

## Dissolution of kraft lignin using Protic Ionic Liquids and characterization



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### ABSTRACT

In the present research three Protic Ionic Liquids (pyridinium formate, pyridinium acetate and pyridinium propionate) were synthesized and tested for the dissolution and subsequent regeneration of kraft lignin. Among the investigated solvents, pyridinium formate showed a higher dissolution capacity (70% w/w) i.e. (710 g/L) at 75 °C within 1 h. The results indicated that the introduced solvent is thermally stable, noncorrosive, possesses low viscosity and is easy to recycle. The dissolution process is purely physical and the physicochemical analysis of the regenerated lignin showed high thermal stability, with reduction in polydispersity and the average molecular weight was reduced from 4119 g/mol to 1249 g/mol. FTIR spectroscopy and <sup>1</sup>H NMR results proved that the regenerated lignin is less degraded. Moreover the O–H vibrations of regenerated lignin showed a weak inter and intramolecular interaction in regenerated lignin, which could positively help in reducing its chemical resistance towards processing for further commercial applications. Due to the higher solubility of lignin and its stability towards recyclability, the pyridinium formate proved that present selective dissolution and regeneration of lignin could significantly enhance the pretreatment techniques for lignocellulosic biomass.

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## 1. Introduction

Lignin is considered as the second most abundant organic, natural compound in the world and is also considered as a renewable source of aromatic and chemical feedstock. The concept of bio refinery comprises the selective separation of the three main polymeric wood components namely, cellulose, hemicellulose and lignin, and their subsequent utilization for the production of fuels and high value added chemicals. Cellulose and hemicellulose fractions can be readily used as a starting material for the production of biofuels and biochemicals, whereas the efficient utilization of lignin presents an ongoing challenge (Zhang, 2008). The separation techniques employed for lignocellulosic biomass components (i.e., cellulose, hemicellulose, and lignin) are mostly conducted in destructive ways to obtain comparatively pure cellulose, which results in degraded lignin that can only be used as a low value by products or burnt as a low-grade fuel (Zhang, 2008; Zakrzewska et al., 2010). Therefore a key challenge remains on the achievement of an effi-

cient, cost effective technology and selective separation of native lignin. Kraft and sulfite processes are the oldest and most common technologies for commercial delignification of wood. However, the high energy inputs and potential pollutants involved (sulfur containing reagents) in the process make it uneconomical. Moreover high temperature and pressure conditions degrade the cellulose structure and lead to the destruction of the fermentable sugar i.e., glucose (Baptista et al. 2008; Gellerstedt and Henriksson, 2008; Vila et al., 2003). Organosolv pulping process has several advantages over sulphite and kraft process through which some of the above-mentioned drawbacks were eliminated (Alriols et al., 2009; Li et al., 2012; Vila et al., 2003). Though it is possible to obtain a sulfur free lignin with minimum degradation, however the major drawbacks of this technique are thermal instability of solvent and high cost for solvent regeneration (Sundquist, 1988). da Costa Lopes et al. (2013a) introduced a fractionation methodology by using 1-ethyl-3-methylimidazolium acetate for wheat straw cooking followed by alkaline extraction at 120 °C for 6 h and the reported lignin contents were very low (i.e., 41.8% cellulose, 25.4% hemicellulose and 8.0% lignin). Later a multiple linear regression model was developed by da Costa Lopes et al. (2013b) based on their experimental results at various operating conditions.

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Lignin is the second most important constituent of lignocellulosic biomass, although far less attention has been given to its recovery. The lignin content in normal hardwood and softwood varies from 20% to 30% and 26% to 32% respectively (Maki Arvela et al., 2010; Sun and Cheng, 2002). Lignin is a highly branched aromatic polymer that binds cellulose and hemicellulose via strong hydrogen bonding and ester linkages, which act as “glue binding” in the whole lignocellulosic biomass. These linkages and molecular interactions cause rigidity and microbial resistance in the lignocellulosic biomass. Furthermore, lignin behaves quite differently in solutions compared to cellulose, as the dissolution mechanisms for lignin and cellulose are different. The solubility of cellulose increases almost linearly with hydrogen bonding strength, but in case of lignin it is reverse (Hart et al., 2015; Horvath, 2006; Lee et al., 2009; Vitz et al., 2009).

Recently Imidazolium based Aprotic Ionic Liquids (AIL's) with short side alkyl chains have been extensively used for the dissolution and delignification of biomass (King et al., 2009; Pu et al., 2007). A comprehensive studies regarding lignocellulose (i.e., cellulose, lignin, and monosaccharides) solubility in IL's was performed by Zakrzewska et al. (2010). Among the IL's investigated, Imidazolium chloride was found to be more suitable for cellulose dissolution, whereas Imidazolium acetate was considered as the best IL for lignin dissolution. It was also concluded that acetate as anion reduces the thermal stability of the solvent. Despite their usefulness, AIL's do have certain drawbacks namely high viscosity and high operating temperature and recoverability etc. Apart from these issues, extended dissolution times are required for processing, (generally >12 h). High viscosity and cost of IL's were reduced by using polar organic solvents as a co-solvent and a variety of co-solvents, including dimethylsulfoxide (DMSO) and *N,N*-dimethylformamide (DMF), have been tested for delignification (Mai et al., 2014; Pinkert et al., 2011; Rinaldi, 2011). However a comprehensive study on the effect of co-solvents is still lacking. Protic Ionic Liquids (PIL's) possess excellent chemical and thermal stability and negligible vapor pressure and they are capable of hydrogen bonding, including proton acceptance and proton donation. Protic IL's are less expensive than traditional Imidazolium-based AIL's. Protic acetate PIL's were studied for delignification of biomass and the lignin extraction was found to be  $\geq 50\%$  w/w. But due to a lower degree of protonation (e.g., less ionicity) of amines by acetic acid protic acetates were found to be thermally unstable (Achinivu et al., 2014). Recently a techno-economic investigation study along with thermal stability comparison was reported for protic ammonium hydrogen sulfate using AIL (i.e., 1-ethyl-3-methylimidazolium acetate) as benchmark and the results are comparable (George et al., 2015). Due to their numerous desirable properties they offer an attractive alternative to conventional nonionic solvents. Based on the disadvantages of the available techniques for complete delignification and regeneration of lignin, in the present research an attempt has been made to use cost effective and easy to synthesize pyridinium based Protic Ionic Liquids with different anionic compounds and hydrogen bond basicity for the selective dissolution of lignin.

For the present research pyridine is selected due to its classic tailored property, through which pyridine can be easily attached to different anions (Scriven and Murugan, 2000) also it has a high mobile proton with a tendency of both electron pair donor and proton acceptor (Shimizu et al., 2000). Pyridine is used in drug formulation, insecticides, plant growth regulator, and other agricultural products etc. (Chaubey and Pandeya, 2011; Haviv et al., 1983; Maga, 1981). In this study carboxylic acid anions are preferably selected due to their advantages; namely, low melting points, low viscosities, and high hydrogen bonding acceptor abilities, all of which should facilitate the dissolution of lignin. Moreover, weak organic acids are less toxic and less corrosive compared to the

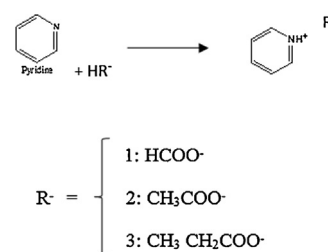


Fig. 1. General scheme of the reaction.

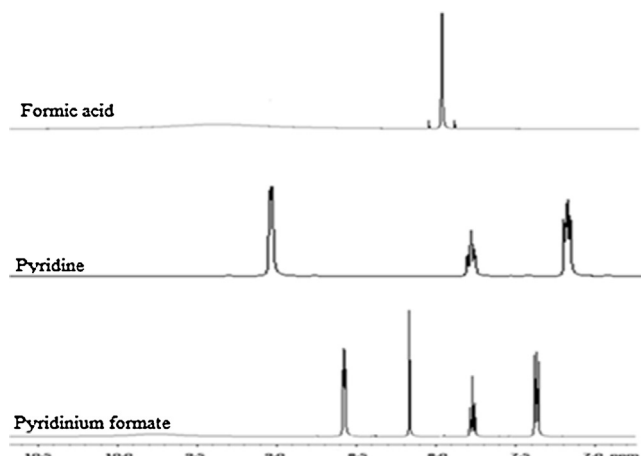


Fig. 2.  $^1\text{H}$  NMR spectra of pyridinium formate and its precursors in  $\text{DMSO-d}_6$ .

mineral acids commonly used for the delignification of the lignocellulose (Li et al., 2012; Zhang et al., 2010; Zhou et al., 2012).

## 2. Material and methods

### 2.1. Materials

The chemicals used for the present research namely, Pyridine, Formic acid, Glacial Acetic acid, Propionic acid, Chemicals for Karl Fischer titration, Dimethyl Sulphoxide ( $\text{DMSO-d}_6$ ) (used as a solvent for NMR samples), Lignin (kraft lignin-indulin AT), Microcrystalline Cellulose (MCC) (with a particle size of 20–150  $\mu\text{m}$ ), Sodium hydroxide, Methanol, Acetone (99% purity), were of analytical grade and purchased from Sigma-Aldrich. All the chemicals were used as received. Triple distilled water was used for the preparation of all aqueous solutions.

### 2.2. Synthesis of pyridinium based Protic Ionic Liquids

Pyridinium based Protic Ionic Liquids are produced when a proton is transferred from a carboxylic acid to pyridine and the general scheme of the reaction is shown in Fig. 1. For the present study three anions are selected based on increasing alkyl chain length i.e.  $[\text{HCOO}^-]$ ,  $[\text{CH}_3\text{COO}^-]$  and  $[\text{CH}_3\text{CH}_2\text{COO}^-]$ , and the PIL's namely pyridinium formate [PyFor], pyridinium acetate [PyAce] and pyridinium propionate [PyPro] respectively were prepared according to the established procedures (Belieres and Angell, 2007). The PIL's thus prepared were kept in the vacuum oven at  $80^\circ\text{C}$  for 48 h, in order to remove the excess moisture, which was formed during the reaction. The oven dried solvent was sealed with laboratory parafilm to prevent any moisture contamination. The characterization analysis using  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ , 500 MHz) (Fig. 2.), TGA (Fig. 3.) and Karl Fischer water content analysis performed on the [PyFor] showed the following results respectively;  $[\delta = 7.37(2\text{H}, \text{d})$ ,

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