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Ionic liquid mediated degradation of lignin to platform chemicals

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1. Introduction

Lignocellulosic biomass is fast emerging as the major renewable feedstock in terms of providing platform chemicals for the future green fuel and chemical industry. However, almost all the efforts in this direction have focused on use of cellulosic components of biomass. Lignin, comprising 10% to 30% of any lignocellulosic biomass, has remained a neglected natural resource. Molecular structure of lignin comprising a network of phenylpropanoids, however, makes it a potential candidate for conversion to platform chemicals and high-octane fuel additives (as gasoline blending agents) such as aromatic hydrocarbons and/or ethers. Most processes used for delignifying biomass produce polymeric or partially depolymerized lignin not ideally suited for biological and chemical transformations. In the present work we attempt to depolymerize lignin derived from alkali treated rice straw and Kraft lignin by using different ionic liquids (ILs). Careful optimization studies in terms temperature and lignin to IL ratio revealed that Benzyl methyl imidazolium sulfonate emerges as the best among the ILs studied.

2. Material and Methods

Ionic liquids: 1-benzyl- 3-methyl imidazolium chloride, 1-butyl- 3-methyl imidazolium sulfonate, 1-butyl- 3-methyl imidazolium bromide, 1-benzyl- 3-methyl imidazolium sulfonate; were synthesized. Alkali Lignin was obtained after ammonia treatment to lignocellulosic biomass¹ while the standard Kraft lignin was obtained from J K Paper Mill, Gujarat.

3. Significant Results and Discussion

Of the several methods possible, the more preferred one for lignin breakdown has been one involving oxidative reactions involving molecular oxygen, hydrogen peroxide or nitric acid. Ionic liquids methyl imidazolium sulfonate; butyl methyl imidazolium sulfonate; benzyl methyl imidazolium sulfonate; and benzyl methyl imidazolium chloride were prepared and used for lignin depolymerization at temperatures in the range of 130-210°C for 30min maximum under aqueous conditions. Degraded compounds were recovered in organic phase through reverse phase chromatography or solvent. The work flow of the process devised and employed is given in Fig 1. A comparison of the results obtained with the synthesized ILs is given in Fig. 2.

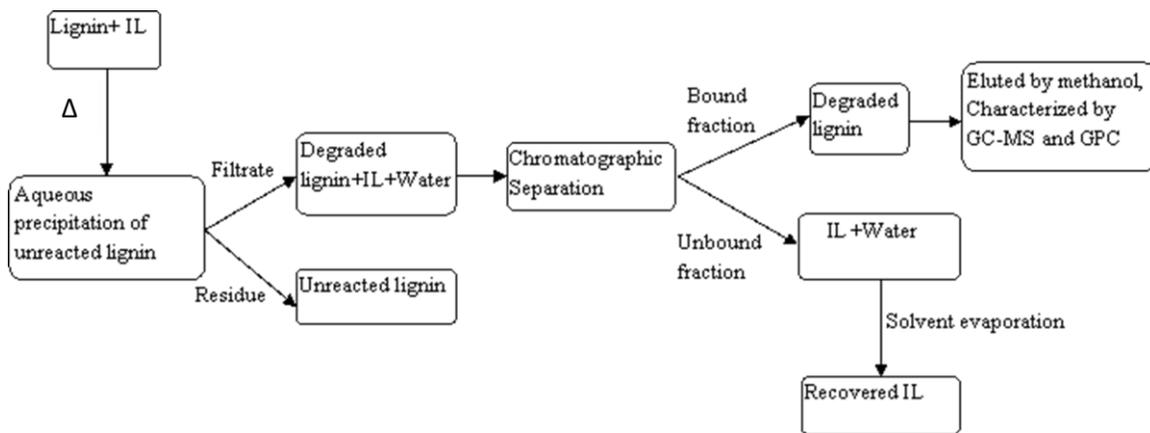


Figure 1: Process Flow Sheet

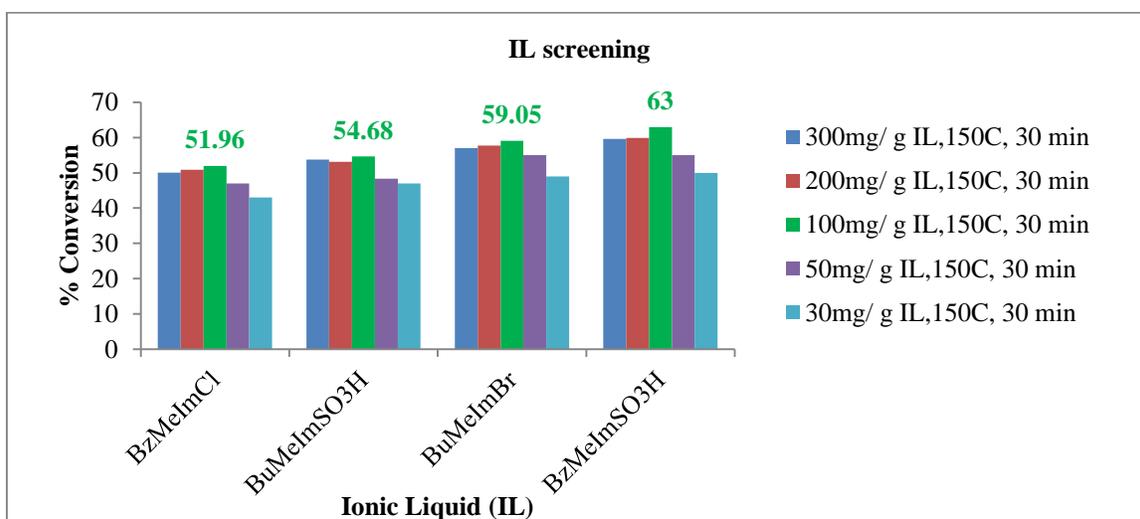


Figure 2: Performance comparison of different ILs for lignin hydrolysis

Characterization

GC-MS and GPC Characterization

Analysis of the degraded lignin on GC-MS indicated formation of aromatics such as phenolic aldehyde, phenolic acids, aliphatic acid and other phenolic compounds as major products. The GC-MS profile and relative abundance are given below as Figure 3 and Table 1. Figure 4 shows the GPC analysis of depolymerized product.

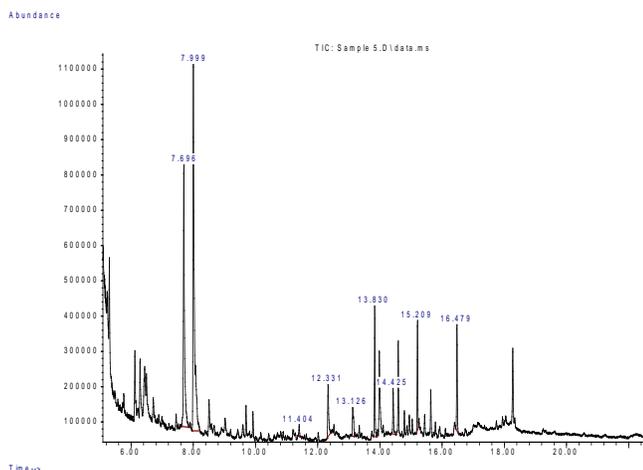


Fig 3: GC-MS Chromatogram for hydrolyzed lignin

Retention time	Name of Compound
7.696	Benzoic acid
7.999	Glycerol
11.4	2,4,6 tri- <i>t</i> butyl benzene thiol
12.331	<i>P</i> -hydroxy benzoic acid
13.126	Phthalic acid
13.8	Vanillic acid
14.425	Protocatechuic acid
15.201	Syringic acid
16.48	Hexadecanoic acid
18.02	Octadecanoic acid

Table 1: List of compounds detected on GC-MS

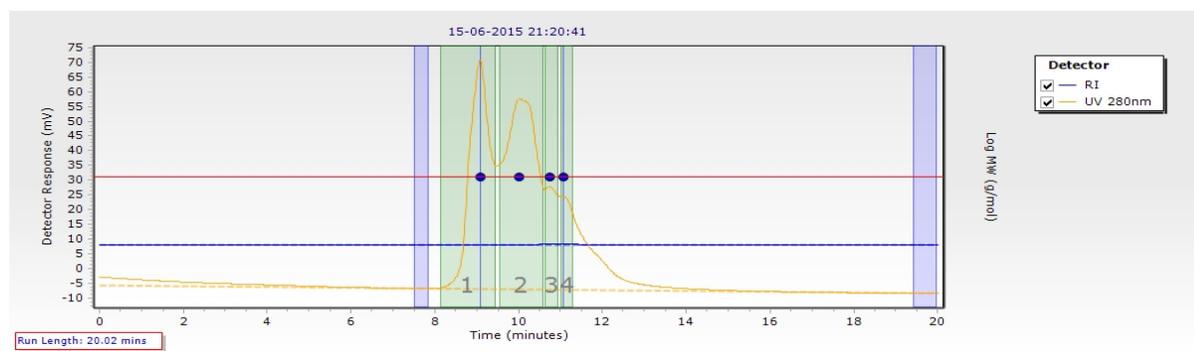


Figure 4: Gel permeation chromatography (GPC)

Determination of molecular weight distribution of degraded lignin (acylated) was estimated on the GPC in THF on a styrene divinylbenzene column (PLgel 5 μ m MIXED-D, 7.5 x 300 mm, Agilent technology), at a flow rate of 1 ml min⁻¹ with UV detection at 280 nm. The GPC data indicates that all degraded lignin products in the MW range of 100-600Da.

4. Conclusions

Different ionic liquids were synthesized for lignin degradation, of which [BZMIM][SO₃H] was found to be promising with conversions in the range of 63% with >90% IL recovery. Degradation lignin products when analyzed by GC-MS were found to contain range of aromatic hydrocarbons, organic acids, aldehydes, phenols and derivatives.

References

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