Supporting Information

Enhanced Delignification of Cornstalk by Employing Superbase TBD in Ionic Liquids

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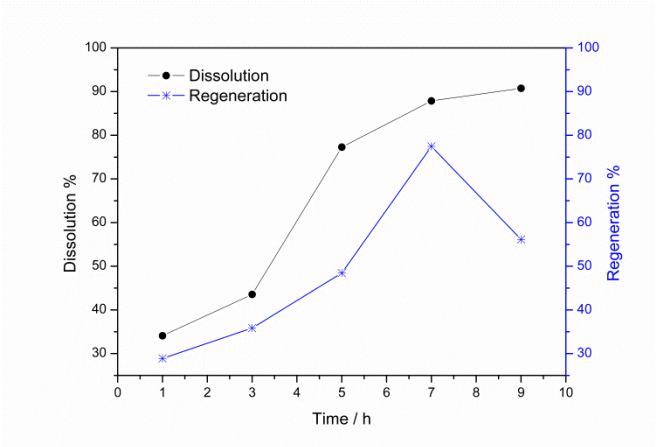
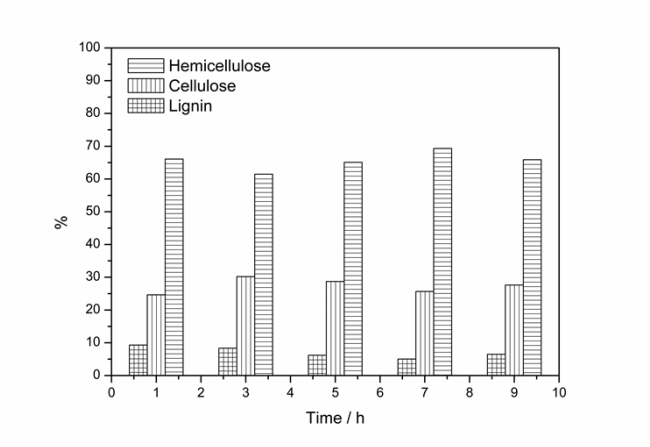
1. Effect of the dissolution time on the cornstalk delignification with [Amim][OAc]



(a)



(b)

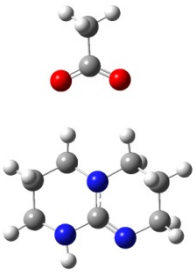
Fig. ESI-1. Effect of the dissolution time on the cornstalk delignification with [Amim][OAc]. Conditions: 0.5 g cornstalk sample (< 0.125 mm), 10 g [Amim][OAc], 130℃, different reaction time, 1.0 wt% additive was added at the beginning of the dissolution, (a) the dissolution % and regeneration %, (b) the components of CRM.

2. Density functional theory (DFT) calculations.

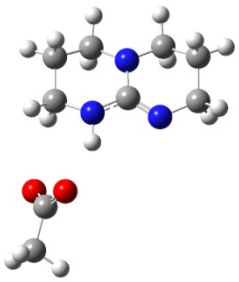
The density functional theory (DFT) calculations were carried out to analyze the interaction of reactants. All calculations were carried out using the Gaussian 03 program. The B3LYP/6-311+G(d, p) method has been used for structure optimizations, and subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0).

Firstly, the interactions of TBD and $[OAc]^-$ was investigated. It was found that there are different energy minimum structures for the coordination TBD with anion via hydrogen bonds (as shown in Figure ESI 2) by calculations. The interaction of TBD with anion will lead to form three kinds of structure A-C. The hydrogen bonds will be formed between oxygen and hydrogen, and these three structures are quite similar in energy. Based on the structure A, the interaction energy of TBD and $[OAc]^-$ was calculated and obtained as 13.1 kcal/mol.

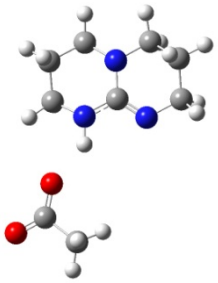
The interaction of TBD and $[Amim]^+$ was investigated, too. It was found that there are different energy minimum structures for the coordination TBD with cation via hydrogen bonds (as shown in Figure ESI 3). Based on the structure A with lowest energy, the interaction energy of TBD and $[Amim]^+$ was calculated and obtained as 17.6 kcal/mol.



A (0.0)

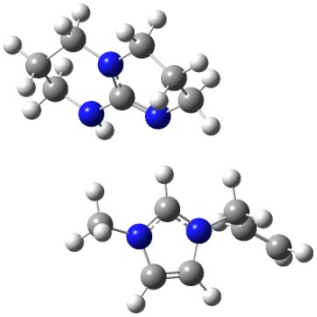


B (1.9)

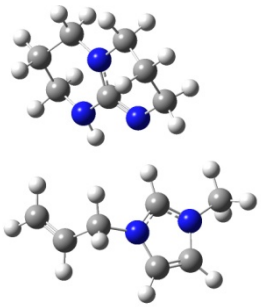


C (2.9)

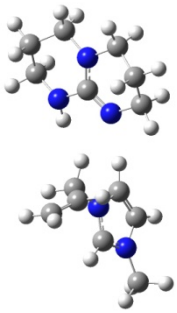
Fig. ESI-2 Optimized structures of TBD and anion with relative energy (kcal/mol).



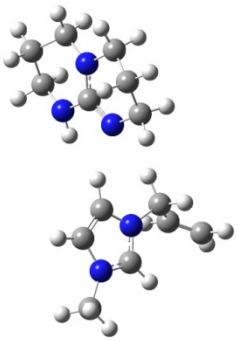
A (0.0)



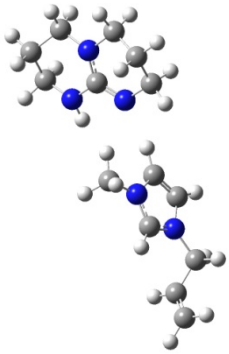
B (0.8)



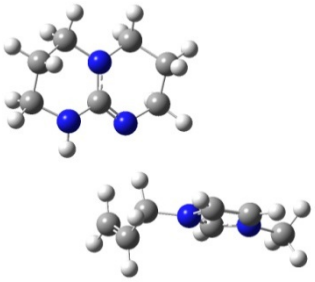
C (3.1)



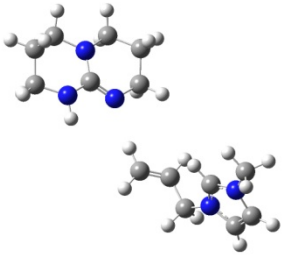
D (3.1)



E (3.4)



F (6.4)

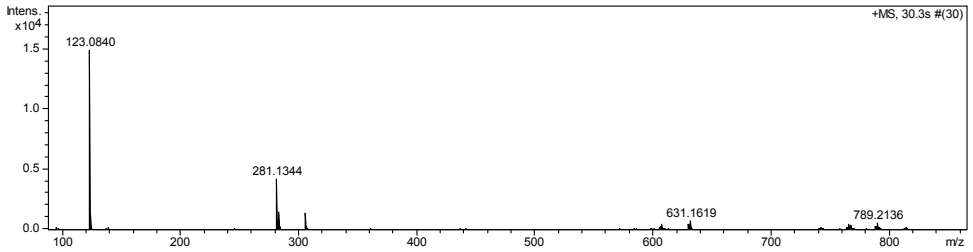


G (10.3)

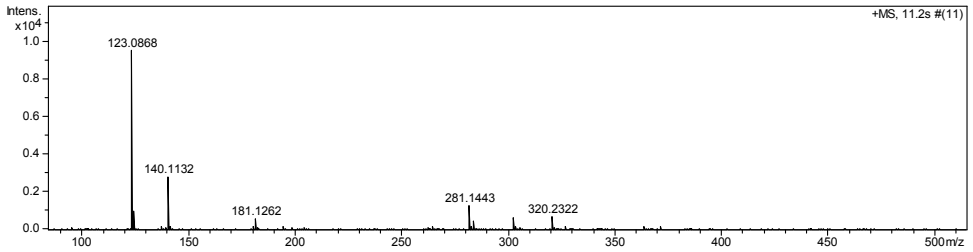
Fig. ESI-3 Optimized structures of cation and TBD by B3LYP/6-311+G(d,p) with relative energy (kcal/mol).

3. MS of [Amim][OAc] +TBD with different mass ratios

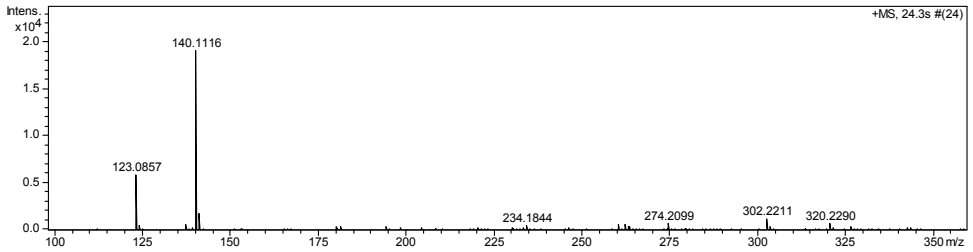
(a) 100% [Amim][OAc] 123: $[Amim]^+$ 281: $2([Amim]+Cl)^+$



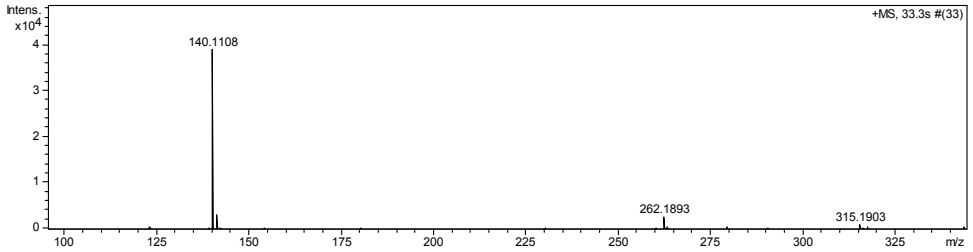
(b) 90 % [Amim][OAc] + 10 % TBD 123: $[Amim]^+$, 140: $(TBDH)^+$



(c) 70 % [Amim][OAc] + 30 % TBD 123: $[Amim]^+$, 140: $(TBDH)^+$



(d) 30 % [Amim][OAc] + 70 % TBD 140: $(TBDH)^+$, 262: $TBD\cdots H^+\cdots[Amim\text{-}H]$



(e) 100 % TBD

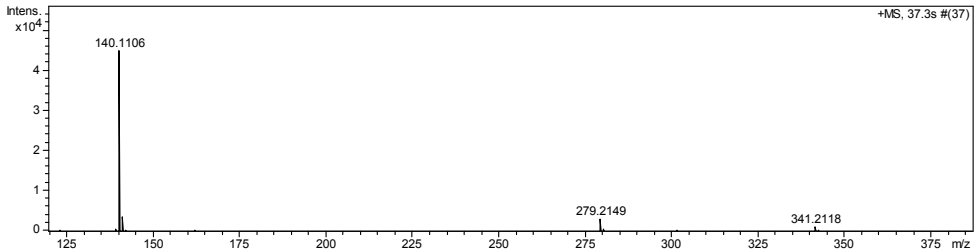


Fig. ESI-4 Mass spectrum of [Amim][OAc] +TBD solution