CRADA Final Report **Date** 11/2/16

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LBNL Report Number 1006449

1. Parties: Compact Membrane Systems, Inc.

2. Title of the Project: "Enhanced Mixed Feedstock Processing Using Ionic Liquids"

3. Summary of the specific research and project accomplishments:
Biomass pretreatment using certain ionic liquids (ILs) is very efficient, generally producing a substrate that is amenable to saccharification with fermentable sugar yields approaching theoretical limits. Although promising, several challenges must be addressed before IL pretreatment technology becomes commercially viable. Once of the most significant challenges is the affordable and scalable recovery and recycle or the IL itself. Pervaporation is a highly selective and scalable membrane separation process for quantitatively recovering volatile solutes or solvents directly from non-volatile solvents that could prove more versatile for IL dehydration than traditional solvent extraction processes, as well as efficient and energetically more advantageous than standard evaporative techniques. In this study we evaluated a commercially available pervaporation system for IL dehydration and recycling as part of an integrated IL pretreatment process using 1-ethyl-3-methylimidazolium acetate ($[C_2C_1Im][OAc]$) that has been proven to be very effective as a biomass pretreatment solvent. We demonstrate that >99.9 wt% $[C_2C_1Im][OAc]$ can be recovered from aqueous solution and recycled at least five times. A preliminary techno-economic analysis validated the promising role of pervaporation in improving overall biorefinery process economics, especially in the case where other IL recovery technologies might lead to significant losses. These findings establish the foundation for further development of pervaporation as an effective method of recovering and recycling ILs using a commercially viable process technology.

4. Deliverables:

Deliverable Achieved	Party (LBNL, Participant, Both)	Delivered to Other Party?
Process optimization for regional feedstocks	Both	Yes
Build CMS Dehydrator	Participant	Yes
Build lab scale regeneration unit	Participant	Yes
Test IL dehydration in IL-water mixtures from biomass hydrolysates	Participant	Yes

Demonstrate IL pretreatment efficiency after IL recycle	Both	Yes
Process optimization – operating temperature and IL	Participant	Yes
Scale-up of process	Both	Yes
Engineering and economic evaluation	Both	Yes

5. Identify publications or presentations at conferences directly related to the CRADA?
None

6. List of Subject Inventions and software developed under the CRADA:
None

7. A final abstract suitable for public release:
The present research aimed to develop an efficient, robust and scalable technology for the dehydration, recovery and reuse of IL after lignocellulosic biomass processing. We conducted pervaporation in place of conventional distillation to recover the [C2C1Im][OAc] after mixed feedstock pretreatment. Compared to vacuum distillation and electrodialysis methods, we found that the IL loss was kept within 0.1 wt% (i.e., >99.9 wt% IL recovery) by using pervaporation, and complete dehydration of IL can be achieved with a maximum water flux of 42.8 kg/h/m2. The recovered [C2C1Im][OAc] can be reused at least five times without significant changes in chemical structure and activity. In addition, the long-term performance stability of the membrane has been demonstrated over sixty dehydration cycles for the same [C2C1Im][OAc]-water mixture. A preliminary technoeconomic analysis highlights the advantage of pervaporation, in conjunction with vacuum distillation, as it could potentially minimize IL losses thereby improving overall economics. This study demonstrates that PV can be extended to much higher water content because the perfluorinated polymer membrane does not swell and therefore is stable when exposed to any water concentration. Also, PV integrates evaporation with a permeation membrane and has the potential to meet the needs for both high selectivity and low IL loss. More efforts are still warranted to improve the permeate flux, selectivity, and stability of the membranes in a more complex separations and scale-up applications with significant prospects in fuels and chemical industries.

8. Benefits to DOE, LBNL, Participant and/or the U.S. economy.
We demonstrate that >99.9 wt% [C_2C_1Im][OAc] can be recovered from aqueous solution and recycled at least five times. A preliminary techno-economic analysis validated the promising role of pervaporation in improving overall biorefinery process economics, especially in the case where other IL recovery technologies might lead to significant losses. These findings establish the foundation for further development of pervaporation as an effective method of recovering and recycling ILs using a commercially viable process technology.

9. Financial Contributions to the CRADA:

DOE Funding to LBNL	$ 0
Participant Funding to LBNL	$ 67,500
Participant In-Kind Contribution Value	$ 80,725
Total of all Contributions	$ 148,225

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