luna CL. They reported that Spezyme hydrolyzed both cellulose and hemicellulose but Primafast primarily hydrolyzed the amorphous cellulose fraction of biomass. With that they have also mentioned that the increased digestibility of cellulose and hemicellulose fractions was enhanced due to synergism between Primafast cellulase and Multifect xylanase rather than from the additional cellulase activity of Multifect xylanase and the glucose yield was increased from 29% to 46% with relatively low xylan hydrolysis of about ~30% for the Primafast/xylanase mixture.

Rohit Arora et al. (2010)[162] shown the effect of time/temperature over IL pretreatment using switchgrass with 1-ethyl-3-methyl imidazolium acetate for pretreatment performance by delignification, xylan and glucan depolymerization, increased in porosity, surface area, cellulase kinetics, and sugar yield. BET surface area estimation showed that surface area of IL-treated switchgrass was increased by a factor of ~30, with a corresponding increase in saccharification kinetics of a factor of ~40. They found that efficient depolymerization of hemicellulose occurred at high temperature despite temperature with highest 73.5% delignification at 160 °C and the kinetics was increased ~6.1 times when compared to 110 °C pretreatment, which was ~39 times higher than the untreated switchgrass.

Sung Ha et al. (2011)[163] conducted a microwave assisted ionic liquid pretreatment for enhanced enzymatic saccharification which chemical characterisation of pretreatment cellulose. They have reported that microwave irradiation helps to decrease the degree of polymerization (50–59 for [C_2mim][OAc] and 40–45 for [C_4mim][Cl]) respectively almost 96% and 97% decreased degree of polymerization, which resulted in higher rate 12-fold of cellulose hydrolysis after [C_4mim][Cl] and [C_2mim][OAc] dissolution after pretreatment with microwave irradiation were 17.1 and 15.6 mg/mL after 24 h. They have correlated this enhancement with Kamlet-Taft parameter and found higher hydrogen bond basicity of $[OAc]^-$ play an essential role in the dissolution of cellulose.

A. Sant'Ana da Silva et al., (2011)[164] conducted a study to determine the dissolvation capability of six ILs using sugarcane bagasse as a feedstock using [Mmim][DMP], [C_2mim][OAc] [C_4mim][NTf_2], [C_4mim][Cl], [Amim][Cl] and 1-ethyl- 3-(hydroxymethyl) pyridine ethyl sulfate ILs with a ratio of 1:20 (wt.%) was pretreated at 120 °C for 2h. Soluble baggage was precipitated using water as anti-solvent They found almost 20.7% of baggage was dissolved in [C_2mim][OAc]. Which on enzymatic saccharification resulted in 80% of glucose yield within 6 h and maximum 90% glucose yield was achieved after 24 h. They showed this increase in glucose yield was attributed due to drastic lignin removal and exposure of cellulose nanofibrils with the high specific surface area (13184 m^2/g) after ionic liquid pretreatment.

An acid catalysed ionic liquid study was conducted by Z. Zhang et al. (2012)[165] with bagasse with 1.2% HCl with [C_4mim][Cl] at 130 °C for 30 min to evaluate the effect of acid. They found that HCl was a more effective catalyst in combination with an ionic liquid to disrupt the cell wall structure than H_2SO_4 or $FeCl_3$ and gave high glucan digestibility (>94%) after 72 h of enzymatic saccharification. They also reported that with increased acid conc. from 0.4% to 1.2% and reaction temperature (from 90 to 130 °C), glucan digestibility was also increased. They showed that addition of acidified water in ionic liquid pretreatment could lead to reduced viscosity and increased high loading, making ionic liquid pretreatment more economic. Further characterization study showed that xylan removal in acidified [C_4mim][Cl] was attributed mainly due to cleavage of β-ether linkages between lignin and hemicellulose and lignin removal was attributed to breaking of β-aryl ether linkages due to high acidity nature of HCl/[C_4mim][Cl] IL and high temperature.

Teck Ang et al. (2012)[166] elucidated [C_2mim][DEP], [C_4mim][Cl] and [C_2mim][OAc] ionic liquids over rice husk. The regenerated biomass were amorphous in nature and was less crystalline with enhanced disrupted surface structure as charactered by XRD, FT-IR, and SEM, which upon enzymatic saccharification resulted higher glucose yield in order of [C_2mim][OAc], (42.1%) followed by [C_2mim][DEP] (39.9%) and [C_4mim][Cl] (28.6%) respectively. Similarly, regenerated cellulose from [C_4mim][DEP] resulted to decrease the crystallinity by 32.0%, followed by [C_2mim][OAc] (34.4%) and [C_4mim][Cl] (37.7%) pretreatments respectively. The FT-IR data showed the absorbance band at 798, 1035, 1457, 1513, 1637, 2919, 3312, and 3750 cm^{-1} for untreated rice husk for lignocelluloses. The intensity around 1035 cm^{-1} in cellulose/hemicellulose corresponds to the C-O stretching vibration.

Işık Haykır et al. (2012)[167] conducted a pretreatment study using [C_2mim][OAc] for the cotton stalk, followed by saccharification and fermentation of the regenerated cellulosic material and fermentation with consecutive ionic recycling. They have reported that digestibility of cotton stalk was increased up to 9-fold upon [C_2mim][OAc] ionic liquid pretreatment.

Sergios K. Karatzos et al (2012) conducted sugar bagasse pretreatment using three imidazolium-based ionic liquid, i.e., $[C_4mim][Cl]$, $[C_2mim][Cl]$ and $[C_2mim][OAc]$ at 130 °C with certain mass balance studies. They reported that $[C_2mim][OAc]$ ionic liquid delignify more efficiently (60%) followed by 50% in $[C_2mim][Cl]$ and 10% $[C_4mim][Cl]$ with addition of water as antisolvent. The enzymatic hydrolysis for 24 h at 15 FPU of commercial enzyme showed highest sugar yield in case of $[C_2mim][OAc]$, (83%) followed by $[C_2mim][Cl]$, (53%) and $[C_4mim][Cl]$,(53%) respectively. With that FT-IR analysis of $[C_2mim][OAc]$ treated cellulose showed the strong characteristic band at 974 cm^{-1} indicative of arabinosyl groups, which confirms the preservation of covalent bonds to arabinosyl moieties during $[C_2mim][OAc]$ dissolution.

K. Ninomiya et al. (2012)[168] demonstrated the dissolution of kenaf powder in five Ils; $[C_4mim][Cl]$), [Amim][Cl], $[C_2mim][Cl]$, $[C_2mim][Dep]$, and $[C_2mim][OAc]$ after ultrasonic pretreatment followed by enzymatic saccharification. They reported almost 20% saccharification for kenaf powders pretreated with $[C_4mim][Cl]$, AmimCl, $[C_2mim][Cl]$, and $[C_2mim][Dep]$ at 110 °C for 120 min. They reported that maximum of 86% saccharification was obtained using $[C_2mim][OAc]$ IL pretreatment after 15 min of the ultrasonic pretreatment conducted at 25 °C, however, 47% saccharification yield was obtained after IL pretreatment only. The XRD analysis showed the cellulose I crystalline structure for native biomass and the crystallinity reduced with ultrasonic pretreatment due to the removal of amorphous hemicellulose and lignin and the crystallinity was found to be 49.4%, 38.8% and 31.5% for the untreated sample, $[C_2mim][OAc]$ treated and $[C_2mim][OAc]$+ultrasound treated cotton stalk for 15 min respectively.

M. Muhammad et al. (2012)[169] showed that $[C_2mim][OAc]$ IL swollen wood biomass in an aqueous solvent for improved solubility of substrates due to lower amounts of lignin/xylan, which show that ionic liquid pretreatment helps in reduction of crystallinity by removal of >20% lignin after IL pretreatment.They also showed that cellulose exists in cellulose I form in native biomass which on ILs pretreatment converts in amorphous form cellulose II, which has a low degree of polymerisation. With that FT-IR spectra of untreated and treated wood fibres indicated the partial removal of lignin/xylan was also removed.

K Torr et al. (2012)[170] reported the impact of [C$_2$mim][OAc] IL treatment on the chemical modification over enzymatic saccharification efficiency over opposite wood, *Pinus radiata* at 120 °C and 155 °C for 3 h. They have found that [C$_2$mim][OAc] IL pretreatment was much more effective in xylan removal from *Pinus radiata,* which increase the overall glucan content. With that, they also found that [C$_2$mim][OAc] ionic liquid pretreatment resulted in condensation of lignin with reduction n cellulose crystallinity and decreased in degree depolymerisation of regenerated biomass. With that, they also reported that >90% of glucan conversion was reported achieved after 24 h of enzymatic hydrolysis or regenerated cellulose-rich material as compared to untreated samples (3–8%).

Joan G. Lynam et al. (2012)[171] demonstrated the dissolution study of rice hull using [C$_2$mim][OAc], 1-hexyl-3-methylimidazolium chloride, ([C$_6$mim][Cl]), and 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) at 110 °C for 8 h. They reported that at optimized condition in [C$_2$mim][OAc] almost 100% lignin was dissolved due to higher hydrogen bond acidity as compare to other ionic liquids, with they also reported that lower melting point and viscosity of [C$_2$mim][OAc], compared to Cl^- containing ILs, may also make it more successful in penetrating a biomass's interior, especially for a silica-shielded biomass such as rice hull. Hemicellulose removal was more pronounce in [C$_2$mim][OAc] (70%), compared to 75% [Amim][Cl] and 60% removal in [C$_6$mim][Cl] ionic liquid.

Similarly, Alejandro Cruz et al. (2013)[172] showed the impact of high solid loading over ionic liquid pretreatment using switchgrass using [C$_2$mim][OAc]. The impact of IL pretreatment was correlated in term of chemical composition, cellulose crystallinity, saccharification kinetics, viscosity with glucose released. The reported the anticipated benefit of increasing the loading levels to 40–50 wt.% is the decrease of the cellulose crystallinity after [C$_2$mim][OAc] pretreatment. They also reported glucan content was increased up to 68% after [C$_2$mim][OAc] treatment as compared to untreated biomass (35%).

Chenlin Li et al. (2013)[173] showed the same study for scale up and evaluation of ionic liquid pretreatment at high solid loading (15% (w/w). They showed that [C_2mim][OAc] treated switchgrass at 15% gave highest glucan (87.5%), xylan (42.6%), low lignin (22.8%) in the regenerated switchgrass. The enzymatic saccharification at 10% solid loading at 150-fold scale of operations (1.5 L vs 0.01 L) resulted 99.8% sugar conversion, with 94.8% and 62.2%, of glucan and xylose yield respectively, with high titers of fermentable sugars (62.1 g/L of glucose and 5.4 g/L cellobiose) in liquid stream. They also reported the overall glucose and xylose in pretreatment and saccharification were 95.0% and 77.1%, respectively with efficient ionic liquid recycling.

Ning Sun et al. (2013)[174] demonstrated a method for extraction of sugars from ionic liquid pretreated slurry using aqueous alkaline solutions by formation of a biphasic system. The extraction efficiency was dependent upon the ratio of sugar and ionic liquid and a maximum of 53% glucose and 88% xylose yield were recovered in the alkali phase. Using [C_2mim][Cl] or [C_4mim][Cl] ionic liquid pretreated slurry with 10 and 15% alkali. Furthermore, they showed that improved sugar yields could be achieved by optimising the acid: water ratio and alkali conc. Similarly, Rogers et al. Also, reported that certain hydrophilic ILs could form an aqueous biphasic system (ABS) in the presence of concentrated kosmotropic salts.

Haykir et al. (2013)[175] demonstrated that 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc] IL pretreatment of cotton stalks at high solid loading is helpful to improve enzymatic saccharification for bioethanol production. They report that 1-ethyl-3-methylimidazolium acetate pretreated cotton stalk have high digestibility and resulted to 82-85% of glucose yield due to reduced crystallinity due to cellulose I to cellulose II transformation of pretreated cotton stalk at high solid loading (15%), which on fermentation by yeast resulted in 74% ethanol yield, when compare to alkaline pretreated biomass which resulted in 46% ethanol yield respectively.

André M. da Costa Lopes et al. (2013)[176] emphasized over wheat straw pretreatment using 1-butyl-3-methylimidazolium thiocyanate ([C_4mim][SCN]), 1-butyl-3-methylimidazolium hydrogensulfate (C_4mim][HSO_4])and 1-butyl-3-methylimidazolium dicyanamide [C_4mim][$N(CN)_2$])ionic liquid for fractionation. They found that fractionation was completely dependent on the acidity of the anion of ionic liquid used, and [C_4mim][HSO_4] was found more effective for dissolution of wheat straw. [C_4mim][SCN], ionic liquid helps to obtained high-purity lignin-rich compare to [C_4mim][N$(CN)_2$], which generate high-purity carbohydrate-rich fractions after precipitation. They have also reported the effect of anion on the extent of lignin removal and found that strong hydrogen bond basicity of anions was helpful for the liberation of lignin. LOI and TCI crystallinity were determined by spectroscopic analysis.

Idi Audu et al. (2013)[177] demonstrated the [C_4mim][OAc] ionic liquid pretreatment for TC at 110 °C for a time from 0.5−24 h. After regeneration, they carried out the enzymatic saccharification for reducing sugar yield and found a maximum of 82.4% reducing sugar yield after 6 h of incubation. With that, they also conducted the IL recycling using acetone/water solvent system as an antisolvent with a recovery of 93%., and showed that about 10% of initial lignin was being accumulated in the liquid stream everytime. Recycled ionic liquid after pretreatment released 84.64 and 57.45 g/100 g of sugars at the first cycle to 52.81 and 29.13 g/100 g at the 20th cycle, respectively.

Tong-Qi Yuan et al. (2013)[178] showed an environmental fissible process for fractionation of hemicellulose and lignin from poplar wood using ionic liquid and mild alkaline pretreatment. They showed that high yield of hemicellulose and lignin (59.3 and 74.4%) were separated respectively for conversion into value-added products. The enzymatic hydrolysis showed high glucose yield (99.2%) compared to native poplar (19.2%). Removal of hemicellulose and lignin showed increased in the surface area, high sugar yield and cellulose I to II transformation. They showed that cellulose content in alkali, IL and alkali+IL pretreated poplar was 51.3, 42.7 and 61.1% respectively with 10.1, 15.2, 3.5% hemicellulose, which showed the synergic effect of alkali and ionic liquid for extraction of hemicellulose.

Jörn Viell et al. (2013)[179] in his study showed the effect of [C_4mim][Cl] and [C_2mim][OAc] ionic liquid pretreatment over spruce and beech wood chips at 115 °C. The cellulose-rich material was precipitated using (1:1 v/v) of acetone/ethanol mixture and enzymatic hydrolysis of regenerated biomass were conducted. The maximum cellulose conversion received was 70.5 and 90.5 w% after 5 and 72 h of saccharification. They concluded that shorter pretreatment time is enough to get same glucose yield.

Yon Sun et al. (2013)[180] conducted the similar study for structure comparison and enhancement of sugar yield via different IL pretreatment of cellulose. They showed the maximum amount of total reducing sugars (80%) was obtained, which was 4.4-6.4-fold increased from first 4 reactions. With that, they reported that the CrI of [Amim]Cl IL treatment cellulose was reduced from 70.2% to 31.2%, which was attributed to cellulose II change, which enabled the cellulase enzymes. In contrary [C_4mim]OAc] ionic liquid did not show any cellulose transformation. SEM analysis showed the formation of the porous and irregular structure after [C_4mim][Cl] and [C_2mim][OAc] ionic liquid. They showed that $MgCl_2$ and H_2SO_4 addition as a catalyst has increased the sugar yield significantly.

P. Weerachanchai et al. (2014)[181] conducted the ionic liquid pretreatment and recycling studies [C_2mim][OAc] and [C_2mim][OAc]/ethanolamine (60/40 vol%) ionic liquid up to 7th cycle and correlated with the sugar released and lignin removal and turnover frequency. They reported that [C_2mim][OAc]/ethanolamine (60/40 vol%) demonstrates superior effectiveness on biomass pretreatment with 99.0–99.9 wt.% of sugar yield than that of [C_2mim][OAc]/ (85.19 to 63.06 wt.%) at the equal quantity of lignin within the pretreatment solvent. In addition, they reported the lower lignin deposition (29.30–76.94 wt.%) in [C_2mim][OAc]/ethanolamine compared with pure ionic liquid (43.93–120.98 wt.%).

Jian Shi et al. (2014)[182] investigated the pretreatment of switchgrass with 50-80% IL-water mixture of [C_2mim][OAc] IL and water at 160 °C. They found that hydrogen bond basicity and the ratio of [C_2mim][OAc] is essential in cellulose dissolution with high extent of lignin and xylan removal, crystallinity reduction with increased cellulose accessibility towards cellulases, for better enzymatic hydrolysis. With that, they also carried out molecular dynamics simulations for cellulose Iβ transformation into cellulose II.

Weng et al. (2014)[183] showed the alkali lignin dissolution and chemical transformations under [C_2mim][OAc] IL pretreatment conditions using poplar alkaline lignin (hardwood lignin) at 110-170 °C, 1–16 hours. Lignin structural transformations were further investigated by 2D-HSQC, GPC analysis, ^{31}P

NMR, and ^{13}C-NMR spectra with proximate and ultimate analysis. Lignin dissolution in IL was confirmed by reduced intensity of aliphatic OH, and increased intensity in phenolic hydroxyl groups, that was attributed due to the breaking of β-O-4 bonding in cellulose chains, while the reduction in -OH intensity was attributed to rearrangement and dehydration. The breaking of β-O-4, β–β and β-5 bonds were confirmed with a decrease of molecular weights with temperature.

Jian Liu et al. (2014)[184] conducted the enzymatic saccharification after [Amim][Cl]/DMSO ionic liquid pretreatment for hardwoods, softwood and agricultural wastes and result showed that Pinewood (PW) gave better solubilization of biomass reaching to the highest ratios of 54.3% and 31.7%, respectively. They also reported that cellulose I crystal structure was transformed into amorphous cellulose II, with maximum glucose conversion of 85.1% and 85.4%, respectively. For comparison, they reported that saccharification of steam-exploded corn stover was 91.5%, and about 7.3-fold higher than the original CS.

Similarly, T. Auxenfans et al. (2014)[185] showed that [C_2mim][OAc] is an effective solvent for the treatment of hardwood and softwood sawdust and can be recycled and reuse 7 times. Pretreatment efficiency was calculated in term of lignin and xylan removal with a morphological study by FT-IR and XRD at 110 °C for 40 min. They showed that sugar yield was enhanced 70% for Spruce, 67–79% for pretreated oak. The compositional study showed that biomass recovery after [C_2mim][OAc] pretreatment for sawdust was 85% with a 25–27% decrease in lignin and of 45–47% in extractives. The removal of lignin was confirmed by FT-IR data with the disappearance of characteristic peaks at 1492 cm^{-1} (g), 1447 cm^{-1} (h) (-C-H aromatic vibrations of lignin) and at 1311 cm^{-1} (i.e. syringyl and guaiacyl condensed lignin) etc. Cellulose I to cellulose II transformation was attributed to reduced intensity at 1089 cm^{-1} for the crystalline plane and increase in intensity at 891 cm^{-1} bands.

Wuan Teh et al. (2015)[186] effectively treated the nut shells (from Macadamia integrifolia) with 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc] ionic liquid for their solubility and found to solubilize 5.5 ± 0.5 wt % of macadamia nutshell. After precipitation and regeneration of macadamia nutshell, they conducted the enzymatic hydrolysis with commercial cellulase for glucose released and found a maximum of 80 ± 15% glucose was released compared to untreated one 1.3 ± 1.0%.

Peng Zhang et al. (2015)[187] showed that certain acidic ionic liquid in a combination of ultrasound pretreatment at a low reaction temperature of 70 °C followed by alkaline extraction could significantly extract lignocellulosic components. Acetone/water (1:1 v/v) was used anti-solvent for cellulose precipitation. The total residue obtained after [C_6mim][Cl] and [C_6mim][HSO_4] was 39.99% and 67.23% respectively, with the maximum amount of lignin was present in solubilized form in the ionic liquid. The yield of S-G-H enriched IL liquid 60.48%, the structure was confirmed by ^{13}C NMR and ^{13}C–^{1}H correlation 2D NMR (HSQC) analysis. With that the conducted the enzymatic saccharification of precipitated cellulose and showed maximum 92.55% of cellulose conversion was achieved. The lignin extraction was correlated with properties of ionic liquid and showed that hydrogen bond capacity and acidity play a major role in the dissolution of lignin and hemicellulose.

Ly Thi Phi Trinh et al., (2015)[188], reported the [C_4mim][Cl] pretreatment of softwood at 130°C for 15hr significantly changes the crystallinity of cellulose, surface morphology and chemical compositions by lignin/xylan removal resulting in better glucan digestibility over 90% of sugar conversion with 78% of highest sugar release. The solid recovery was decreased from 90 to 73% due to the dissolution of amorphous lignin with a decrease in glucan/xylan recovery (53%/49%) with an increase in temperature.

A. George et al. (2015)[189] synthesised a series of new protic ionic liquids based upon the [HSO_4]$^-$ anion. The pretreatment performance of [HSO_4]$^-$ ILs were compared with 1-ethyl-3-methylimidazolium acetate ionic liquid in term of highest saccharification yields. The result showed that the hydrolysis yield for the triethylammonium hydrogen sulphate was 75% as effective as [C_2mim][OAc]. The enhanced saccharification was correlated with lignin removal and cellulose decrystallization, mass recovery, glucan/lignin recovery. Feng Xu et. al. (2016)[14] have used some biocompatible ionic liquids, i.e., cholinium based ILs, for corn stover and switchgrass pretreatment using cholinium acetate [Ch][OAc], cholinium lysinate [Ch][Lys], and cholinium aspartate $[Ch]_2[Asp]$ at 140 °C for 1-3h followed by simultaneous saccharification and fermentation. They have shown corn stover treated with ([Ch][Lys]) IL pretreatment have highest more than 80% glucose conversion over 30% solid loading.

Meenatchi et al. (2016)[190] conducted the dissolution studies using commercial cellulose powder (Avicel) at 5 wt.% loading in $[C_6mim]CH_3CH(OH)COO^-$, $[Heim]CH_3CH(OH)COO^-$, $[Hbim]CH_3CH(OH)COO^-$,$[Hmim]CH_2(OH)COO^-$,$[Heim]CH_2(OH)COO^-$,$[Hbim]CH_2(OH)COO^-$] ionic liquids between 40 to 80 °C. They found that $[Heim]CH_3CH(OH)COO^-$ and $[Heim]CH_2(OH)COO^-$ dissolve up to 5 wt.% within 20 and 30 min, respectively at 80 °C. and decreases with increasing temperature with cellulose structure transformation of native crystalline cellulose I to amorphous cellulose II.

K. Cheenkachorn et al. (2016)[191] demonstrated that the $[C_2mim][OAc]$ IL pretreatment of rice straw at 128.4 °C for 71.83 min at 5% w/w solid loading followed by enzymatic hydrolysis using commercial enzymes. The data showed enhancement of enzymatic hydrolysis of IL-pretreated rice straw with a maximum glucose yield of 90% yield. With that, they also did some ionic recycling study using methanol, water, acetone as antisolvent for precipitation of dissolved cellulose. The recyclability of $[C_2mim][OAc]$ IL after pretreatment using methanol as an anti-solvent showed >90% efficiency without any modification.

Similarly, Chang et al. (2016)[192] conducted a study for rice straw pretreatment using 1-butyl-3-methylimidazolium chloride IL assisted with 1% sodium dodecyl sulphate (SDS) and 1% cetyl trimethyl ammonium bromide (CTAB) and found to increased lignin removal to 49.48% and 34.76%, respectively. Surface morphological study of native and pretreated rice straw was conducted using XRD, FT-IR and SEM for cellulose morphological and crystallinity measurement after ionic liquid pretreatment.

Chen Liu et al. (2016)[193] demonstrated the ionic liquid processing of rice straw with three ionic liquids and compared with instant catapult steam explosion (ICSE). The effect of pretreatment severity and the ionic liquid was evaluated in term of surface morphology, chemical composition, crystallinity index, thermostability, and glucose yield after enzymatic hydrolysis. Results showed that addition of 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc] have enhanced the glucose yield by 70.35%, 73.38% (1-butyl-3-methylimidazolium chloride, [C_2mim]Cl) and 74.01% (1-butyl-3-methylimidazolium chloride, [C_4mim]Cl), due to removal of lignin/xylan when compared with untreated rice straw.

Amal A. Elgharbawy et al. (2016)[194] showed the application of ionic liquid as an emerging solvent for biomass processing. Moniruzzaman and Ono et al. (2012)[169] have used [C_2mim][OAc] to study the dissolving ability for wood and for enzymatic saccharification. They showed the delignification of wood chips using [C_2mim][OAc] ionic liquid followed by laccase enzymatic hydrolysis resulted to purified cellulose from wood biomass in an aqueous buffer medium and that delignification efficiency was enhanced in presence of 2.5 wt.% IL without any change in cellulose composition. With that, they also reported that dissolution of biomass was attributed to the disruption of hydrogen linkage between lignin-carbohydrate complex with solubilization of hemicellulose and lignin. Hence, the cellulose content was enhanced by 73.1% after regeneration and lignin were reduced by 9.8%, as compared to native wood (29.3%). TGA study showed that obtained cellulose-rich material has high thermal stability due to cellulose structure transformation.

Kraipat Cheenkachorn et al. (2016)[191] used [C_2mim][OAc] IL for pretreatment of rice straw at 128.4 °C for 71.83 min at 5% w/w loading mass ratio. The pretreated straw was precipitated with methanol, water, and acetone, as antisolvent, which has the different capability of cellulose recovery. The pretreated straw was further undergone enzymatic saccharification, which gave about 90% of glucose yield. They also reported showed that IL can be recycled almost five times, which retain almost 90% of the pretreatment efficiency with methanol.

Ai Asakawa et al. (2016)[195] showed the effect of a biocompatible ionic liquid, i.e. cholinium acetate for bagasse pretreatment with certain organic solvents. The sugar yield for [Ch][OAc] pretreated biomass was 91.0%, which was increased with DMSO addition, reaching a maximum value of 97.4% at a [Ch][OAc]/DMSO ratio of 1:1 after pretreatment at 130 °C for 180 min. They also showed that combination DMSO with biocompatible ILs helps to reduce 50% of the amount used of [Ch][OAc], with enhanced removal of hemicelluloses and lignin compared to the [Ch][OAc] treatment alone. The crystallinity was not much affected by solvent addition. The SCB pretreated with [Ch][OAc]/DMSO (1:1 w/w) showed 69.9% of ethanol yield.

Uju et. al. (2016)[196] showed that bagasse pretreatment with peracetic acid followed by 1-buthyl-3-methylimidazolium chloride [C_4mim][Cl]-HCl hydrolysis, improved the cellulose hydrolysis from 20 to 70% after 1.5 h and 80% cellulose conversion without acid pretreatment. They further reported that Cl^- in [C_4mpy][Cl] attributed to reducing to cellulose crystallinity by cellulose transformation from one crystal cellulose to another amorphous cellulose with reducing the degree of polymerization. Similarly, Morales-delaRosa et al., (2012)[197] reported that the enzymatic saccharification of regenerated cellulose with [C_4mim][Cl] in the presence of 20 wt.% HCl (1.66 M) at 125 and 105 °C results in 99.8% of glucose yield.

Yuan et.al. (2017)[198], conducted a systematic study to understand the different interactions, correlations between biomass structure and biomass loading during [C_2mim][OAc] ionic liquid pretreatment of poplar and eucalyptus at 110 °C for 3 h at different biomass loadings. After pretreatment, they have hydrolyzed the pretreatment biomass using cellulose enzymes characterised the treated biomass for biomass crystallinity and porosity by X-ray diffraction (XRD) and small angle neutron scattering (SANS), respectively and found that pretreated biomass has pores radii ranging from ~25 to 625 Å, which is a consequence of ionic liquid pretreatment. SANS showed that small pores contributed to less to increase the porosity of biomass compared to the large pore. They have also correlated the enzymatic saccharification with pores and crystallinity. SANS data show that smaller pores contributed less to the increased porosity than larger pores after IL pretreatment. They have also reported that crystallinity of biomass was reduced after ionic liquid pretreatment due to cellulose I crystalline form of cellulose II amorphous form.

Samuel Kassaye et. al. (2017)[37] have characterized the dilute acid followed by [C_2mim][Cl] ionic liquid pretreatment of bamboo by FT-IR, XRD, SEM, TGA and Elemental analysis techniques to investigate the effect of the pretreatment severities over properties native and pretreated bamboo in term of lignin/xylan removal, crystallinity reduction, surface morphology and for thermal stability analysis. They have found that [C_2mim][Cl] ionic liquid pretreatment resulted in lignin and hemicellulose removal, the crystallinity and structural complexity of bamboo biomass were reduced which resulted in high >80% total reducing sugars.

Dannie et. al. (2017)[199] have shown that lignocellulosic biomass that fractionation of lignocellulosic biomass into its constituents, cellulose, lignin and hemicellulose and is important for any biomass to biofuels conversion process. The cellulose embedded in recalcitrance matrix can be solubilized using deep eutectic ionic liquid solvent due to tunability solvent properties of ionic liquids with a proper selection of their cation/anion, their low volatility and high thermal stability.

Yuan et al. (2017)[198] recently conducted at study to understand interactions among biomass loading during IL pretreatment, biomass type and biomass structures using 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) IL and white poplar and eucalyptus as a feedstock to pretreat at 110 °C for 3 h at 5, 10, 15, 20 and 25 wt.% biomass loading followed by enzymatic saccharification. They have measured the structure changes during IL pretreatment crystallinity and porosity measurement by XRD and SANS, ranging from ~25 to 625 Å. They found that small pores contributed less to the increased porosity than larger pores after IL pretreatment and hence enhanced the enzymatic saccharification. XRD data showed the change in the crystalline structure of cellulose due to intercalation of IL molecules between (110) and (101) planes.

M. Smuga et al. (2017)[200] conducted the optimisation study using different pretreatment conditions and enzymatic hydrolysis of rye straw using [C_2mim][OAc] ionic liquid for rye straw. Maximum reducing sugars was obtained 120 °C, 2h pretreatment with 10 mL/10 g DM of ionic liquid/rye straw. Reducing Sugars 27.54 g/L was obtained after enzymatic saccharification of pretreated rye straw at 50 °C for 72 h.

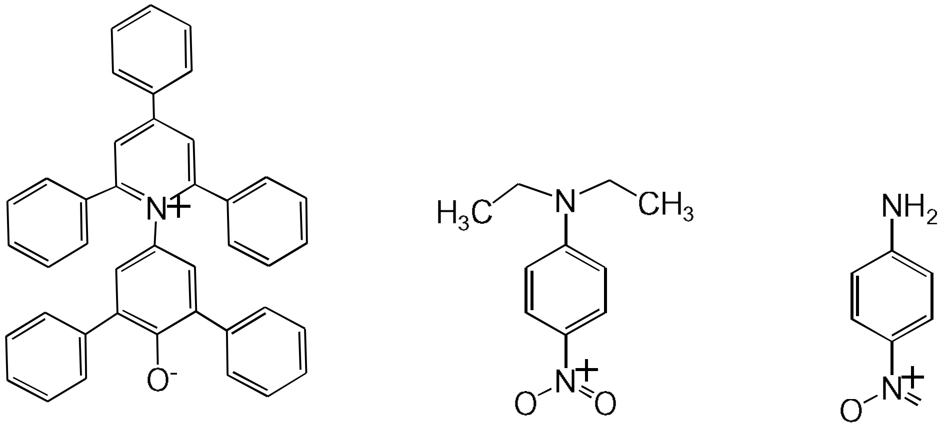
K. Chang et al. (2017)[201] described the pretreatment of rice straw with 1-Allyl-3-methylimidazolium chloride as IL assisted by different surfactants (nonionic-, anionic-, cationic- and bio-surfactant) to visualise the effect on lignin removal. They found that bio-surfactant + IL-pretreated rice straw showed significant lignin removal (26.14%) and exhibited higher cellulose conversion (36.21%) compared with untreated (16.16%) rice straw.

Bian Jing et al (2014)[202] correlated the sugar released after enzymatic hydrolysis in term of physical and chemical changes in cellulose structure after [C_2mim][OAc] IL pretreatment at 90 °C. They reported that XRD, TGA, FT-IR and SEM data showed that glucan content of pretreated biomass was increased from 80.0–83.3% to 91.6–92.8%, with a decreased degree of polymerization from 974–1039 to 511–521. XRD data showed a sharp decrease in cellulose crystallinity due to the transformation from cellulose I to cellulose II. With that, they also mentioned that regenerated cellulose had higher surface area during the pretreatment. Furthermore, in conclusion, they reported IL pretreatment helps to increase the cellulose disruption with high glucose conversion yield of 95.2%.

2.3 PROPERTIES OF CATION AND ANION OF IONIC LIQUID

Ionic liquids (ILs), in particular, is organic salts with melting points of <100°C, are mainly composed of organic cations (i.e. pyridinium, imidazolium and quaternary ammonium species) and organic/inorganic anion (i.e., halogen, acetate and some other polyatomic inorganic species)[203].

Ionic liquids is being used in biomass processing for biomass solubilization due to its unique solvation properties such hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β) and polarizability (π^*) are miscible in water due to strong hydrogen bond ability[204], E_T^N, normalized polarity parameter and thermal stability at ~300 °C.[203, 205] They have calculated the solvatochromic parameters (E_T^N, π^*, β, and α) have been determined from the corresponding chemical probe wave numbers for binary mixtures of propan-2-ol, propan-1-ol, ethanol, methanol, and water with recently synthesized IL (2-hydroxyethyl ammonium formate) at 25 °C by measuring the absorbance using three dye, i.e., 4-Nitroanisole and 4-nitroaniline and Reichardt's dye.



(i) (ii) (iii)

Figure 2.2 4-Nitroanisole and 4-nitroaniline and Reichardt's dye

The understanding of these properties helped to understand the capability of certain anion and cation of solvent for their hydrogen bond basicity (β), the contribution of specific (e.g., H-bonding) and non-specific probe–solvent interactions, which reflect the strength of particular ionic liquid for biomass solubilization.

The α parameter, hydrogen bond acidity of the ionic liquids are largely dependent on nature of cation, which highly depends upon the capability to donate a hydrogen atom, with the presence of the acidic C-H in the 2-position of imidazolium ring from a cation and become nucleophilic in nature.[206] They showed that small addition of ionic liquid in propan-2-ol, the α parameter was attributed due to hydrogen bond interactions between the ionic liquid and -OH of propanol, which makes it highly polar in nature and acts as a strong hydrogen bond donor than the individual.

In 2002 Rogers et al. demonstrated the concept of carbohydrate dissolution in ILs, particularly cellulose. They reported 1-butyl-3-methylimidazolium chloride [C_4mim][Cl] as the best IL to dissolve cellulose among the ones studied. Furthermore, the dissolution could be improved when microwave irradiation was applied (up to 25 wt.% solubility), although possibly higher polymer degradation could be obtained under microwave radiation when compared with conventional heating conditions. Since then, this new type of solvent has been described for the dissolution of cellulose and biomass lignocellulosic derivatives such as wood (hardwood and so wood) and grass.

Ionic liquid dissolution mainly depends on the particle size (which can inhibit the dissolution of the IL into the interior of the biomass), the content of lignin, hemicellulose and cellulose present in the biomass sample, the nature of the native cellulose (cellulose crystallinity and degree of polymerization), operating conditions (temperature, reaction time, biomass loading) and type of heating (conventional, microwave or sonication).

Tam Nguyen et al. (2010)[59] they have to test the desolvation of rice straw in ammonia and compared with ionic liquid pretreatment for better enzymatic saccharification using [C_4mim]Cl, ([C_2mim][Cl]), 1 ([C_2mim][OAc]) ionic liquid. [C_4mim][Cl], [C_2mim][OAc], [C_2mim][Cl] and [C_2mim][Su] with 1:20 ratio at 130 °C, for 24 h. They have reported that the highest cellulose recovery (82%) was obtained after 24 h while the increased solubility time to 48 h caused a decrease in the cellulose recovery (76%) in the case of [C_2mim][OAc]) ionic liquid pretreatment. With that, they have also conducted the recycling study of [C_2mim][OAc] and found that cellulose recovery increased from 74% up to 89% till 20th cycle.

T.V. Doherty et al. (2010)[207] have reported that physicochemical parameters of ionic liquid are essential for an effective pretreatment. They have investigated the relationship between the solvatochromic properties, i.e. Kamlet–Taft Parameter (α, β, and π^*) solvent polarity parameters by varying the cation and anion of ionic liquid, i.e., [C_2mim][OAc], [C_4mim][$MeSO_4$]) and [C_2mim][OAc]) and found that β-parameter of anion detrimental factor for pretreatment efficacy. OAc containing ILs with high (β>1.0) removed >32% of lignin from maple wood flour with a significant reduction in cellulose crystallinity, resulting in >65% glucose yields after 12 h cellulase hydrolysis. Comparatively, [C_4mim][MeSO4] with small (β=0.60) resulted in only 19% lignin removal without affecting any change in cellulose crystallinity and sugar yield was very low compared to [C_2mim][OAc] wood flour.

Patanjali Varanasi et al. (2012)[208] showed that solvatochromic properties of any solute-substrate help to understand the hydrogen bond interaction. They have quantified the Kamlet-Taft parameters to determine the hydrogen-bond accepting capacities at these temperatures to understand the mechanism for lignin dissolution mechanisms at different pretreatment temperatures and time. They have shown that IL pretreatment preferentially removes S-lignin at 160 °C, and G-lignin at 120 °C. Hydrogen bond basicity (β) at higher temperatures suggests that the acidic hydrogen bond in the C2 position of [C_2mim][OAc] is released and hence it behaves like acid pretreatment at a higher temperature.

Bahcegul et al., (2012)[209] showed that ionic liquid pretreatment of cotton stalks with different particles sizes (<0.15 mm, 0.15–0.5 mm, 0.5–1.0 mm and 1.0–2.0 mm) using 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc] and 1-ethyl-3-methylimidazoliumchloride [C_2mim][Cl] followed by the enzymatic hydrolysis of pretreated biomass. They found that small size (<0.15 mm) [C_2mim][OAc] pretreatment, gave lowest glucose yield (57%) compared with glucose released with larger particle sizes (71%). On the contrary, they found that [C_2mim][Cl] IL pretreatment functioned more efficiently with cotton stalks having smaller particle sizes (<0.15 mm and 0.15–0.5 mm) where increasing the biomass particle size further caused a decrease in the glucose yield from approximately 49% to 33%, unlike the [C_2mim][OAc] pretreatment.

Z. Zhang et al. (2013)[210] have conducted a study using acid-catalysed ionic liquid pretreatment on solubilization of sugarcane bagasse using [C_4mim][CH_3SO_3], [C_4mim][CH_3SO_4], [C_2mim][Cl] and [C_4mim][Cl]. They showed that lower pH of aqueous ILs (from 6.0 to 0.4) have increased xylan and lignin removal, which increased the glucan digestibility by >90% after 72h. With that, they also reported that ILs with β>1.0 were found to be better for biomass dissolution.

Moniruzzaman et al. (2013)[211] studied the cellulose dissolution using cellulose different ILs (1-ethyl-3-methylimidazolium acetate [C_2mim][OAc], 1-n-butyl-3-methylimidazolium chloride [C_4mim][Cl], 1-ethyl-3-methylim-imidazolium diethyl phosphate [C_2mim][DEP], 1-allyl-3-methylimidazolium chloride [Amim][Cl], and 1-ethyl-3-methylimidazolium hydrogen sulfate [C_2mim][HSO_4] using corn stover as feedstock, followed by enzymatic hydrolysis of regenerated biomass. They found that [C_2mim][OAc] pretreatment resulted in the highest reduction of crystallinity and opening of the structure. Cellulose digestibility was enhanced to 69.7% compared with 21.1%

for untreated corn stover. The authors have also explained the mechanism of dissolution of cellulose by interacting the cation and anion of [C_2mim][OAc] IL, which is helpful in disruption of inter/intramolecular hydrogen bonding leading to higher amorphous cellulose sites that are consequently more accessible to the enzymes. They also characterised the pretreated biomass by FTIR, SEM, and XRD to show the changes in crystallinity and higher amorphous sites.

Using [C_4mim][OAc] as pre-treatment solvent, Cheng et al. (2014)[125] also has studied the physicochemical changes of biomass samples (switch grass and corn stover) by TGA. IL pretreatment increased the cellulose II polymorph by increasing the CC of the recovered cellulose material. Cheng et al. (2014) showed that the thermal stability of the cellulose II polymorph can be higher than native cellulose if considerable depolymerization does not occur during the pre-treatment.

Ngoc Mai et al. (2014)[212] conducted a study for ionic liquid/co-solvent pretreatment of rice for better saccharification efficiency using [C_2mim][OAc], [C_4mim][Cl] and [C_2mim][DMP] ionic liquids and DMSO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA) as co-solvent. They reported that IL/cosolvent system could enhance the dissolution of hemicellulose and lignin. For example, IL/DMSO resulted in 70% and 37% of hemicellulose and lignin dissolution, compared to 24% and 33% of pure [C_2mim][OAc] respectively. They attributed the high solubility due to reduced viscosity and high hydrogen bond basicity of IL/DMSO mixture. Enzymatic saccharification showed that the highest glucose and xylose released were 10.4 and 5.1 mg/mL, respectively after microwave-assisted [C_2mim][OAc]-DMSO treated-RS, compared with untreated rice straw of 2.3 and 0.9 mg/mL respectively.

Koo et al. (2014)[213] have independently studied the dissolution of cell wall components (cellulose, hemicellulose and lignin) using [C_2mim][OAc] with polar aprotic co-solvent (DMSO, DMF and DMA (dimethyl sulfoxide, dimethylacetamide, dimethylformamide, respectively). They found that combination of [C_2mim][OAc]/DMSO (1:1) dissolve this carbohydrate in many extents and was further studied using rice straw. They found that this cosolvent mixture improved lignin dissolution and decreased the cellulose crystallinity with cellulose I transformation to cellulose II with better enzymatic saccharification compared to neat [C_2mim][OAc] pre-treatment.

J. C. del Valle et al.(2015)[206] conducted similar study to evaluate the solvent properties of and 1-(1-butyl)-3-methylimidazoliumhexafluorophosphate [C_4mim][PF_6], 1-(1-butyl)-3-methylimidazolium tetrafluoroborate, [C_4mim][BF_4] ionic liquids. They showed the effect of the size of anion [PF_6]$^-$ and [BF_4]$^-$ over same cation ([C_4mim]$^+$, [PF_6]$^-$ being in a larger size than [BF_4]$^-$ have less interaction with water molecules and hence have poor dissolution capability for cellulose.

K Ninomiya et al. (2015)[169] conducted a [C_2mim][OAc] pretreatment and compared with a biocompatible ionic liquid [Ch][OAc], with that they also conducted they study over ionic liquid inhibition on cellulase, yeast for saccharification and fermentation. The of IL-treated bagasse resulted in 90 and 60% of glucose and xylose irrespective to [Ch][OAc] and [C_2mim][OAc] ionic liquid pretreated biomass. The cellulose activity and yeast growth curve were found to be (32, 16 wt.%) and (3.1 wt.%, 0.3 wt.%) for [Ch]OAc] and [C_2mim][OAc]. Ethanol yield of sugar obtained for bagasse were 60% and 24% for [Ch][OAc] and [C_2mim][OAc], respectively after 2 washed. They study showed that [Ch][OAc] was much more tolerable to ionic liquid conc.and could be hydrolyzed and fermented in water wash compared to [C_2mim][OAc].

Similarly, Juan M. Padró et al. (2016)[214] also quantified solvatochromic parameters of certain ionic liquids, i.e 1-hexyl-3-methyl imidazolium hexafluorophosphate, trihexyl-(tetradecyl)phosphonium bromide, trihexyl-(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide 1-octyl-3-methyl imidazolium hexafluorophosphate, , N-octylpyridinium tetrafluoroborate, 2-hydroxyethylammonium formate, 2-hydroxypropylammonium formate, trihexyl-(tetradecyl)phosphonium chloride, 1-octyl-3-methyl imidazolium tetrafluoroborate, trihexyl-(tetradecyl)phosphonium dicyanamide and 1-butyl-3-methyl imidazolium hexafluorophosphate using kamlet Taft parameters as discussed in above references.

Safia Mohtar et al. (2017)[215] conducted a study for biomass solubilization and fractionation [C_4mim][Cl] for oil palm empty fruit bunch

(OPEFB). They showed that during [C_4mim][Cl] treatment, the cellulose crystal structure and lignin-carbohydrate structure were shattered and fractionation occurred during regeneration with acetone/water (1:1, v/v) addition and a maximum amount of cellulose (52.72±1.50) wt.%, hemicellulose (27.17±1.68) wt.% and lignin (16.82 ± 1.15) wt.% fractions were extracted. The morphological study was conducted with FT-IR, SEM, TGA and XRD, CP/MAS etc. TGA study showed that high degradation temperature for cellulose for its high cellulose content followed by hemicellulose and lignin fractions. GPC analysis showed to lower molecular weight. distribution due to degradation of hemicellulose and lignin during the ionic liquid pretreatment.

Hyungsup Kim et al. (2016)[216] compared the influence of acetate and chloride anion on structure of ionic liquid pretreatment of MCC, cotton, hemp and acacia biomass using [C_2mim][OAc] and [C_2mim][Cl] ionic liquids at 80 and 120 °C. The influence of the pretreatment on the composition, the molecular structure, and the crystalline structure was observed using FT-IR compositional analysis, TGA, rheological behavior, and XRD. FT-IR spectral analysis of native and the pretreated MCC, cotton, hemp and acacia showed the different characteristic peaks of lignin and hemicellulose in the lignocelluloses appeared at 1732 cm^{-1} (C=C, unconjugated stretching, hemicellulose), 1515-1505 cm^{-1} (C=C, aromatic symmetrical stretching, lignin), 1425 cm^{-1} (C=C stretching in aromatic groups, lignin and hemicellulose) and 1240 cm^{-1} (C-O, aryl group, lignin), the intensity of these band was decreased for [C_2mim][OAc] followed by [C_2mim][Cl] pretreated biomass. With that they have also reported that lignin removal efficiency was decreased by type of biomass, for example, lignin removal efficiency in case of cotton was 70% after [C_2mim][OAc] at 120 °C.

2.4 MECHANISM OF CELLULOSE SOLUBILIZATION IN IONIC LIQUIDS

Cellulose is highly crystalline and polar molecule with OH and H functional groups, which are involved in strong inter/intramolecular hydrogen bonding network, hence are very difficult to dissolve in conventional solvents. Ionic liquid anion has high hydrophilic, basicity, which is responsible for interacting inter/intramolecular hydrogen bonding with cellulose chains, which led to disrupting the intra/intermolecular hydrogen bond network between cellulose chains.[217]

Ionic liquids solvatochromic properties like, Kamlet–Taft parameters, viscosity and surface tension, which will be discussed in detail in the upcoming chapters in details are important parameters for cellulose dissolution.

Björn Lindman et al. (2010)[218] showed that cation of an ionic liquid interacts with cellulose chain and lignin via hydrophobic interactions with. Hydrogen at C-2 proton in the imidazolium moiety is highly acidic and are assume participate in hydrogen cellulose OH groups during cellulose dissolution in (1:1) stoichiometric ratio. Imidazolium-based ionic liquids interact with OH of cellulose ILs through a variety of different interactions, including dispersive, π–π, n–π, hydrogen bonding, dipolar, and ionic/charge–charge interactions.

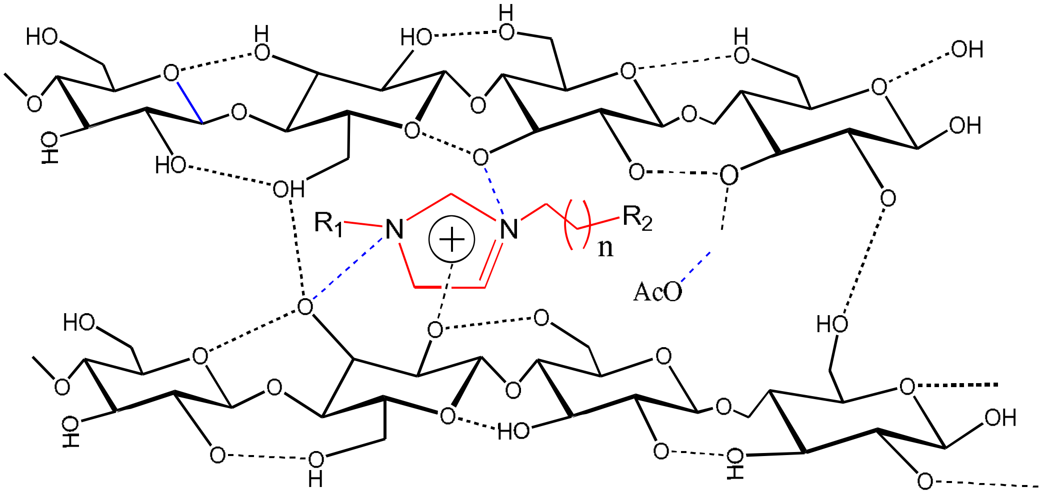


Figure 2.3 Interaction of imidazolium ionic liquid with OH groups of cellulose

Chenlin Li et al. (2010)[219] conducted a comparative analysis of dilute acid and 1-ethyl-3-methylimidazolium acetate ionic liquid pretreatment using switchgrass and compared with delignification, saccharification efficiency and saccharide yield. They found that ionic liquid pretreated switchgrass resulted in almost 100% sugar yield compare to acid treated (80%). With that, they also reported that ionic liquid pretreatment removed 69.2% of total lignin with 12.0% of acid-soluble lignin and 57.2% of Klason lignin compared with dilute acid pretreatment, which removed 22.4% and 13.7% of acid-soluble lignin and 8.7% of Klason lignin. The crystallinity of untreated switchgrass was (26.2 CrI), which was increased to CrI (39.1) in ionic liquid pretreatment but decreased too much extent in the case of ionic liquid pretreatment due to cellulose II amorphous transformation.

Du Hongbo et al. (2011)[220] conducted a study using quantum mechanics to see the interaction of imidazolium acetate and chloride based ionic liquid and OH of cellulose with anions and found that imidazolium cation of ionic liquid reacts with the acetate anion to generate a carbene, which is highly reactive intermediate, which was supposed to react with OH of cellulose to initiate the dissolution in ionic liquid with stronger hydrogen bonds formation between $[OAc]^-$ and OH of cellulose due to interaction of ion pairing via H-bonding and electrostatic interactions.

Similarly, Z. Ding et al. (2012)[221] theoretical and experimental investigated the dissolution and regeneration of cellulose in 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$), using (1,4)-dimethoxy-β-D-glucose as a model compound. They have found that hydrogen bonding of $[C_2mim][OAc]$ with glucose (Glu) is much stronger than that of Glc with Glc. They also found that this interaction reduced the intra/intermolecular hydrogen bonding between cellulose I change and are weakened or even destroyed by the addition of water. The regenerated cellulose was further characterised by FT-IR, XRD, TGA and SEM for crystalline structure change to cellulose II.

Liu et al. (2012)[222] conducted the similar study to investigate the mechanism of cellulose in 1-allyl-3-alkylimidazolium chloride ionic liquids by increasing carbon atoms ($n \leq 6$) of alkyl chains on a cationic 3-imidazole ring. With that they showed that 1-allyl-3-alkylimidazolium chloride with asymmetrical structure on the two sides of a cationic 3-imidazole ring (i.e., n = 1, 2, 6) exhibited higher alkalinity, lower thermal stabilities, and showed better solubility to the cellulose samples at 60–120 °C than those with symmetrical structures (n=3, 4). The cellulose samples treated by 20% (w/w) ethylenediamine solution showed better solubility in 1-allyl-3-ethyl, hexyl-imidazolium chloride ionic liquids than that treated with 20% (w/w) NaOH solution at 5 °C for 72 h. XRD and TGA analysis indicated that 002 planes apparent crystallite size as well as the thermal stability of the regenerated cellulose samples from the ionic liquids decreased significantly compared with the untreated cellulose samples.

Hui Tan et al. (2012)[223] correlated the cellulose digestibility of [C_4mim][Cl] IL oil palm with crystallinity, the degree of polymerization, specific surface area and with xylan and lignin removal. They also reported that cellulose digestibility of untreated oil palm after enzymatic hydrolysis was 22.57% and highest 99.78% was obtained after ionic liquid [C_4mim][Cl] at 80 °C with 8 wt.% solid loading for 3 h retention time. Crystallinity index/lateral order index (LOI) was calculated using absorbance at peaks 1430 and 897 cm^{-1}, with that they also reported that lignin content also plays an important role in the effectiveness of an ionic liquid in disrupting crystalline structure of cellulose.

Zenghui Qiu et al. (2012)[224] showed the impact of [C_2mim][OAc] ionic liquid pretreatment of energy cane bagasse conducted at 5% (w/w) solid loading at 120 °C for 30 min, followed by enzymatic hydrolysis of cellulose-rich material. And the pretreatment severity was calculated in term of structural modification, changes in chemical composition and glucose released after enzymatic hydrolysis. They reported that ionic liquid pretreatment helped to remove (32.0%) of lignin. The regenerated bagasse shows higher cellulose and hemicellulose digestibility (87.0%, 64.3%) than untreated (5.5% and 2.8%) or water-treated (4.0% and 2.1%) energy cane bagasse, respectively. The surface morphological study was further examined by FT-IR and XRD analyses.[225]

Shao-Ni Sun et al. (2012)[226] showed that in any biological conversion the pretreatment essential step to remove biomass recalcitrance for the productions of biofuels. They have demonstrated a pretreatment study using ionic liquid for corncob with 1-ethyl-3-methylimadazolium acetate [C_2mim][OAc] and/or H_2O/dimethyl sulfoxide (DMSO) followed by alkaline extraction to fractionate dissolve hemicelluloses and characterized them with gel permeation chromatography (GPC), thermogravimetric analysis (TGA), high-performance anion-exchange chromatography (HPAEC), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR). The showed that ionic liquid pretreatment helped to extract higher average molecular weight hemicellulose (196 230−349 480 g/mol) than without IL pretreatment (Mw, 96 260 g/mol. Furthermore, by FT-IR and NMR study they showed that extracted hemicellulose has (1→4) linked β-D-xylopyranosyl backbone substituted with arabinofuranosyls attached to O-2 and O-3 and with 4-O-methyl-α-D-glucuronic acid also linked to O-2.

Yuling Zhao et al. (2013)[227] showed the effects of the same anionic structure with varying cation of different ionic liquid on the dissolution of cellulose in ionic liquids by molecular simulation. They had found that strong hydrogen bonds were formed between anions of the ILs and OH proton of cellulose. They found that Cl^- anion and O atom of $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ are better hydrogen bond acceptors with a high electronegativity of hydrogen bond acceptor, the steric effect of alkyl chain length and an electron-withdrawing group of the anion. They suggested that hydrogen bond interaction between the ionic liquid anion and cellulose OH decreased with increasing chain length due to the steric effect. With that they also reported that hydrogen bonding capability of ionic liquid anion decreased in the order: $Cl^- > [CH_3COO]^- > [(CH_3O)_2PO_2]^- > [SCN]^- > [PF_6]^-$.

Airong Xu et al. (2014)[228] showed that 1-butyl-3-methylimidazolium acetate/dimethyl sulfoxide ($[C_4mim][OAc]$/DMSO) could dissolve cellulose significantly. They studied the cellulose dissolution in 1-butyl-3-methylimidazolium acetate $[C_4mim][OAc]$ and in $[C_4mim][OAc]$/DMSO-d_6 (Deuterated dimethyl sulfoxide)/cellulose solution to reveal the mechanism of cellulose dissolution in true $[C_4mim][OAc]$/DMSO solvent using ^{13}C NMR. They indicated that both cation and anion of $[C_4mim][OAc]$ in $[C_4mim][OAc]$/DMSO solvent dominate cellulose dissolution, and DMSO mainly serves to dissociate the ion pairs in $[C_4mim][OAc]$ into solvated cations and anions. Moreover, the hydrogen bonding interaction of anion of $[C_4mim][OAc]$ with cellulose hydroxyl proton is much stronger than that of the cation of $[C_4mim][OAc]$ with cellulose hydroxyl oxygen.

Similarly, Cao et al. (2016)[229] demonstrated the interaction of cellulose with acetate-based ILs and proposed a mechanism for cellulose solubilization using NMR spectra and DFT methods using cellobiose as cellulose substrate with $[C_4mim][OAc]$ ionic liquid. They found that cooperation of strong hydrogen bonding and van der Waals interactions between cellobiose and ILs cation and anion, correlated with thermodynamic analysis with an increase in dissolution temperature. They found the drastic shift in chemical shifts of ^1H and ^{13}C of hydrogen of hydroxyl in cellobiose, which is replaced by $[C_4mim]^+$ cation and form stronger hydrogen bonds with $[OAc]^-$ anion during dissolution. In the meanwhile, oxygen of hydroxyl in cellobiose forms weaker hydrogen bonds with an H-2 proton in $[C_4mim]^+$ cation.

H. Satria et al. (2017)[230] demonstrated the process for ionic liquid pretreatment using acidic ionic with H_2SO_4 and 1-(1-butylsulfonic)-3-methylimidazolium hydrosulfate $[(HSO_3)_4C_4C_1im]HSO_4]$ at 100 °C under microwave heating. Enzymatic hydrolysis of regenerated biomass was carried out and highest glucose (80%) and xylose (100%) were reported respectively and was attributed to the catalytic activity of the $[(HSO_3)_4C_4C_1im]HSO_4]$. Similarly, high sugar yield, 77% and 102%, were obtained for glucose and xylose respectively using H_2SO_4, with the addition of addition of $[(SO_3)_4C_4C_1im]$.