Lignin Depolymerization with Novel Brønsted Acidic Ionic Liquid

Zheng-Yen Wang, Babasaheb M. Matsagar, Kevin C.-W. Wu*
Department of Chemical Engineering, National Taiwan University, Taiwan
**Corresponding author: kevinwu@ntu.edu.tw*

Abstract: Among the conversion of lignocellulosic biomass, the valorization of lignin gives much attention as the structure of lignin is composed of phenolic units. However, due to its rigid and complex structure the depolyerization of lignin is challenging. By applying novel Brønsted acidic ionic liquid (BAIL) such as 1-methyl-3-(3-sulfopropyl)-imidazolium trifluoromethanesulfonate ([C_3SO_3HMIM][OTf]), higher yield of THF soluble product can be achieved (56 *wt%*) under 120 ℃ in 1 h, showing its good performance on depolymerizing lignin. Besides, BAIL can be successfully separated from reaction mixture.

Keywords: lignin, depolymerization, Brønsted acid ionic liquid

1. Introduction

Due to higher reserve amount and better accessibility of lignocellulosic biomass, it is expected to valorize it for the synthesis of platform chemicals. Lignocellulosic biomass comprises lignin, cellulose and hemicellulose. Among of them, lignin is 3-D cross-linked structure made up of aromatic phenolic biopolymer and drawing much interest in converting into valuable phenolic chemicals, oligomers as polymer composites, etc. However, due to its complex aromatic structure, the depolymerization of lignin is more challenging and severe condition (high temperature, high pressure) is necessary. Thus, catalysis is regarded as a key enabling technology for fulfilling the promise of lignin valorization.

Ionic liquids (ILs) are homogeneous catalyst and perform better than most of solid catalyst. The properties of ILs such as Brønsted acidity, solubility, etc. can be tuned. One of the advantage of IL is its lower vapor pressure hence it is environmentally green solvent. Therefore, acidic ILs are suitable candidate as a catalyst for biomass conversion. Mineral acids (HCl, H_2SO_4, etc.) are homogeneous catalysts reported in the literature for biomass conversion are not recyclable and corrosive. On the other hand, the BAILs (homogeneous catalyst) used for the biomass conversion are environmentally safer and can be recycled. Here we demonstrate the use of [C_3SO_3HMIM][OTf] BAIL for the depolymerization of lignin. The trifluoromethanesulfonic acid as super acid and common in other acid catalyzed reactions (e.g. esterification), is applied to synthesize novel BAIL. The [C_3SO_3HMIM][OTf] BAIL showed better performance for lignin depolymerization (56 *wt%*) compared to [C_3SO_3HMIM][HSO_4] BAIL (10 *wt%*).

2. Experimental

For the synthesis of [C_3SO_3HMIM][OTf] BAIL, first 1-methylimidazole was dissolved in toluene. Then toluene solution containing 1-methylimidazole was added slowly (20 min) into 1, 3-propanesultone in equal molar concentration at 0 ℃. The solution was refluxed in toluene for 12 h with during refluxing it is stirred at 400 rpm. The resulting solution was then filtered and zwitterion ion was obtained as white solid. After drying the zwitterion in lyophilizer overnight, trifluoromethanesulfonic acid was mixed with zwitterion in equal molar concentration and stirred at 100 ℃ for 12 h which results in desired IL which then dried in lyophilizer for 10 h.

Catalytic reactions were conducted in high pressure reactor (Taiatsu, Japan). Typically, 0.25 g IL, 0.25 g alkali lignin (Sigma Aldrich) and 25 mL water/methanol solution (1/5 *v/v*) were charged into reactor. Then the solution in the reactor was heated to desired temperature with slow stirring (100 rpm). Once the desired temperature reached the stirring speed increased to 600 rpm. After completion of reaction methanol/water solution was removed with rotary evaporator. Then THF was added in the residue for extracting THF soluble products. THF solution is then filtered and further analyzed with GPC and GC.

3. Results and discussion

The $[C_3SO_3HMIM][OTf]$ BAIL shows a higher THF soluble product (56 *wt%*) formation compared with $[C_3SO_3HMIM][HSO_4]$ BAIL (10 *wt%*). This implies that by changing anion in BAILs the THF soluble product yield can be increased. The reaction performed without catalyst showed only 4.5 *wt%* THF soluble products yield. Even $[C_3SO_3HMIM][HSO_4]$ BAIL possesses higher Hammett acidity (H_0) than $[C_3SO_3HMIM][OTf]$ BAIL, the THF soluble product yield is not improved because too high acidity also accelerates recombination reaction. On the other hand, $[C_3SO_3HMIM][OTf]$ has optimized acidity, so the activity on depolymerization reaction is better.

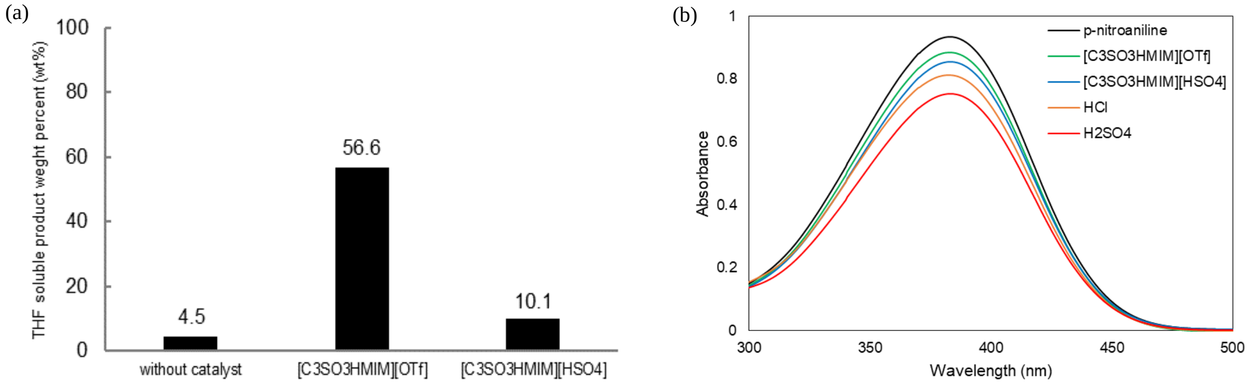

Figure 1.(a) Depolymerization of lignin with BAIL. Reaction conditions: alkali lignin (0.25g), catalyst (0.25g), H_2O/CH_3OH (1/5 *v/v*), 120 ℃, 1 h. **(b)** UV-vis spectra for measuring H_0 of various catalysts.

catalyst	λ_{max}	[I]%	$[IH^+]\%$	H_0
blank	0.934	100.00	0.00	-
$[C_3SO_3HMIM][OTf]$	0.886	94.82	5.18	2.25
$[C_3SO_3HMIM][HSO_4]$	0.855	91.54	8.46	2.02
HCl	0.814	87.11	12.89	1.82
H_2SO_4	0.753	80.53	19.47	1.61

Table 1. Hammett acidity (H_0) for different acidic catalysts used in this study.

4. Conclusions

We successfully synthesized a new novel $[C_3SO_3HMIM][OTf]$ BAIL and utilized for lignin depolymierzation reaction. Furthermore, the activity of $[C_3SO_3HMIM][OTf]$ BAIL was compared with $[C_3SO_3HMIM][HSO_4]$ BAIL. The results exhibited that $[C_3SO_3HMIM][OTf]$ BAIL performs better compared to $[C_3SO_3HMIM][HSO_4]$ BAIL. The higher THF soluble products (56 *wt%*) are obtained using $[C_3SO_3HMIM][OTf]$ BAIL under 120 ℃ in 1 h. The $[C_3SO_3HMIM][OTf]$ BAIL used in present study is environmentally safer promising catalyst for lignin depolymerization under lower temperature.

References

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