We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



4

The application of ionic liquids in dissolution and separation of lignocellulose

Jianji Wang[1], Yong Zheng[1] and Suojiang Zhang[2]
[1]*School of Chemical and Environmental Sciences, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007*
[2]*Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190*
[1, 2]*P. R. China*

1. Introduction

There are many problems in traditional chemical industry, such as environmental pollution, low production efficiency and high energy consumption. Nowadays, energy and environment become two main bottlenecks in the development of chemical industry. As non-renewable fossil resource, petroleum and coal are still widely used in the modern world. The excessive use of fossil resource will accelerate the deterioration of environment. Therefore, it is necessary to find new kinds of energy for the sustainable development and environmental protection.

Biomass is renewable, environmentally friendly and abundant in the natural world. According to the statistics, the total energy produced from photosynthesis is nearly ten times more than that of fossil fuel used in the world every year. However, the utilization rate of biomass energy is less than 1%. Although the preparation of ethanol from glucose and starch has already been employed in industry for a long time, the universal shortage of food restricts the application of this method in the large-scale production of clean energy. Therefore, it is very important to produce green energy and bio-products from lignocellulose which is the most abundant biomass (Pu et al., 2008; Zhu, 2008). Lignocellulose is hard to be dissolved and separated with common solvents due to its complex structure, strong intra- and inter-molecular hydrogen bonding. Traditional acid and basic systems used in the lignocellulose industry are environmentally polluted, and can not be recycled (Li et al., 2007). Therefore, development of new efficient solvents is the first step for the transformation and utilization of lignocellulose.

As novel green solvents, ionic liquids (ILs) have many attractive properties, including negligible vapor pressure, non-flammability, thermal stability and recyclability, and have been used in organic synthesis, electrochemistry, catalysis, extraction and among others (Qian et al., 2005; Dupont et al., 2002; Scurto et al., 2002; Kubo et al., 2002). In 2002, Rogers and co-workers (Swatloski et al., 2002) found that some hydrophilic ILs are effective solvents for the dissolution of cellulose. The high solubility of cellulose in the ILs attracts great attention of the scientists and engineers in the world. Since then, significant progress

has been made for the dissolution of cellulose and lignin as well as for the separation of lignocellulose components by using ILs (Zhu et al., 2006; Seoud et al., 2007; Winterton, 2006).
This chapter aims to provide a summary of our current state of knowledge in this field. Therefore, after a brief introduction to the structural features of the main components (cellulose, hemicellulose and lignin) of lignocellulose and the unusual physico-chemical properties of ionic liquids, the recent progress in the dissolution and separation of lignocellulose components with ILs is reviewed. The dissolution mechanism of cellulose in ILs and the regeneration and reuse of the ILs have also been discussed. At the end of this chapter, the challenges we have to face have been addressed and some suggestions are given for the future work.

2. The structural features and physico-chemical properties of lignocellulose components and ionic liquids

In this section, we will have a brief introduction to the structural features of cellulose, hemicellulose and lignin and the unusual physico-chemical properties of ionic liquids. This is designed to lay the foundation for the discussion of the major issues in the next sections.

2.1 The main components of lignocellulose and their structural features

Existed as plant cell wall, lignocellulose is mainly composed of cellulose, hemicellulose and lignin. These components have different proportions in various green plants. Generally speaking, the percentages of cellulose, hemicellulose and lignin are approximately 30~50%, 10~40% and 5~30%, respectively, in lignocellulose (McKendry, 2002). Cellulose is embedded in the network of lignin and hemicellulose which are connected by hydrogen and covalent bonds (Sun et al., 2005).
Cellulose is a typical biopolymer composed of *a-D*-glucopyranoside units linked by *β*-1,4 glycosidic bonds (see Figure 1) (Zhang et al., 2006). The degree of polymerization (DP) of natural cellulose always ranges from 1000 to 1000000 (Champagne & Li, 2009). The crystal structure of cellulose is very compact owing to its complex and extensive hydrogen bond networks which are hard to be broken. Consequently, cellulose is insoluble in common solvents.

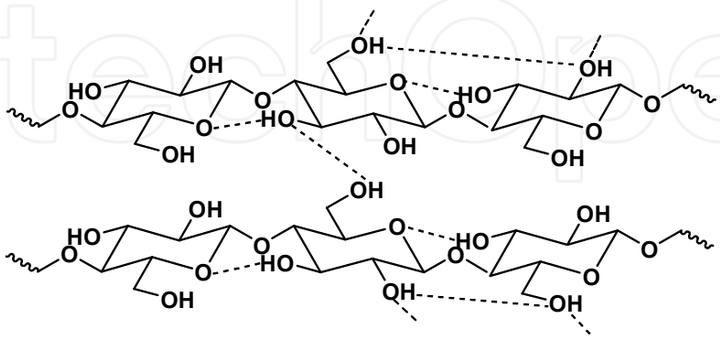
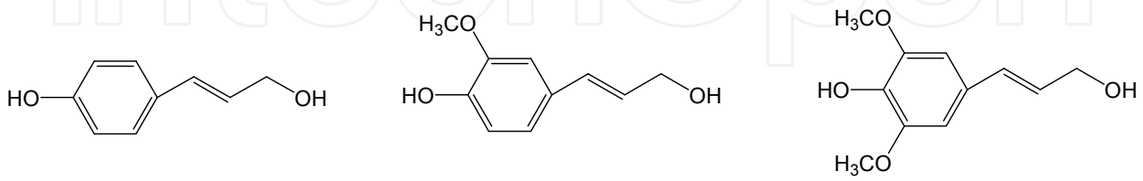


Fig. 1. The structure of cellulose. (Zhang et al., 2006)

Unlike cellulose, hemicellulose is not only a heteropolymer, but also a branched polymer. It is usually polymerized from different monomers, such as hexoses (glucose, mannose and galactose), pentoses (arabinose, xylose) and uronic acids (Vegas, et al., 2004). Because of its

amorphous structure and lower molecular weight, hemicellulose is more prone to be hydrolyzed by catalysts than cellulose (Liao et al., 2004).

The structure of lignin is much more complex than that of cellulose and hemicellulose. Lignin is a mixture made from the random oxidative coupling of *p*-hydroxycinnamyl monolignols (Río et al., 2008). There are three primary monolignols: *p*-coumaryl, coniferyl- and sinapyl alcohols (see Figure 2) (Hayatsu et al., 1979). As the three monolignols are incorporated into lignin, *p*-hydroxyphenyl, guaiacyl and syringyl units are formed. This makes lignin to have a cross-linked structure, strong chemical bonds and complex compositions. Accordingly, lignin is quite resistant to many chemicals, external forces and degradation.

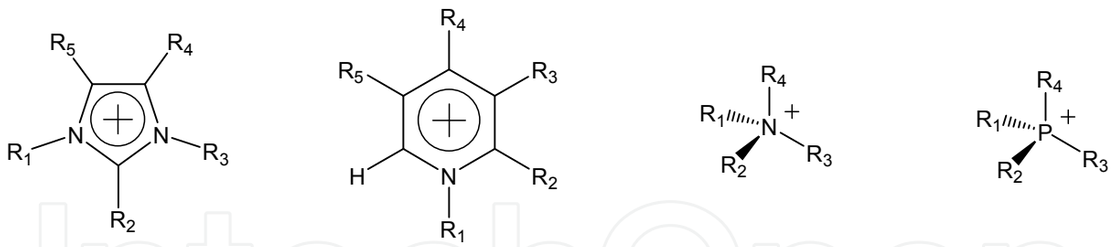


(a) (b) (c)

Fig. 2. The structures of three primary monolignols: (a) *p*-coumaryl alcohol, (b) coniferyl alcohol, (c) sinapyl alcohol. (Hayastu et al., 1979)

2.2 The structural features and physico-chemical properties of ionic liquids

In general, ILs are a class of organic salts that exist as liquids at the temperatures below 100°C. They are composed of organic cations and inorganic/organic anions. According to the structure of cations, these liquid salts can mainly be divided into imidazolium-, pyridinium-, quaternary ammonium- and quaternary phosphonium-based ionic liquids (see Figure 3).



(a) (b) (c) (d)

Fig. 3. The common structures of ILs' cations: (a) imidazolium, (b) pyridinium, (c) quaternary ammonium, (d) quaternary phosphonium.

Compared with traditional solvents, ILs have many excellent physico-chemical properties. These properties can be summarized as follows (Larsen et al., 2000; Zhao et al., 2002):

1) High thermal stability. The decomposition temperatures of many ILs can be more than 300°C.
2) Broad liquid range from -200 to 300°C, and excellent dissolution performance for organic, inorganic compounds and polymer materials.
3) Immeasurable vapor pressure and non-flammability under common conditions.
4) High conductivity and wide electrochemical window of 2~5 V.
5) Designable structures and properties for various practical applications.

It was shown that imidazolium-based ILs have better performance for the dissolution and separation of lignocellulose components than other ILs under the same conditions. This is probably due to the lower melting points, lower viscosity, higher thermal stability and unique structure of the imidazolium-based ILs. On the other hand, ILs are efficient in dissolution and separation of lignocellulose when they contain Cl^- (chloride), $[HCO_2]^-$ (formate), $[CH_3CO_2]^-$ (acetate, Ac^-), $[NH_2CH_2CO_2]^-$ (aminoethanic acid), $[CH_3SO_4]^-$ (methylsulfate), $[RR'PO_2]^-$ (phosphonate), $[Me_2C_6H_3SO_3]^-$ (xylenesulphonate) anions and so on.

3. The dissolution of cellulose and lignin in ionic liquids

The recent progress in the dissolution of lignocellulose components with ILs is summarized in this section. The main content includes the influence of cationic structure and anionic type of the ILs on the dissolution of cellulose, lignin and hemicellulose, the possible dissolution mechanism, and the recovery and reuse of ILs.

3.1 The dissolution of cellulose in ionic liquids

It was first discovered (Graenacher, 1934) in 1930s that cellulose could be dissolved in molten *N*-ethylpyridinium chloride. However, little attention was paid to this finding at that time. With the remarkable progress in the research and development of ILs, more and more researchers have recognized the importance of this field. Until 2002, study first shown that some imidazolium-based ILs could dissolve cellulose efficiently at low temperature (≤100°C) (Swatloski et al., 2002). Since then, more interesting results have been reported during the past few years (Zhang et al., 2005; Fukaya et al., 2006; Fukaya et al., 2008; Vitz et al., 2009; Xu et al., 2010), as shown in Table 1.

IL	Solubility (w/w %)	Experimental condition	Ref.
[Bmim]Cl	10	Heating at 100°C	Swatloski et al., 2002
[Bmim]Cl	25	Microwave heating	Swatloski et al., 2002
[Amim]Cl	5	Heating at 80°C within 30 min	Zhang et al., 2005
[Amim]Cl	14.5	Heating at 80°C after a longer dissolution time	Zhang et al., 2005
[Amim][HCO_2]	10	Heating at 60°C	Fukaya et al., 2006
[Emim][(MeO)HPO_2]	10	Heating at 45°C within 30 min	Fukaya et al., 2008
[Emim][(MeO)HPO_2]	2~4	Room-temperature within 3~5 h	Fukaya et al., 2008
[Emim][Et_2PO_4]	14	Heating at 100°C within 1 h	Vitz et al., 2009
[Bmim]Ac	15.5	Heating at 70°C	Xu et al., 2010
[Bmim][$HSCH_2CO_2$]	12	Heating at 70°C	Xu et al., 2010
[Bmim]Ac/LiAc	19	Heating at 70°C	Xu et al., 2010

Table 1. The dissolution of cellulose in some ILs. [a]

[a]: The cellulose samples used in these studies usually differed in DP, molecular weight or crystal structure.

It can be seen that in the ILs studied, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) shown excellent dissolution capability for cellulose. The solubility of cellulose in [Bmim]Cl was as high as 10% (w/w) at 100°C, which increased to 25% under microwave heating. Cellulose could be easily regenerated from the IL+ cellulose solutions by the addition of 1% water, while ILs could be recycled and reused after purification.

Some task-specific ILs have also been used to dissolve cellulose. For example, allyl-based ILs 1-allyl-3-methylimidazolium chloride ([Amim]Cl) and 1-allyl-3-methylimidazolium formate ([Amim][HCO_2]) were synthesized successively (Zhang et al., 2005; Fukaya et al., 2006). These ILs have lower melting points, lower viscosity and stronger dissolution capabilities for cellulose than those of the common imidazolium-based ILs with the same anions. 5% of cellulose (DP≈650) could be dissolved readily in [Amim]Cl at 80°C within 30min. After a longer dissolution time, 14.5% of cellulose solution can be obtained. If [Amim][HCO_2] was used as the solvent, the solubility of cellulose was as high as 10% at 60°C.

To reduce the production cost and improve the thermal stability of ILs, a series of alkylimidazolium ILs containing phosphonate-based anions have been synthesized (Fukaya et al., 2008; Vitz et al, 2009). These ILs include 1-ethyl-3-methylimidazolium methyl methylphosphonate ([Emim][(MeO)$MePO_2$]), 1-ethyl-3-methylimidazolium dimethyl phosphate ([Emim][$(MeO)_2PO_2$]), 1-ethyl-3-methyl-imidazolium methyl phosphate ([Emim][(MeO)HPO_2]), 1-ethyl-3-methylimidazolium diethyl phosphate ([Emim][Et_2PO_4]) and 1,3-dimethylimidazolium dimethyl phosphate ([Dmim][Me_2PO_4]). The preparation of these ILs could be accomplished by only one step with high conversion efficiency. As the main experimental material, alkylphosphate was cheap, less toxic and easy to purchase. The low melting points and viscosity of phosphonate-based ILs facilitated the dissolution of cellulose. It was reported that 10% of microcrystalline cellulose could be dissolved in [Emim][(MeO)HPO_2] within 30 min at 45°C (Fukaya et al., 2008). Even without pretreatment and heating, the solubility of cellulose could still reach 2~4%. A later research revealed that [Emim][Et_2PO_4] had the ability to dissolve up to 14% of cellulose at 100°C (Vitz et al., 2009). Furthermore, the regenerated cellulose from [Emim][Et_2PO_4] shown a much lower degradation than those regenerated from other ILs.

Our team has been working on the research of ILs for many years and gets much experience in the dissolution of cellulose in ILs (Xu et al., 2010). In our work, a series of ILs based on Brønsted anions, such as Ac^-, [$NH_2CH_2CO_2$]$^-$, [$HSCH_2CO_2$]$^-$ (thioglycollate) and [$OHCH_2CO_2$]$^-$ (glycollate) were synthesized and used to dissolve cellulose. Among these ILs, [Bmim]Ac and [Bmim][$HSCH_2CO_2$] were found to be the most efficient solvents for the dissolution of microcrystalline cellulose. The solubilities of cellulose were as high as 15.5% and 13.5% at 70°C, respectively. An enhanced dissolution of cellulose has been achieved by the addition of 1% of lithium salt into the IL solution. These lithium salts include LiAc, LiCl, LiBr, $LiClO_4$ and $LiNO_3$. For example, the solubility of microcrystalline cellulose could increase to 19% in [Bmim]Ac containing 1% of LiAc.

3.2 The dissolution mechanism of cellulose in ionic liquids

The excellent dissolution capability of ILs for cellulose inspires many researchers to explore the possible mechanism. In the early studies, it was widely believed that the ions, especially anions of the ILs could effectively break the extensive intra- and inter-molecular hydrogen bonding network in cellulose. Consquently, cellulose was finally dissolved in the ILs (Swatloski et al., 2002; Zhang et al., 2005; Fukaya, et al., 2006). Based on this hypothesis, the

interaction between ILs and cellulose was investigated by ^{13}C and $^{35/37}Cl$ NMR relaxation measurements (Remsing et al., 2006). They found that the carbons C-4'' and C-1' of $[Bmim]^+$ cation shown a slight variation in the relaxation times as the concentration of cellobiose in [Bmim]Cl increased (see Figure 4). Meanwhile, the value changes in ^{13}C T_1 and T_2 indicated that the $[Bmim]^+$ did not have specific interaction with cellobiose. However, the $^{35/37}Cl$ relaxation rates for the anion Cl^- was more dependent on the cellobiose concentration, which implied that Cl^- interacted strongly with cellobiose. Their study proved the presence of 1:1 hydrogen bonding between Cl^- and carbohydrate hydroxyl proton. Similar conclusions have also been obtained by computer modeling in a later literature (Novoselov et al., 2007).

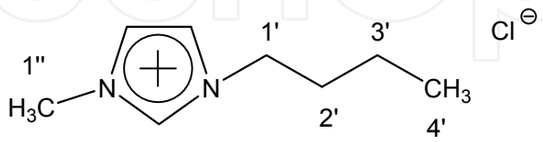


Fig. 4. The structure and numbering of [Bmim]Cl. (Remsing et al., 2006)

In our recent work, the effects of anionic structure and lithium salts addition on the dissolution of microcrystalline cellulose has also been studied through ^1H NMR, ^{13}C NMR and solvatochromic UV/vis probe measurements (Xu et al., 2010). It was known that the ^1H NMR chemical shift of proton H-2 in the imidazolium ring reflects the hydrogen bond accepting ability of the ILs' anions. When the H in the Ac^- anion of [Bmim]Ac was replaced by an electron-withdrawing group, such as -OH, -SH, $-NH_2$ or $-CH_2OH$, the solubility of microcrystalline cellulose and ^1H NMR chemical shifts of proton H-2 decreased. This indicates that the ILs whose anions have strong hydrogen bond accepting ability are more efficient in dissolving cellulose. Furthermore, the enhanced dissolution of cellulose achieved with the addition of lithium salts suggests that the interaction between Li^+ and the hydroxyl oxygen of cellulose can break the intermolecular hydrogen bonds of cellulose.

3.3 The dissolution of lignin in ionic liquids

Lignin is more difficult to be dissolved than the other components of lignocellulose because of its strong covalent bonds and complex structure. Pu and his co-workers have determined solubilities of the lignin isolated from a southern pine kraft pulp in some ILs, including 1,3-dimethylimidazolium methylsulfate ($[Mmim][MeSO_4]$), 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ($[Hmim][CF_3SO_3]$), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($[Bm_2im][BF_4]$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim][PF_6]$) and among others (Pu et al., 2007) (see Table 2).

IL	Temperature (°C)	Solubility (g/L)
$[Mmim][MeSO_4]$	50	344
$[Hmim][CF_3SO_3]$	70	275
$[Bmim][MeSO_4]$	50	312
[Bmim]Cl	75	13.9
[Bmim]Br	75	17.5
$[Bm_2im][BF_4]$	70-120	14.5
$[Bmim][PF_6]$	70-120	insoluble

Table 2. Solubilities of lignin in some ILs. (Pu et al., 2007)

The work of Pu and his co-workers shown that softwood lignin could be dissolved in [Mmim][$MeSO_4$] and [Bmim][$MeSO_4$] at room temperature. The solubilities of lignin in these ILs were about 74 g/L and 62 g/L, respectively. When heated up to 50~70°C, lignin sample was dissolved more rapidly in [Mmim][$MeSO_4$], [Bmim][$MeSO_4$] and [Hmim][CF_3SO_3] with solubilities ranging from 275 g/L to 344 g/L. For $[Bmim]^+$ based ILs, the solubilities of lignin followed the order: $[MeSO_4]^-$ > Cl^- > Br^- >> PF_6^-. Therefore, it can be concluded that anions of ILs have important effect on the dissolution of lignin. ILs always have a poor dissolution capability for lignin when they contain larger sized non-coordinating anions, such as PF_6^-.
Owing to the complex structure and strong intra-molecular interactions of lignocellulose, the natural lignin in wood is much more difficult to be dissolved than the pure lignin. However, it is necessary to develop efficient solvents for the dissolution of natural lignin in order to promote the application of lignocellulose. Accordingly, the dissolution of lignin-rich wood in ILs has been studied (Kilpeläinen et al., 2007). It was found that wood chips could be partially dissolved in some ILs, such as [Bmim]Cl. Wood sawdust sample was easier to be dissolved in ILs and its solubilities were both 8% in [Bmim]Cl and [Amim]Cl at 110°C. A 5% of Norway spruce momechanical pulp (TMP) solution could be formed in 1-benzyl-3-methylimidazolium chloride ([Bzmim]Cl) at 130°C (see Table 3). The order of dissolution efficiency of lignocellulose in ILs was: ball-milled wood powder > sawdust ≥ TMP fibers >> wood chips. It can be inferred that the particle size of wood sample is vital to the wood solubilization. As the structure of wood sample is incompact, ILs are easy to diffuse into the wood's interior and break the intermolecular forces, resulting in a higher solubility of wood.

IL	Wood sample [a]	Solubility (w/w%)	Dissolution condition
[Amim]Cl	Norway spruce sawdust	8	Heating at 110°C, 8h
[Amim]Cl	Ball-milled Southern pine powder	8	Heating at 80°C, 8h
[Bmim]Cl	Norway spruce sawdust	8	Heating at 110°C, 8h
[Bmim]Cl	Norway spruce TMP	7	Heating at 130°C, 8h
[Bmim]Cl	Wood chips	Partially soluble	Heating at 130°C, 8h
[Bzmim]Cl	Norway spruce TMP	5	Heating at 130°C, 8h

Table 3. The dissolution of wood samples in ILs. (Kilpeläinen et al., 2007)
[a]: The wood samples have been subjected to some mechanical pre-treatment before use.

Another study shown that 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) had a higher solvation power for lignin-rich wood than [Bmim]Cl and many other ILs (Sun et al., 2009). Nearly 5% (w/w) of southern yellow pine (total lignin content: 31.8%) or red oak (total lignin content: 23.8%) could be dissolved in [Emim]Ac after mild grinding at 110°C. As the authors analyzed, two main reasons might account for these results. Firstly, the inter- and intra-molecular hydrogen bonds in wood can be efficiently disrupted by the stronger basicity of acetate anion; Secondly, the low melting point and low viscosity of [Emim]Ac facilitate the dissolution of wood.

4. The separation of the main components of lignocellulose with ionic liquids

The efficient separation of the main components of lignocellulose is very important for the utilization of lignocellulose. Although it is difficult to achieve this goal, researchers have explored the possibility for the separation of lignocellulose components with ILs, and some important results have been reported.

4.1 The separation of cellulose from lignocellulose with ionic liquids

It was reported that wood could be regenerated from imidazolium-based IL (such as [Bmim]Cl, [Amim]Cl and [Bzmim]Cl) + wood solutions as an amorphous mixture of its original components after the addition of water (Kilpeläinen et al., 2007). Using cellulase as catalyst, the regenerated cellulose of wood could be converted into glucose, and the hydrolysis percentage of cellulose was about 60%. This provides a new way for the separation of the cellulose of lignocellulose

Cellulose can also be separated from lignocellulose with [Bmim]Cl based on the different solubilities of the main components of lignocellulose (Fort et al., 2007). Their work shown that some untreated wood (oak, eucalyptus, poplar and pine) could be partially dissolved in [Bmim]Cl at 100°C. After the removal of un-dissolved materials, cellulose could be regenerated from [Bmim]Cl + lignocellulose solutions by the addition of one to two volumes of the precipitation solvents, such as 1:1 acetone-water solutions, dichloromethane and acetonitrile. Yields of the reconstituted cellulose ranged from 30 to 60%. Through the characterization of ^{13}C NMR and IR spectrum, the regenerated cellulose was found to be free of lignin and hemicellulose. The properties of cellulose obtained in this way was similar to those of microcrystalline cellulose regenerated from [Bmim]Cl + cellulose solutions.

4.2 The separation of lignin from lignocellulose with ionic liquids

Some researchers have studied the separation of lignin from lignocellulose-rich wood with ILs (Lee et al., 2009). In their work, [Emim]Ac was first used to pretreat 5% (w/w) of wood flour at 90°C for 24h. The mixture was washed with water to remove the extract from the residual wood flour solids. After the evaporation of water, [Emim]Ac solution was reused for the pre-treatment of wood flour, and the lignin concentration was increased (see Table 4). Furthermore, chemically unmodified and highly hydrophobic lignin could be easily precipitated from concentrated lignin + [Emim]Ac solutions by the addition of excess water.

Reuse of [Emim]Ac	Extracted lignin content (g/kg) [a]	Digestibility of pretreated wood flour (%)
0	6.9	95.7
1st	14.2	92.1
2nd	21.3	92.7
3rd	28.4	92.7
4th	35.6	90.2

Table 4. Reuse of [Emim]Ac for the pre-treatment of wood flour. (Lee et al., 2009)
[a]: Determined by Indulin AT (kraft lignin) standard.

Lignin can also be separated from lignocellulose with xylenesulphonate- and benzoate-based ILs (Upfal et al., 2005). As indicated by Upfal et al., lignin-containing material (bagasse and wood pulp) could be dissolved in ILs, such as 1-ethyl-3-methyl-imidazolium xylenesulphonate ([Emim][XS]), tetrabutylammonium xylenesulphonate ([TBA][XS]) and tetrabutylammonium benzoate ([TBA][Bz]) in the temperature range of 100~180°C. After the complete dissolution of lignin-containing material, the solid cellulosic components were filtered and a clear lignin/IL solution was formed. Then, lignin could be separated by precipitation and extraction methods. In the former method, lignin was precipitated from lignin + IL solutions by the addition of water, and adjustment of temperature and/or pH of the solutions. In the latter method, lignin could be extracted into immiscible organic solvents, such as polyethylene glycol, and then separated by distillation. In this way, 60~86% of the lignin component was separated from lignocellulosic materials and the ILs could be regenerated and reused in the separation process (see Table 5).

IL	pH	Lignin removed (%)	Recovered IL (%) [b]
[Emim][XS]	6	70.65	102
[Emim][XS]	4	64.46	101
[TBA][XS]	4.5	70.61	90
[TBA][XS]	9	65.26	84
[TBA][Bz]	7	68.39	48
[TBA][Bz]	4.5	74.15	56

Table 5. The efficiency in the removal of lignin from bagasse and in the recovery of ILs (Upfal et al., 2005). [a]

[a]: The temperature of dissolution was from 100 to 180°C.

[b]: Based on lignin recovery as calculated by Kappa number determination.

4.3 The separation of both cellulose and lignin from lignocellulose with ionic liquids

Cellulose and lignin can be separated from lignocellulosic materials with ILs according to the results of a patent (Myllymaki & Aksela, 2005). In their work, lignocellulose-rich wood and straw which had not been subjected to any chemical or mechanical pulping process were used as experimental materials. Lignocellulosic materials were first dissolved in [Bmim]Cl under microwave heating at the temperatures range from 80 to 170°C and/or under pressure. Then, lignin was separated from IL + lignocellulose solutions by extraction, and cellulose could be separated from the remained solutions by the addition of water or ethanol.

Unlike Myllymaki et al. who used natural lignocellulose as experimental materials, Lateef's group used cellulose/lignin mixtures as the model lignocellulosic materials to investigate the separation of cellulose from lignin with ILs (Lateef et al., 2009). Three ionic liquids 1-(2-cyanoethyl)-3-methylimidazolium bromide ([Cmim]Br), 1-propyl-3-methylimidazolium bromide ([Pmim]Br) and [Bmim]Cl were synthesized and used as solvents. A mixture of cellulose and lignin was dissolved in each of these ILs at 80~90°C. After the saturated solution of cellulose/lignin was created, cellulose was regenerated by the addition of water

(see Figure 5). The remained solution of lignin in IL was concentrated by the distillation of water under reduced pressure. Then, lignin could be precipitated by the addition of ethanol (see Figure 6). The recovery yields of cellulose and lignin were 98~99% and 83~97%, respectively. In general, this work shows us a good example for the separation of natural lignocellulose with ILs.

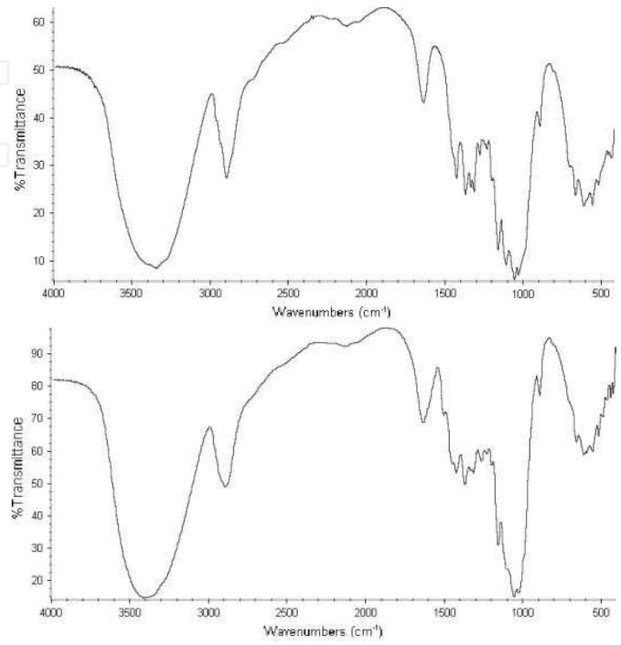


Fig. 5. FTIR spectra: (a) pure cellulose, (b) recovered cellulose from [Bmim]Cl. (Lateef et al., 2009)

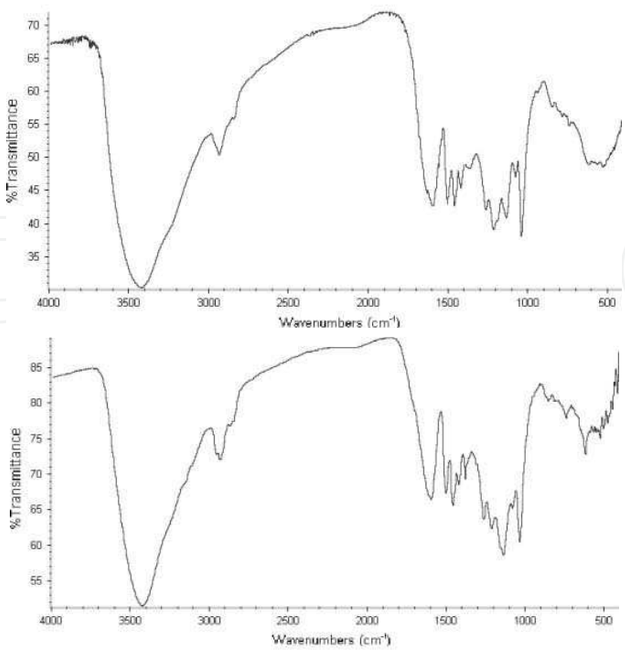


Fig. 6. FTIR spectra: (a) pure lignin, (b) recovered lignin from [Bmim]Cl. (Lateef et al., 2009)

From the discussion above, it can be concluded that the main components (cellulose, lignin and hemicellulose) of lignocellulose can be separated by various experimental methods. The typical process for the separation of lignocellulose with ILs is summarized in Figure 7.

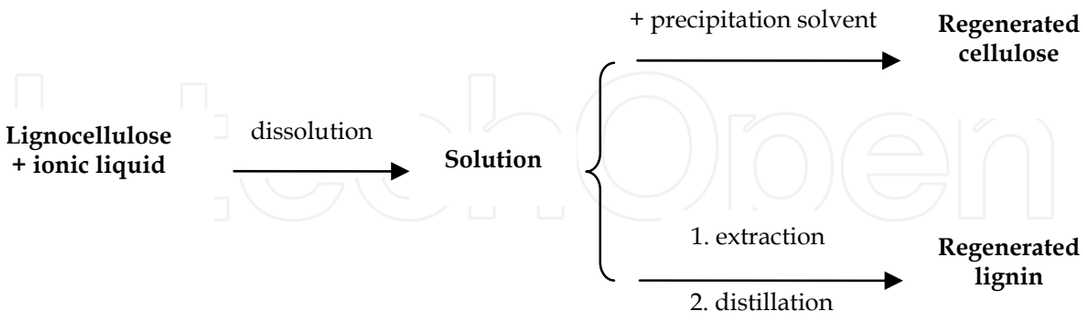


Fig. 7. The typical process for the separation of lignocellulose with ILs.

5. Future challenges

Because of the worldwide energy shortage and environmental pollution, we have to make full use of lignocellulose in order to develop clean energy and bio-products in the future. ILs have played a important role in the production of clean energy owing to their excellent physico-chemical properties and outstanding performance in the dissolution and separation of lignocellulose. However, the research on this area is still at its infant stage and some problems have to be solved. In the future work, the following main issues are suggested.

1) To study the interaction mechanism between ILs and cellulose, hemicellulose or lignin further through macroscopic and microcosmic methods, and to know how cations and anions of the ILs disrupt the cross-linked structure, and the intra- and inter-molecular hydrogen bonding of lignocellulose.

2) To develop the knowledge of the relationship between the structure of ILs and their dissolution performance for cellulose, hemicellulose and lignin, and then to design and prepare more new task-specific ILs which are ought to have low viscosity, low melting points and high dissolution and separation capability for lignocellulose.

3) To develop inexpensive methods for the recovery and recycle of ILs, and to promote the applicaiotn of mircowave heating and other intensification technologies in the dissolution and separation of lignocellulose components with ILs.

4) To investigate the effect of precipitation solvents on the crystalline state and thermo-physical properties of regenerated cellulose, hemicellulose and lignin, and then to regulate the structure and properties of the regenerated components for different applications.

6. References

Pu, Y.; Zhang, D.; Singh, P. M. & Ragauskas, A. J. (2008). The new forestry biofuels sector. *Biofuels Bioprod. Bioref.*, Vol. 2, Issue 1, (January 2008) 58-73, ISSN 1932-104X

Zhu, S. (2008). Use of ionic liquids for the efficient utilization of lignocellulosic materials. *J. Chem. Technol. Biotechnol.*, Vol. 83, Issue 6, (June 2008) 777-779, ISSN 0268-2575

Li, D.; Li, K.; Ma, Y.; Gong, G. & Qu, F. (2007). Progress in studies of dissolution of cellulose with ionic liquid. *Synthetic Fiber in China*, Vol. 36, Issue 2, (February 2007) 28-32, ISSN 1001-7054

Qian, W.; Jin, E.; Bao, W. & Zhang, Y. (2005). Clean and highly selective oxidation of alcohols in an ionic liquid by using an ion-supported hypervalent iodine(III) reagent. *Angew. Chem. Int. Ed.*, Vol. 44, Issue 6, (January 2005) 952-955, ISSN 1433-7851

Dupont, J.; Souza, R. F. D. & Suarez, P. A. Z. (2002). Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.*, Vol. 102, Issue 10, (August 2002) 3667-3692, ISSN 0009-2665

Scurto, A. M.; Aki, S. N. V. K. & Brennecke, J. F. (2002). CO as a separation switch for ionic liquid/organic mixtures. *J. Am. Chem. Soc.*, Vol. 124, Issue 35, (August 2002) 10276-10277, ISSN 0002-7863

Kubo,W.; Kitamura,T.; Hanabusa, K.; Wada, Y. & Yanagida, S. (2002). Quasi-solid-state dye-sensitized solar cells using room temperature molten salts and a low molecular weight gelator. *Chem. Commun.*, Issue 4, (January 2002) 374-375, ISSN 1359-7345

Swatloski, R. P.; Spear, S. K.; Holbrey, J. D. & Rogers, R. D. (2002). Dissolution of cellose with ionic liquids. *J. Am. Chem. Soc.*,. Vol. 124, Issue 18, (April 2002) 4974-4975, ISSN 0002-7863

Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y. & Wu, G. (2006) Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chem.*, Vol. 8, Issue 4, (March 2006) 325-327, ISSN 1463-9262

Seoud, O. A. E.; Koschella, A.; Fidale, L. C.; Dorn, S. & Heinze, T. (2007). Applications of ionic liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules*, Vol. 8, Issue 9, (August 2007) 2629-2647, ISSN 1525-7797

Winterton, N. (2006). Solubilization of polymers by ionic liquids. *J. Mater. Chem.*, Vol. 16, Issue 44, (October 2006) 4281-4293, ISSN 0959-9428

McKendry, P. (2002) Energy production from biomass (part 1): overview of biomass. *Biores. Technol.*, Vol. 83, Issue 1, (May 2002) 37-46, ISSN 0960-8524

Sun, X.; Sun, R.; Fowler, P. & Baird, M. S. (2005) Extraction and characterization of original lignin and hemicelluloses from wheat straw. *J. Agric. Food Chem.*, Vol. 53, Issue 4, (February 2005) 860-870, ISSN 0021-8561

Zhang, S.; Lv, X. et al. (2006). *Ionic liquids-from basic research to application in industry*. Science Press, ISBN 7-03-016882-8, Beijing

Champagne, P. & Li, C. (2009). Enzymatic hydrolysis of cellulosic municipal wastewater treatment process residuals as feedstocks for the recovery of simple sugars. *Biores. Technol.*, Vol. 100, Issue 23, (December 2009) 5700-5706, ISSN 0960-8524

Vegas, R.; Alonso, J. L. Domínguez, H. & Parajó, J. C. (2004). Processing of rice husk autohydrolysis liquors for obtaining food ingredients. *J. Agric. Food Chem.*, Vol. 52, Issue 24, (November 2004) 7311-7317, ISSN 0021-8561

Liao, W.; Liu, Y.; Liu, C. & Chen, S. (2004). Optimizing dilute acid hydrolysis of hemicellulose in a nitrogen-rich cellulosic material-dairy manure. *Biores. Technol.*, Vol. 94, Issue 1, (August 2004) 33-41, ISSN 0960-8524

Río, J. C. D.; Rencoret, J.; Marques, G.; Gutiérrez, A.; Ibarra, D.; Santos, J. I.; Barbero, J. J.; Zhang, L. & Martínez, Á. T. (2008). Highly acylated (acetylated and/or *p*-coumaroylated) native lignins from herbaceous plants. *J. Agric. Food Chem.*, Vol. 56, Issue 20, (September 2008) 9525-9534, ISSN 0021-8561

Hayatsu, R.; Winans, R. E.; Mcbeth, R. L.; Scott, R. G.; Moore, L. P. & Studier, M. H. (1979). Lignin-like polymers in coals. *Nature*, Vol. 278, (March 1979) 41-43, ISSN 0028-0836

Larsen, A. S.; Holbrey, J. D.; Tham,F. S. & Reed, C. A. (2000). Designing ionic liquids: imidazolium melts with inert carborane anions. *J. Am. Chem. Soc.*, Vol. 122, Issue 30, (July 2000) 7264-7272, ISSN 0002-7863

Zhao, D.; Wu, M.; Kou, Y. & Min, E. (2002). Ionic liquids: applications in catalysis. *Catal. Today*, Vol. 74, Issue 1, (May 2002) 157-189, ISSN 0920-5861

Grenacher, C. (1934). Cellulose solution. US Patent Office, Pat. No. 1943176

Zhang, H.; Wu, J.; Zhang, J. & He, J. (2005). 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: a new and powerful nonderivatizing solvent for cellulose. *Macromolecules*, Vol. 38, Issue 20, (September 2005) 8272-8277, ISSN 0024-9279

Fukaya, Y.; Sugimoto, A. & Ohno, H. (2006). Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates. *Biomacromolecules*, Vol. 7, Issue 12, (November 2006) 3295-3297, ISSN 1525-7797

Fukaya, Y.; Hayashi, K.; Wada, M. & Ohno, H. (2008). Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. *Green Chem.*, Vol. 10, Issue 1, (November 2008) 44-46, ISSN 1463-9262

Vitz, J.; Erdmenger, T.; Haensch, C. & Schubert, U. S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chem.*, Vol. 11, Issue 3, (January 2009) 417-424, ISSN 1463-9262

Xu, A.; Wang, J. & Wang, H. (2010). Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. *Green Chem.*, Vol. 12, Issue 2, (November 2009) 268-275, ISSN 1463-9262

Remsing, R. C.; Swatloski, R. P.; Rogers, R. D. & Moyna, G. (2006). Mechanism of cellulose dissolution in the ionic liquid 1-*n*-butyl-3-methylimidazolium chloride: a ^{13}C and $^{35/37}Cl$ NMR relaxation study on model systems. *Chem. Commun.*, Issue 12, (February 2006) 1271-1273, ISSN 1359-7345

Novoselov, N. P.; Sashina, E. S.; Petrenko, V. E. & Zaborsky, M. (2007). Study of dissolution of cellulose in ionic liquid by computer modeling. *Fibre Chem.*, Vol. 39, Issue 2, (March 2007) 153-158, ISSN 0015-0541

Pu, Y.; Jiang, N. & Ragauskas, A. J. (2007). Ionic liquid as a green solvent for lignin. *J. Wood Chem. Technol.*, Vol. 27, Issue 1, (January 2007) 23-33, ISSN 0277-3813

Kilpeläinen, I.; Xie, H.; King, A.; Granstrom, M.; Heikkinen, S. & Argyropoulos, D. S. (2007). Dissolution of wood in ionic liquids. *J. Agric. Food Chem.*, Vol. 55, Issue 22, (October 2007) 9142-9148, ISSN 0021-8561

Sun, N.; Rahman, M.; Qin, Y.; Maxim, M. L.; Rodríguez, H. & Rogers, R. D. (2009). Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methyl-imidazolium acetate. *Green Chem*., Vol. 11, Issue 5, (March 2009) 646-655, ISSN 1463-9262

Fort, D. A.; Remsing, R. C.; Swatloski, R. P.; Moyna, P.; Moyna, G. & Rogers, R. D. (2007). Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-*n*-butyl-3-methylimidazolium chloride. *Green Chem*., Vol. 9, Issue 1, (January 2007) 63-69, ISSN 1463-9262

Lee, S. H.; Doherty, T. V.; Linhardt, R. J. & Dordick. J. S. (2009). Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. *Biotechnol*. *Bioeng*., Vol. 102, Issue 5, (April 2009) 1368-1376, ISSN 0006-3592

Upfal, J.; Macfarlane, D. R. & Forsyth, S. A. (2005). Solvents for use in the treatment of lignin-containing materials. WO Pat, 2005/017252, (February 2005)

Myllymaki, V. & Aksela, R. (2005). Dissolution method for lignocellulosic materials. WO Pat, 2005/017001, (February 2005)

Lateef, H.; Grimes, S.; Kewcharoenwong, P. & Feinberg, B. (2009). Separation and recovery of cellulose and lignin using ionic liquids: a process for recovery from paper-based waste. *J. Chem*. *Technol*. *Biotechnol*., Vol. 84, Issue 12, (August 2009) 1818-1827, ISSN 0268-2575



Clean Energy Systems and Experiences

Edited by Kei Eguchi

ISBN 978-953-307-147-3
Hard cover, 178 pages
Publisher Sciyo
Published online 05, October, 2010
Published in print edition October, 2010

This book reports the latest developments and trends in "clean energy systems and experiences". The contributors to each chapter are energy scientists and engineers with strong expertise in their respective fields. This book offers a forum for exchanging state of the art scientific information and knowledge. As a whole, the studies presented here reveal important new directions toward the realization of a sustainable society.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Jianji Wang, Yong Zheng and Suojiang Zhang (2010). The Application of Ionic Liquids in Dissolution and Separation of Lignocellulose, Clean Energy Systems and Experiences, Kei Eguchi (Ed.), ISBN: 978-953-307-147-3, InTech, Available from: http://www.intechopen.com/books/clean-energy-systems-and-experiences/the-application-of-ionic-liquids-in-dissolution-and-separation-of-lignocellulose

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License, which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen