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Ionic Liquids for Utilization of Waste Heat from Distributed Power Generation Systems

Final Report

8/1/05-7/31/08

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Objectives

The objective of this research project was the development of *ionic liquids* to capture and utilize waste heat from distributed power generation systems. Ionic Liquids (ILs) are organic salts that are liquid at room temperature and they have the potential to make fundamental and far-reaching changes in the way we use energy. In particular, the focus of this project was fundamental research on the potential use of IL/CO_2 mixtures in absorption-refrigeration systems. Such systems can provide cooling by utilizing waste heat from various sources, including distributed power generation. The basic objectives of the research were to design and synthesize ILs appropriate for the task, to measure and model thermophysical properties and phase behavior of ILs and IL/CO_2 mixtures, and to model the performance of IL/CO_2 absorption-refrigeration systems.

Accomplishments

All of the milestones for this project have been achieved. This includes those for Year 1 (8/1/05-7/31/06) and Year 2 (8/1/06-7/31/07) of the project. Note that the project was given a one-year no-cost extension so the completion date was 7/31/08. The emphasis of Year 1 is the IL/CO_2 systems and the emphasis of Year 2 is the IL/water systems.

Task 1 Milestones

- We selected, synthesized, purified and analyzed four ionic liquids for this project.
- 1-hexyl-3- methylimidazolium bis(trifluoromethyl)sulfonylimide ([hmim][Tf_2N]) is immiscible with water but has a high CO_2 solubility. Therefore, it was considered for the IL/CO_2 absorption refrigeration system.
- 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtSO_4$]), 1-ethyl-3-methylimidazolium triflate ([emim][TfO]), and 1-ethyl-3-methylimidazolium trifluoroacetate ([emim][TFA]) are totally miscible with water and were investigated for IL/water absorption refrigeration systems.

Task 2 Milestones

- We measured pure component properties for all of the ILs investigated. This included pure component densities, melting points, glass transition temperatures, heat capacities, thermal decomposition temperatures, viscosities and thermal conductivities. The corrosivity of the ILs (with and without water and CO_2) were measured by an outside laboratory.
- Molecular simulation was used to predict some of the properties. A new method for prediction melting points from molecular simulation was developed.
- The results from these measurements and simulations can be found in many of the progress reports and in the publications that resulted from this project. All of the pure component properties were reasonable. The corrosivity was acceptably low, except with copper.
- The molecular simulations gave good values for many of the pure component properties, agreeing well with the experimental results.

Task 3 Milestones

- Measurements were made of mixture properties (IL + water and IL + CO_2), including heats of mixing, densities, and viscosities.
- Diffusivities were measured by PGNMR for the IL + water systems by an outside laboratory.
- We determined that molecular simulations of the IL + water systems were generally not sufficiently quantitative so experimental measurements were the primary results used for those systems.
- Although not in the original proposal, we also measured the vapor-liquid equilibrium of the IL + water systems. This was necessary to determine the liquid phase nonideality (i.e., activity coefficient) which, in turn, was needed to calculate the enthalpies and coefficients of performance for the IL + water absorption refrigeration systems.

Task 4 Milestones

- We developed simple correlations for all of the thermodynamic data.
- We found that the NRTL equation provided an adequate representation of the IL + water liquid phase nonideality.
- Conventional equation of state models were not able to adequately represent all of the necessary thermodynamic data.
- Reliable computational techniques were developed for parameter estimation.
- Using a combination of experiments data, simulation data, correlations and models, we assembled tables of all the thermodynamics necessary to analyze the absorption refrigeration systems.

Task 5 Milestones

- We developed a mathematical model of the conventional lithium bromide/water and ammonia/water absorption refrigeration systems.
- We developed equivalent mathematical models for both steady state and transient operation of the IL + water and IL + CO2 absorption refrigeration systems.

Task 6 Milestones

- Using all the thermodynamic information collected, simulated, modeled and tabulated, we calculated the ideal coefficient of performance (COP) of an absorption refrigeration cycle for three different ionic liquid/H_2O pairs over a variety of operating temperatures and compared to the ideal COP of a traditional LiBr/H_2O absorption refrigeration cycle. As can be seen in Figure 1 and 2, there are two important observations that can be made.

  (a) Firstly, all three ionic liquid/H_2O pairs produce **a more efficient absorption refrigeration cycle** than LiBr/H_2O.

  (b) Secondly, it is also of note that the COPs for the IL/H_2O pairs do not decrease as quickly with increasing generator temperature compared to that of LiBr/H_2O. This flatter curve allows for much higher COP than the LiBr system as the generator temperature is increased. This allows for a much more efficient cycle for higher waste heat temperatures.

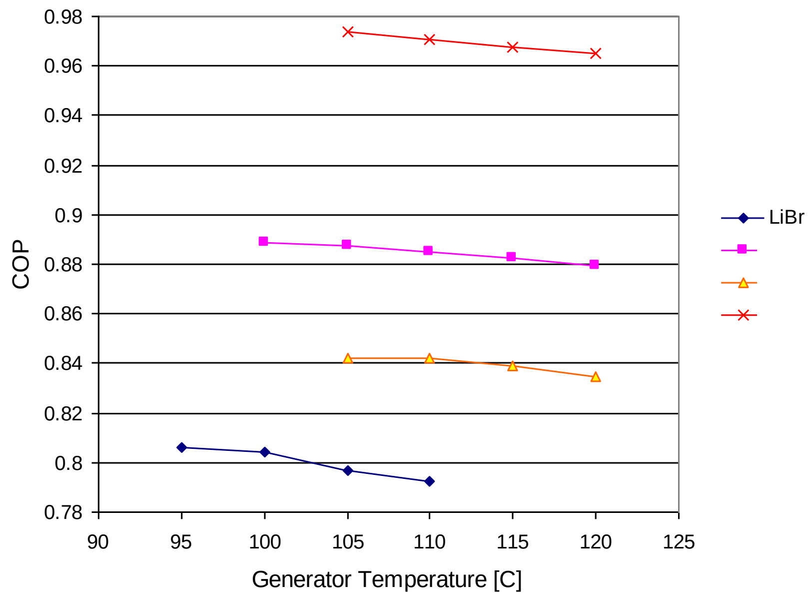

Figure 1 Coefficient of Performance of a heat-operated absorption refrigeration cycle for various generator temperatures, with evaporation, condensation, and absorption occurring at T_e = 5 °C, T_c = 50 °C, and T_a = 40 °C, respectively. The three different ionic liquids are compared with LiBr/water and all function as the absorbent while H_2O is used as the refrigerant.

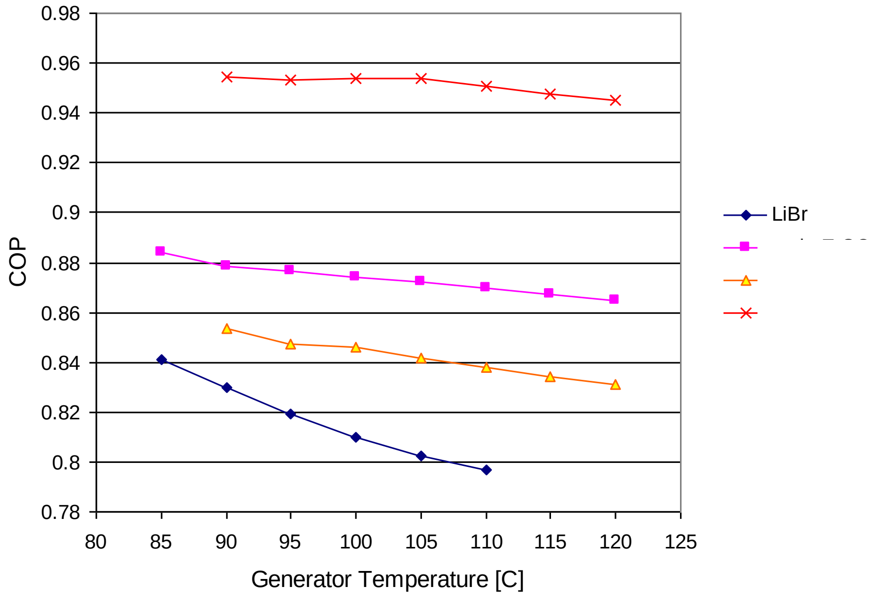

Figure 2 Coefficient of Performance of a heat-operated absorption refrigeration cycle for various generator temperatures, with evaporation, condensation, and absorption occurring at T_e = 5 °C, T_c = 50 °C, and T_a = 30 °C, respectively. The three different ionic liquids are compared with LiBr/water and all function as the absorbent while H_2O is used as the refrigerant.

- Using all the thermodynamic information collected, simulated, modeled and tabulated, we calculated the ideal COP of an absorption refrigeration cycle for the ionic liquid – CO_2 system. For the calculations, appropriate condenser, evaporator, and absorber temperatures were chosen and the generator temperature was varied to demonstrate its effect on the system's COP.

For specific operating conditions, the evaporator was maintained at T_e = 270 K to allow for sub-zero chilling, a condition not possible using the typical LiBr/H_2O or IL/H_2O systems. The absorber was maintained at T_a = 300 K, the lowest temperature at which the IL/CO_2 mixture data was available. Together, the absorber and evaporator form the low-pressure side of the absorption refrigeration system and, for these operating temperatures, operate at a pressure of ~32 bar (determined by the evaporator temperature).

The high pressure side consists of the generator and condenser and the pressure is dictated by the condenser temperature. In this simulation, a condenser temperature of T_c = 282 K was chosen to allow for sub-critical operation (using pure CO_2 as the refrigerant) as well as to maintain a reasonable operating pressure of ~44 bar. The COP results are shown below in Figure 3.

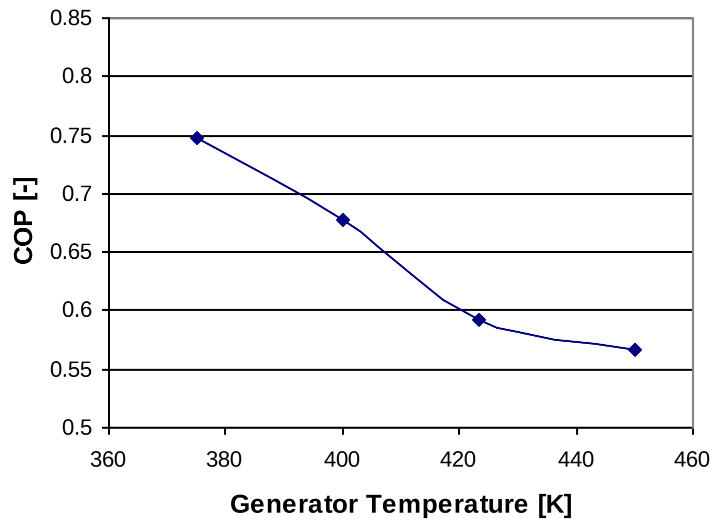

Figure 3: COP for an IL/CO_2 absorption refrigeration loop, with T_a = 300 K, T_c = 282 K, and T_e = 270 K.

The COP data behaves as is expected with performance decreasing with increasing generator temperature. Performance is lower than that of a traditional LiBr/H_2O system or the alternative IL/H_2O system and seems to decrease much more quickly with increasing generator temperature. Additionally, the system operates at fairly high pressures of approximately 32 and 44 bar, for the low and high pressure sides, respectively. However, the benefit of an IL/CO_2 system is its ability to chill to below 273 K using an environmentally friendly absorber/refrigerant pair, a task not possible using the standard LiBr/H_2O and H_2O/NH_3 systems or the alternative IL/H_2O system.

Task 7 milestones

- Since it was clear that we would not receive a third year of funding to build and operate a mini-scale plant, it was determined that design of this unit was not necessary for the project.

Conclusions

In this project we determined that **absorption refrigeration systems using ionic liquid/water have higher theoretical COPs than any commercially available systems**. The ionic liquid/CO_2 system had lower COPs and we do not recommend further development of that system. Numerous publications resulted from this work, as detailed below. Unfortunately, several other groups submitted patent applications prior to our application so we do not own the intellectual property on this invention. Nonetheless, the results of this project are extremely useful to advancing this highly promising technology. We continue to communicate with several companies, including Evoniks and DuPont, who are working to commercialize the technology.

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