Distillable Ionic Liquids/Deep Eutectic Solvents for an Effective Recycling and Recovery Approach

Ezinne C. Achinivu[1,2]* (eachinivu@lbl.gov), Mood Mohan[1,2], Anthe George[1,2], Blake Simmons[1,3] and **John Gladden**[1,2]

[1]Deconstruction Division, Joint Bio Energy Institute, Emeryville, California; [2]Biomass Science and Conversion Technology, Sandia National Laboratories, Livermore, California; and [3]Biological Systems and Engineering Division, Lawrence Berkeley National Laboratory, Berkeley, California

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Project Goals:

Establish the scientific knowledge and new technologies to transform the maximum amount of carbon available in bioenergy crops into biofuels and bioproducts. Our current research focuses on developing recyclable IL pretreatment technologies while simultaneously facilitating the efficient depolymerization of both polysaccharides and lignin.

Developing a low-cost and high efficiency lignocellulosic biomass deconstruction process is a critical step towards the widespread adoption of lignocellulosic biofuels. Ionic liquids (ILs) and deep eutectic solvents (DESs) are novel alternative solvents for biomass pretreatment and conversion, and they are most notably one of the most effective methods for producing lignin and high yields of fermentable sugars for bioenergy production. Despite their commercial potential, the cost of IL/DES utilization (typically associated with their synthesis, purification and reuse/recycling) is a significant problem that must be addressed before an affordable IL/DES-based process is commercially viable. Therefore, this study features the use of ***distillable*** solvents for the development of an integrated biomass pretreatment approach that combines effective pretreatment with a simplistic and energy efficient recovery/recycling method.

Protic ionic liquids (PILs) that are formed with the combination of ***organic ammonium-based cations*** and ***organic carboxylic acid-based anions*** are an attractive group of solvents worth considering for this process. PILs are acid-base conjugate ILs that can be synthesized via the direct addition of their acid and base precursors. Additionally, when sufficient energy is employed, they can dissociate back into their neutral acid and base precursors, while the PILs are re-formed upon cooling. This presents a suitable way to recover and recycle the ILs after their application.

The PIL - hydroxyethylammonium acetate - [Eth][OAc] - has already been demonstrated as an effective solvent for biomass pretreatment and is also relatively cheap due to its ease of synthesis.[1] Therefore, this PIL and chemically analogous PILs were studied for their distillability, as well as, their effect on biomass deconstruction in a one-pot/consolidated process. Preliminary results indicate a PIL recovery of 98% for "neat" IL distillation of [Eth][OAc]), followed by PIL recovery [~80-85%] after biomass pretreatment with 15% biomass loading. Following the PIL removal, the

residual biomass was saccharified to generate ~74% total sugars (compared to ~78% sugars for -One pot and ~91% sugars- Early separation).

This is a promising proof of concept that supports our approach for distilling ionic liquids as a recovery method. Once optimized, this will launch our research into economic regimes, making an IL-based biorefinery a realizable goal.

References

1. Sun, J.; Konda, N. V. S. N. M.; Parthasarathi, R.; Dutta, T.; Valiev, M.; Xu, F.; Simmons, B. A.; Singh, S. One-Pot Integrated Biofuel Production Using Low-Cost Biocompatible Protic Ionic Liquids. *Green Chem.* **2017**, *19* (13), 3152–3163. https://doi.org/10.1039/C7GC01179B.

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