A METHOD FOR COMPARISON OF ABSORPTION HEAT PUMP WORKING PAIRS

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ABSTRACT

Screening analyses based on thermodynamic and heat transfer principles are conducted for a single-effect absorption heat pump to enable the comparison of working pairs on the basis of performance and component size. After a broad survey of working pairs in the literature, in which 83 are discovered, forty-two are analyzed for cooling mode operation, and ten are analyzed for heating mode operation. Working pairs with water as the refrigerant are the most favorable thermodynamically in cooling mode, although some of them require more heat transfer area due to higher viscosity. Working pairs with alcohol refrigerants are most favorable thermodynamically in heating mode, although working pairs with ammonia as the refrigerant yield much more compact systems. The analysis methods developed here can also be applied to newly-characterized absorption working pairs to allow comparison with those previously investigated in the literature.

1. INTRODUCTION

The growing demand for space-conditioning, coupled with the multi-faceted concerns about the environmental impact of such systems has led to an ongoing search for the best working fluids for different thermodynamic cycles for varying ranges of operating conditions. For vapor absorption cycles, natural and synthetic refrigerants have been investigated, and absorbents of interest have ranged from inorganic salts to molecular liquids to ionic liquids (ILs). In most cases, the investigators of new working pairs make a comparison between their working pair and one or two others, most often $\text{NH}_3\text{-H}_2\text{O}$ and $\text{H}_2\text{O-LiBr}$. Fewer investigators have analyzed larger numbers of working pairs.

Tyagi and Rao (1984) carried out a thermodynamic comparison of 26 working pairs with NH_3 , SO_2 , R21, R22, and methylamine as the refrigerants in the cooling mode at a fixed set of operating conditions. Yokozeki (2005) performed a thermodynamic analysis of 25 working pairs with synthetic refrigerants and organic absorbents and compared the performance to that of $\text{NH}_3\text{-H}_2\text{O}$ and $\text{H}_2\text{O-LiBr}$ at a fixed set of operating conditions. Yokozeki and Shiflett (2007b, a, 2010) published a series of papers calculating the cooling mode performance of $\text{H}_2\text{O-IL}$ and $\text{NH}_3\text{-IL}$ working pairs, again at a fixed set of operating conditions. Ruiz et al. (2014) investigated six $\text{NH}_3\text{-IL}$ working pairs at the same set of operating conditions. Saravanan and Maiya (1998) investigated an absorption chiller with 16 working pairs, many of which used multi-component absorbents, with water as the refrigerant. They allowed the temperatures of the cycle components to vary independently. Kim et al. (2012) performed thermodynamic analyses for 14 working pairs with water or synthetic refrigerants and IL absorbents. They allowed the desorber temperature to vary but fixed the temperatures of the other components. Popp et al. (2015) developed a screening method for $\text{H}_2\text{O-IL}$ working pairs, which they then applied to 74 potential

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4 working pairs, but they did not carry the analysis to the calculation of thermodynamic
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6 performance data; rather, their approach was based solely on thermophysical properties.
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9 As researchers continue to investigate new working fluids for absorption cycles, it is
10 important to have a general analysis method that can be applied to any working pair, allowing
11 newly-discovered working pairs to be compared with those previously investigated. Such an
12 analysis method allows comparison at two different levels: first, a thermodynamic performance
13 comparison for a working fluid pair with full characterization of its thermodynamic properties
14 (i.e., density, vapor-liquid equilibrium, enthalpy); and second, a heat transfer analysis that
15 captures non-equilibrium behavior not described by the thermodynamic analysis for a working
16 pair with full characterization of its thermophysical properties (i.e., thermodynamic properties,
17 viscosity, and thermal conductivity).
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31 Here, a general thermodynamic analysis is carried out on a single-effect absorption heat
32 pump cycle to determine its thermodynamic figures of merit when operating in the cooling and
33 the heating mode. This analysis is then applied to working pairs from the literature for a given set
34 of operating conditions to develop the basis of a working pair database with which future
35 working pairs can be compared. Those working pairs with their thermophysical properties
36 characterized are then subjected to a heat transfer analysis to determine the transfer area required
37 to realize the desired system.
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48 **2. THERMODYNAMIC MODELING**

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The absorption heat pump cycle considered in this work is shown in Figure 1. In its simplest form, an absorption heat pump consists of a desorber, where refrigerant vapor is removed from solution by the addition of heat; a condenser, where refrigerant vapor rejects heat to change to a condensed liquid phase; an evaporator, where the refrigerant receives heat to change to a vapor phase; and an absorber, where the refrigerant vapor is absorbed into solution and the heat of absorption is rejected. A solution pump is used to pressurize the high-refrigerant-concentration solution leaving the absorber to the desorber pressure, while throttling valves are used to expand the low-refrigerant-concentration solution leaving the desorber to the absorber pressure and to expand the condensed refrigerant leaving the condenser to the evaporator pressure. In some working pairs, the absorbent has a non-negligible vapor pressure, which results in an appreciable absorbent content in the vapor leaving the desorber. Because this can lead to unreasonably large temperature glide in the condenser and/or the evaporator, a rectifier is used to remove the absorbent from the vapor phase. In addition, a solution heat exchanger (SHX) is used to recover sensible heat from the low-

refrigerant-concentration solution and preheat the high-refrigerant-concentration solution flowing to the desorber (Herold et al., 1996). The aforementioned system is analyzed by performing mass, species, and energy balances on each component. System operating conditions are set by specifying the outlet temperatures of

Figure 1: Single-effect absorption cycle schematic

the absorber, desorber, condenser, and evaporator and the SHX effectiveness. For this generalized screening analysis, the following assumptions are made:

1. The high-refrigerant-concentration solution leaving the absorber, low-refrigerant-concentration solution leaving the desorber, refrigerant leaving the condenser, and refrigerant leaving the evaporator are in saturated states at their respective component temperatures.
2. There is no pressure drop between components.
3. The vapor leaving the desorber is at the desorber outlet temperature and pressure.
4. Saturated liquid reflux flows from the rectifier to the desorber at a temperature 10°C below the desorber temperature.
5. The solution pump is ideal, and the solution flowing through the pump is incompressible.
6. The fluid flowing through the evaporator and condenser is pure refrigerant.
7. The throttling valves operate isenthalpically.

The above assumptions place the thermodynamic analysis on the simpler end of the spectrum. However, the analysis developed here is not intended as a design tool but rather as a screening and comparison method, which will yield the correct relative merits of the various working pairs while retaining simplicity in the analysis.

In the analysis, the rectifier (if necessary) and condenser are treated as a single component. This is primarily to allow a fair comparison between working pairs that require rectification and those that do not. Consider an $\text{NH}_3\text{-H}_2\text{O}$ system that requires rectification and an $\text{NH}_3\text{-LiNO}_3$ system that does not. If the two systems are operating at the same desorber temperature and the rectifier and condenser are treated separately, the refrigerant in the $\text{NH}_3\text{-H}_2\text{O}$ system will leave the rectifier at a lower temperature than the refrigerant in the $\text{NH}_3\text{-LiNO}_3$

system leaves the desorber. Because of this, the condenser load in the $\text{NH}_3\text{-H}_2\text{O}$ system will be lower than the condenser load in the $\text{NH}_3\text{-LiNO}_3$ system, even though the total high-pressure heat rejection will be higher in the former due to the higher heat of vaporization of H_2O .

The circulation ratio for an absorption heat pump cycle is defined as the ratio of flow through the pump to flow of the refrigerant through the condenser and evaporator.

$$f \equiv \frac{\dot{m}_{hr}}{\dot{m}_r} \quad (1)$$

The relation between the circulation ratio and the vapor-liquid equilibrium behavior of the working pair is determined by performing a mass and species balance on the absorber.

$$\dot{m}_{lr} + \dot{m}_r = \dot{m}_{hr} \quad (2)$$

$$\dot{m}_{lr} w_{lr} + \dot{m}_r = \dot{m}_{hr} w_{hr} \quad (3)$$

In the above equation, w refers to the mass fraction of refrigerant, the subscript lr refers to the low-refrigerant-concentration solution, and the subscript hr refers to the high-refrigerant-concentration solution. It is worth noting that, for consistency, all working pairs were analyzed here using the mass fraction of *refrigerant*, even though some working pairs, for example $\text{H}_2\text{O-LiBr}$, are commonly reported in the literature on the basis of the mass fraction of absorbent. Solving Equations 2 and 3 simultaneously and substituting in the expression from Equation 1 yields a relation for circulation ratio in terms of the refrigerant concentrations.

$$f = \frac{1 - w_{lr}}{w_{hr} - w_{lr}} \quad (4)$$

The circulation ratio is important, as working pairs with high circulation ratios require significantly more heat transfer area in the absorber, desorber, and SHX.

For all energy equations, heat transferred is defined as positive into the system, and work transferred is defined as positive into the system. The heat transferred in the absorber is given by performing an energy balance on the absorber.

$$-\dot{Q}_a = \dot{m}_r h_{v,e} + \dot{m}_{lr} \left(h_{lr} - \varepsilon_{SHX} \frac{(\dot{m}\Delta h)_{max}}{\dot{m}_{lr}} \right) - \dot{m}_{hr} h_{hr} \quad (5)$$

Normalizing by the refrigerant mass flow rate, applying the overall species balance to eliminate the low-refrigerant-concentration solution mass flow rate term, and substituting in Equation 1 yields

$$-q_a = h_{v,e} + (f - 1) \left(h_{lr} - \varepsilon_{SHX} \frac{(f\Delta h)_{max}}{f - 1} \right) - fh_{hr} \quad (6)$$

In Equation 6, $h_{v,e}$ is the enthalpy of the refrigerant vapor leaving the evaporator, h_{lr} is the enthalpy of the low-refrigerant-concentration solution leaving the desorber, h_{hr} is the enthalpy of the high-refrigerant-concentration solution leaving the absorber, and $(f\Delta h)_{max}$ is the maximum heat transfer rate in the SHX normalized to the refrigerant mass flow rate.

The heat transferred in the desorber is calculated by performing an energy balance on the desorber.

$$\dot{Q}_d = \dot{m}_{lr} h_{lr} - \dot{m}_{hr} \left(h_{hr} + \varepsilon_{SHX} \frac{(\dot{m}\Delta h)_{max}}{\dot{m}_{hr}} \right) + \dot{m}_v h_v - \dot{m}_\ell h_\ell \quad (7)$$

The subscript v refers to vapor leaving the desorber, while the subscript ℓ refers to liquid entering the desorber from the rectifier. The mass and species balances on the rectifier are as follows:

$$\dot{m}_v = \dot{m}_\ell + \dot{m}_r \quad (8)$$

$$\dot{m}_v y_v = \dot{m}_r + \dot{m}_\ell w_\ell \quad (9)$$

where y is used instead of w for the mass fraction in the vapor to denote that it is in the vapor phase. Solving Equations 8 and 9 simultaneously yields the following expressions for the vapor and liquid mass flow rates normalized by the refrigerant mass flow rate.

$$\frac{\dot{m}_v}{\dot{m}_r} = \frac{1 - w_\ell}{y_v - w_\ell} \quad (10)$$

$$\frac{\dot{m}_\ell}{\dot{m}_r} = \frac{1 - y_v}{y_v - w_\ell} \quad (11)$$

Substituting Equations 10 and 11 into Equation 7, normalizing by the refrigerant mass flow rate, and substituting in the definition of the circulation ratio yields

$$q_d = (f - 1)h_{hr} - f \left(h_{hr} + \varepsilon_{SHX} \frac{(f \Delta h)_{max}}{f} \right) + \frac{1 - w_\ell}{y_v - w_\ell} h_v - \frac{1 - y_v}{y_v - w_\ell} h_\ell \quad (12)$$

The energy balance for the rectifier and condenser, which are combined for the purposes of this analysis as discussed above, is

$$-\dot{Q}_c = \dot{m}_v h_v - \dot{m}_\ell h_\ell - \dot{m}_r h_{\ell,c} \quad (13)$$

where $h_{\ell,c}$ is the enthalpy of saturated liquid leaving the condenser. Substituting Equations 10 and 11 into the above equation and normalizing by the refrigerant mass flow rate yields

$$-q_c = \frac{1 - w_\ell}{y_v - w_\ell} h_v - \frac{1 - y_v}{y_v - w_\ell} h_\ell - h_{\ell,c} \quad (14)$$

The energy balance on the evaporator, normalized by the refrigerant mass flow rate, is

$$q_e = h_{v,e} - h_{\ell,c} \quad (15)$$

The SHX is analyzed using an effectiveness, which is specified when choosing the operating conditions for the cycle. Using this, the heat transfer in the heat exchanger is

$$\dot{Q}_{SHX} = \varepsilon_{SHX} \dot{Q}_{SHX,max} \quad (16)$$

where

$$\dot{Q}_{SHX,max} = \min \{ \dot{m}_{hr} \Delta h_{hr}, \dot{m}_{lr} \Delta h_{lr} \} \quad (17)$$

In Equation 17, the enthalpy difference is between the enthalpy of the solution at a given composition and the desorber temperature and the enthalpy at the same composition and the absorber temperature. Dividing both sides through by the refrigerant mass flow rate yields

$$q_{SHX,max} = (f \Delta h)_{max} = \min \{ f \Delta h_{hr}, (f-1) \Delta h_{lr} \} \quad (18)$$

Pump work is calculated based on the assumptions of an ideal pump operating on an incompressible fluid of density ρ_{hr} to increase its pressure by Δp .

$$w_p = f \frac{\Delta p}{\rho_{hr}} \quad (19)$$

The thermodynamic performance of an absorption cycle is described by the coefficient of performance (COP). For a cooling cycle, this is the ratio of heat input at the evaporator to heat input in the desorber and the pump work. Because the pump work is small in relation to the heat input, the electrical work was directly used here; in specific situations, if necessary, this could be modified using a thermal-to-electrical conversion factor.

$$COP_c = \frac{h_{v,e} - h_{\ell,c}}{(f-1)h_{lr} - f \left(h_{hr} + \varepsilon_{SHX} \frac{\min \{ f \Delta h_{hr}, (f-1) \Delta h_{lr} \}}{f} \right) + \frac{1-w_{\ell}}{y_v - w_{\ell}} h_v - \frac{1-y_v}{y_v - w_{\ell}} h_{\ell} + f \frac{\Delta p}{\rho_{hr}}} \quad (20)$$

For a heating cycle, the COP is the ratio of heat rejected to heat input in the desorber and the pump work.

$$\text{COP}_h = \frac{h_{v,e} + (f-1) \left(h_{hr} - \varepsilon_{SHX} \frac{(f \Delta h)_{max}}{f-1} \right) - f h_{hr} + \frac{1-w_\ell}{y_v-w_\ell} h_v - \frac{1-y_v}{y_v-w_\ell} h_\ell - h_{\ell,c}}{(f-1) h_{hr} - f \left(h_{hr} + \varepsilon_{SHX} \frac{\min \{ f \Delta h_{hr}, (f-1) \Delta h_{lr} \}}{f} \right) + \frac{1-w_\ell}{y_v-w_\ell} h_v - \frac{1-y_v}{y_v-w_\ell} h_\ell + f \frac{\Delta p}{\rho_{hr}}} \quad (21)$$

For this analysis, heat rejected includes the heat rejected in the absorber and condenser-rectifier.

It should be noted that in cycles that require rectification, the heat rejected during rectification is often used to preheat the high-refrigerant-concentration solution; not including this method of heat recovery impacts the COP of those working pairs that require rectification. However, a heat exchanger between the desorber and condenser could be used to recover some of the superheat (as often implemented in multiple-effect cycles) for fluids that do not require rectification.

With these two expressions, it is possible to calculate the COP of an absorption cycle with relatively little thermodynamic data, which is particularly advantageous for a broad screening study such as this. The only information required is component operating temperatures (in turn governed by heat source/sink temperatures), which then determine the required pressures, SHX effectiveness, and high and low refrigerant concentration solution concentrations and enthalpies. The available density information is used to establish circulation rates and pump work.

3. HEAT TRANSFER ANALYSIS

The thermodynamic analysis described above provides an important picture of cycle performance. However, in many cases, the constraints of an application require that the device be of reasonable size. In general, the size of a heat pump is closely related to the surface area required for its heat exchangers, which can be calculated by

$$A = \frac{\dot{Q}}{U \Delta T} \quad (22)$$

where $\dot{Q}$ is the heat transfer rate, U is the overall heat transfer coefficient, and ΔT is a representative temperature difference.

For heat exchangers with the same representative temperature difference, the ratio of required areas can be calculated by

$$\frac{A_1}{A_2} = \frac{\dot{Q}_1 U_2}{\dot{Q}_2 U_1} \quad (23)$$

A more general analysis can be carried out if the ratios of heat transfer rates and overall heat transfer coefficients in Equation 23 can be calculated in such a way that they are independent of the target heating or cooling load of the system. This is relatively straightforward for the ratio of heat transfer rates – the mass flow rate of refrigerant can be calculated for an arbitrary load by dividing the load by the numerator of Equation 20 for cooling or Equation 20 for heating. This mass flow rate can then be multiplied by the specific component heat loads found in the thermodynamic analysis to yield an expression for the heat load in any component for any working pair. This expression depends only on the thermodynamic properties and the load and is directly proportional to the latter. Thus, the ratio of the heat transfer rates for any two working fluid pairs only depends on their thermodynamic properties.

To allow a similar procedure to be used for the ratio of overall heat transfer coefficients, some simplifications must be made. These simplifications affect the numerical values calculated for the required heat transfer area, but they do not affect the trends. As the purpose of the methods developed here is to allow comparison of different working fluid pairs and not a complete engineering design analysis, such simplifications are deemed acceptable.

For a heat exchanger for which the thermal resistance of the wall separating the internal and external fluids may be neglected, the overall heat transfer coefficient can be calculated using

$$\frac{1}{UA} = \left(\frac{1}{h_i A_i} + \frac{1}{h_o A_o} \right) \quad (24)$$

In Equation 24, the subscript i refers to the internal side of the heat exchanger, which is the side containing the working fluid for the absorption cycle, and the subscript o refers to the external side of the heat exchanger, which is the coupling fluid side. Considering a case where the internal and external areas are the same (without preferential enhancement of one side), this yields an expression relating the overall heat transfer coefficient to its internal and external counterparts.

$$\frac{1}{U} = \frac{1}{h_i} + \frac{1}{h_o} \quad (25)$$

Taking the ratio of two overall heat transfer coefficients calculated using Equation 25 yields the following expression.

$$\frac{U_1}{U_2} = \frac{\left(\frac{1}{h_{i,2}} + \frac{1}{h_o} \right)}{\left(\frac{1}{h_{i,1}} + \frac{1}{h_o} \right)} \quad (26)$$

In Equation 26, the external heat transfer coefficients are assumed to be the same for both working pairs, which is equivalent to assuming that the geometries and heat transfer conditions on the coupling fluid sides are the same. The form of this ratio indicates that it would be extremely difficult to calculate on a general basis. Assuming the same heat transfer geometry for both working fluid pairs results in an expression of the form

$$\frac{U_1}{U_2} = \frac{f(\dot{m}_2, \mu_2, \rho_2, k_2, \dots) + g(\dot{m}_{cf}, \mu_{cf}, \rho_{cf}, k_{cf}, \dots)}{f(\dot{m}_1, \mu_1, \rho_1, k_1, \dots) + g(\dot{m}_{cf}, \mu_{cf}, \rho_{cf}, k_{cf}, \dots)} \quad (27)$$

There are no factors common to both terms in the numerator and both terms in the denominator; thus, numerical values for all terms must be calculated to obtain the ratio. If the case where the

external heat transfer coefficients are very high is considered ($g \rightarrow 0$) (i.e., with a focus on the working fluid portion of the cycle, often viewed as the “sealed system” in actual implementation), Equation 27 reduces to

$$\frac{U_1}{U_2} = \frac{f(\dot{m}_2, \mu_2, \rho_2, k_2, \dots)}{f(\dot{m}_1, \mu_1, \rho_1, k_1, \dots)} \quad (28)$$

With a single term in the numerator and denominator, the ratio is more tractable, making it possible to eliminate common factors such as the target load as long as the functional form of f is a single term. This is deemed to be an acceptable approximation because it will not affect the trends. For a function of the form given in Equation 27, with the values of the first terms in the numerator and denominator fixed and the values of the second terms allowed to vary, for all finite, positive values of g , the solution will remain on the same side of unity. As $g \rightarrow \infty$, the ratio will converge to unity. Thus, even for cases where the external heat transfer coefficient has a non-negligible effect on the overall heat transfer coefficient, the trends in heat transfer area resulting from this analysis will be correct.

Calculation of heat transfer coefficients requires the specification of the geometry over which the heat transfer is taking place. For this study, vertical, flat plate, falling-film heat exchangers are selected for the absorber, desorber, condenser-rectifier, and evaporator. Many of the working fluid pairs operate at sub-atmospheric pressures; therefore, a geometry with extremely low pressure drop is required. The pressure drop for the SHX is less restricted; thus, a simple flat plate heat exchanger geometry is selected.

Working pairs that operate at pressures above atmospheric have a wider range of geometries available to them that allow the use of forced convection. The effects of the use of such components is discussed in more detail below, but it is expected that they could improve

performance and/or compactness of the cycle in most cases, making the aforementioned analysis with falling-film heat exchangers a worst-case scenario for these working pairs.

The correlations used for heat transfer must be single term correlations to allow computation of ratios that are not dependent on the target heating or cooling load. When heat transfer is laminar, the heat transfer coefficient decreases with increasing mass flow rate due to increased thickness of the film. When film flow is wavy or turbulent, the heat transfer coefficient increases with increasing mass flow rate as additional mechanisms for thermal and species mixing become more prominent. Without specifying the mass flow rate, it is difficult to determine whether laminar or turbulent correlations should be used; however, it is assumed here that laminar heat transfer coefficients can be used for the mass flow rates found in small-capacity systems, such as for single-family homes, while turbulent heat transfer coefficients should be used for large-capacity systems, such as those installed in industrial facilities. For the laminar flow case, the following correlations were used. For components with condensation, Nusselt film theory was used with the assumption that liquid density is much greater than vapor density (Nusselt, 1916).

$$h = 1.47k_L \left(\frac{4\dot{m}}{L} \right)^{-1/3} \left(\frac{\rho_L^2 g}{\mu_L} \right)^{1/3} \quad (29)$$

For components with evaporation, the laminar correlation of Chun and Seban (1971) was used.

$$h = 0.821k_L \left(\frac{4\dot{m}}{L\mu_L} \right)^{-0.22} \left(\frac{g}{\nu_L^2} \right)^{1/3} \quad (30)$$

For the turbulent flow case, the following correlations were used. For components with condensation, the correlation of Grober et al. (1961) is used.

$$h = 0.0131 k_L \left(\frac{4\dot{m}}{L\mu_L} \right)^{1/3} \left(\frac{g}{v_L^2} \right)^{1/3} \quad (31)$$

For components with evaporation, the turbulent correlation of Chun and Seban (1971) is used.

$$h = 3.8 \times 10^{-3} k_L \left(\frac{4\dot{m}}{L\mu_L} \right)^{0.4} \left(\frac{v_L}{\alpha_L} \right)^{0.65} \left(\frac{g}{v_L^2} \right)^{1/3} \quad (32)$$

In the above equations, the subscript L is for the liquid properties, the variable L is the width of the vertical flat plate, and g is gravitational acceleration. Considering the plate width to be the same for all working fluid pairs and solving for the mass flow rate using the target load, Equations 29-32 can be simplified such that the heat transfer coefficients are proportional to expressions that only depend on the thermophysical properties of the working fluid pairs and the specific heating or cooling load.

$$h \propto k_L \left(\frac{\rho_L^2 q}{\mu_L \dot{m}_r} \right)^{1/3} \quad (33)$$

$$h \propto k_L \left(\frac{\dot{m}}{\mu_L q} \right)^{-0.22} \left(\frac{1}{v_L^2} \right)^{1/3} \quad (34)$$

$$h \propto k_L \left(\frac{\dot{m}}{\mu_L q} \right)^{1/3} \left(\frac{1}{v_L^2} \right)^{1/3} \quad (35)$$

$$h \propto k_L \left(\frac{\dot{m}}{\dot{m}_r} \right)^{0.4} \left(\frac{\nu_L}{\alpha_L} \right)^{0.65} \left(\frac{1}{\nu_L^2} \right)^{1/3} \quad (36)$$

Equations 33 and 35 are used for components with condensation or absorption, while Equations 34 and 36 are used for components with evaporation or desorption. In these equations, q is the specific heating load – that is the cycle heating load normalized by the mass flow rate of refrigerant. The ratio between the mass flow rate through the component in question and the refrigerant mass flow rate is unity for flow through the condenser and evaporator and equal to the circulation ratio for flow through the absorber and desorber. Assuming the circulation ratio rather than the circulation ratio minus one shifts the point at which the laminar to turbulent transition happens but otherwise does not affect the results.

For the SHX, the Nusselt number used is that for laminar, fully-developed flow between infinite parallel flat plates (assuming that the flow would be divided into multiple small-hydraulic-diameter passages that would generally lead to laminar flow) with uniform heat flux.

$$h = 8.235 \frac{k_L}{D_h} \quad (37)$$

Combining the expressions developed above yields expressions that are proportional to the area of each of the components, such that taking ratios of these expressions provides a comparison of component sizes for different working fluid pairs.

The thermophysical properties for the desorber area calculation are calculated at the desorber temperature and the high-refrigerant-solution concentration. Those for the absorber area calculation are computed at the absorber temperature and the low-refrigerant-solution concentration. For the SHX, properties are computed at the average of the desorber and absorber temperatures.

In cooling mode, the specific heat load is

$$q = h_{v,e} - h_{\ell,c} \quad (38)$$

while in heating mode, it is

$$q = h_{v,e} + (f-1) \left(h_{hr} - \varepsilon_{SHX} \frac{(f\Delta h)_{max}}{f-1} \right) - fh_{hr} + \frac{1-w_{\ell}}{y_v-w_{\ell}} h_v - \frac{1-y_v}{y_v-w_{\ell}} h_{\ell} - h_{\ell,c} \quad (39)$$

The mass flow rate of refrigerant is inversely proportional to the specific heat load.

$$\dot{m}_r \propto \frac{1}{q} \quad (40)$$

Combining the results from the analysis developed to this point and substituting them into Equation 22 yields a general expression proportional to the required heat transfer area of any component. It should be noted that the terms proportional to the convective heat transfer coefficient may be used in this expression.

$$A \propto \frac{\dot{m}}{\dot{m}_r} \frac{q_i}{q} \frac{1}{h} \quad (41)$$

In the above expression, q_i is the specific heat load for the component under investigation.

4. PROPERTY ESTIMATION

Wherever possible, properties were calculated directly from correlations published in the literature. When these were not available, the following techniques were used to estimate the thermophysical properties of working pairs.

When enthalpy-concentration-temperature data are unavailable for a given working pair, the enthalpy is calculated using a mass-based average and adding the enthalpy of mixing.

$$h = \sum_i w_i h_i + h_e \quad (42)$$

Reference states for the enthalpy were chosen based on the conditions specified in the literature, the temperature at which the excess enthalpy was measured or calculated, or a convenient reference point. Excess enthalpy data were unavailable for some working fluid pairs. These are noted in the results section.

When density data are unavailable for a working fluid pair, the mixture density is calculated ideally using a mass-based average.

$$\rho = \sum_i w_i \rho_i \quad (43)$$

When viscosity data are unavailable for a working fluid pair, the mixture viscosity is calculated using the component viscosities (Bloomfield and Dewan, 1971).

$$\ln \mu = \sum_i x_i \ln \mu_i \quad (44)$$

When thermal conductivity data are unavailable for a working fluid pair, the mixture thermal conductivity is calculated using the component thermal conductivities (Latini et al., 1996).

$$k = \sum_i w_i k_i - 0.72 w_1 w_2 |k_1 - k_2| \quad (45)$$

Table 1: Cycle Operating Conditions

	Cooling Mode	Heating Mode
Absorber Temperature (T_a)	50°C	50°C
Condenser Temperature (T_c)	50°C	50°C
Evaporator Temperature (T_e)	5°C	-23°C
SHX Effectiveness (ε_{SHX})	0.95	0.95

5. OPERATING CONDITIONS

To apply the thermodynamic model developed above, the temperatures in the absorber, desorber, condenser, and evaporator must be specified, along with the SHX effectiveness. A closest approach temperature (CAT) difference of 5°C is chosen for the components providing heating (i.e., the condenser-rectifier and absorber), as they are assumed to be hydronically coupled. A CAT of 15°C is chosen for the evaporator to reflect the typically larger thermal resistance between the sealed system components and the ambient. The temperature of the ambient is taken from the most stringent set of test conditions for heating in AHRI Standard 210/240-2008. The desorber temperature is varied to find a maximum in COP. The operating conditions are summarized in Table 1.

6. RESULTS AND DISCUSSION

Eighty-three (83) potential working pairs were investigated. The refrigerants investigated were restricted to those with zero ozone depletion potential and global warming potential below 100 (relative to CO₂, 100-year time horizon), which excluded most synthetic refrigerants from the analysis. Due to a lack of data or unfavorable thermodynamics, not all working pairs were analyzed. All working pairs investigated are listed in Tables A1 and A2 of the Appendices. For all working pairs with sufficient data to carry out a thermodynamic analysis, a parametric study was carried out using the Engineering Equation Solver software platform (Klein, 2015) in which the desorber temperature was varied.

Working fluid pairs with a near-complete set of property data are analyzed thermodynamically; however, they are marked with the following symbols: an asterisk (*) is used to denote working fluid pairs without excess enthalpy data; a dagger (†) is used to denote working fluid pairs without vapor-phase composition data. These missing data are expected to affect cycle performance in the following ways.

For working pairs lacking excess enthalpy data, the effect of adding those data can range from minimal to significant. The exclusion of the excess enthalpy is unlikely to affect the COP strongly for a working pair with a small swing in refrigerant concentration and an excess enthalpy that does not depend strongly on temperature. Conversely, for a working pair with a large swing in refrigerant concentration or strongly temperature-dependent excess enthalpy, failing to include this will result in large changes to the enthalpies of the solution leaving the absorber and desorber, which will in turn significantly impact the COP. For working pairs with positive excess enthalpies, the enthalpy difference between the absorber and desorber will decrease when compared with the calculated enthalpy difference when excess enthalpy is not considered. This results in a lower energy requirement to change the state of the solution from the state at the absorber outlet to the state at the desorber outlet, lowering the desorber heat duty and raising the COP. For working pairs with negative excess enthalpies, the opposite will occur.

For working pairs with a volatile absorbent lacking vapor-phase composition data, the inclusion of those data will generally result in a decrease in COP. The third and fourth terms in Equation 12 indicate that as the mass fraction of refrigerant in the vapor phase decreases, the heat load required to generate the same amount of refrigerant will increase due to refrigerant lost in the reflux. The magnitude of the increase depends on the heats of vaporization of the refrigerant and the absorbent. In a working fluid pair like $\text{NH}_3\text{-H}_2\text{O}$, for which the heat of vaporization of the absorbent is almost twice that of the refrigerant, there will be a more substantial impact on the COP than in a working fluid pair like $\text{H}_2\text{O-}[\text{mmim}][\text{DMP}]^{\dagger}$, where the heat of vaporization of the absorbent is less than one-quarter that of the refrigerant.

6.1. Cooling Mode Thermodynamic Analysis

Figure 2 shows the COP as a function of desorber temperature for several of the working pairs analyzed when operating the cycle in cooling mode at the specified operating conditions. In

general, the curves begin at a relatively low COP due to a small refrigerant concentration swing and high circulation ratio. The COP values quickly increase to a maximum as the desorber temperature increases and then decrease more slowly as the desorber temperature continues to increase. This is due to competing phenomena. As the desorber temperature increases, the refrigerant swing between the high refrigerant concentration solution and low refrigerant concentration solution increases, allowing for increased effect. However, the solution requires additional energy to reach the higher desorber temperature. When the increase in required energy input exceeds the additional effect provided, the COP reaches a maximum. There are some curves that are truncated before achieving their maxima, for example, the curves for $\text{H}_2\text{O-LiBr}$ and $\text{H}_2\text{O-(LiBr+1,3-Propanediol)}^{*\dagger}$. These curves are for working fluid pairs with a solid or partially solid absorbent that undergoes crystallization when the desorber operates above a threshold temperature.

Figure 2 also shows that different working fluids have different source temperatures for which they can perform optimally. For example, at temperatures below about 122°C , the performance of $\text{H}_2\text{O-[mmim][DMP]}^\dagger$ exceeds that of $\text{H}_2\text{O-[bmim][BF}_4\text{]}$. Depending on the source temperature, a working fluid pair with a lower maximum COP that operates optimally at a lower temperature could be more efficient than one that has a higher maximum COP at a higher temperature.

Thus, in operating conditions where the

Figure 2: Cooling COP vs desorber temperature for various working fluids

source temperature is limited, working pair choice is governed by the COPs achievable at temperatures at or below the source temperature rather than the maximum possible COP for the working pair. The shapes of the curves vary between working fluid pairs as well. NH_3 - H_2O and TFE-Quinoline show a fairly pronounced peak and a sharp decrease with increasing temperature, while H_2O -[bmim][BF_4] shows a much weaker temperature dependence near its peak COP.

Figure 3 shows the maximum COP for each of the working pairs with sufficient data available to complete a thermodynamic analysis, colored by refrigerant. All of the best five working pairs use water as a refrigerant, in part due to water having the highest heat of vaporization of the refrigerants considered. However, the thermodynamics of mixture composition also play a role. Ammonia and methanol have approximately the same heat of vaporization, but all of the working pairs that use methanol as a refrigerant save one have a higher COP than those that use ammonia.

The nature of the absorbent plays an important role in determining cycle performance as

Figure 3: Maximum cooling COP of evaluated working pairs

well. Three types of single-component absorbents are investigated: molecular liquids, salts, and ILs, the last of which are salts with low melting temperatures. Under the conditions considered in this analysis, every working pair with a COP > 0.52 uses either a salt or an IL as the absorbent, except H₂O-(LiBr+1,3-Propanediol)^{*†} and H₂O-(LiBr+MEA)^{*†}. The negligible vapor pressure of these absorbents allows the generation of a pure refrigerant stream without the need for rectification. The two exceptions are primarily salt-based, but it is expected that they will demonstrate lower performance due to vaporization of the volatile portion of the absorbent and subsequent rectification when the vapor phase composition data are taken into account.

6.2. Heating Mode Thermodynamic Analysis

The heating COP is shown as a function of desorber temperature for the working pairs capable of operating in the heating mode in Figure 4. Because of the low evaporator temperature, working pairs that use water as a refrigerant are eliminated; this removes 13 working pairs from consideration. The extreme temperature difference between the low-pressure components (73°C) necessitates low refrigerant concentrations in the absorber. Many of the working pairs investigated suffer from incompatible thermodynamics in which the equilibrium refrigerant concentration at the desorber temperature and pressure is higher than the equilibrium refrigerant concentration at the absorber temperature and pressure.

Figure 4: Heating COP vs desorber temperature for evaluated working pairs

Upon comparison of Figure 2 and Figure 4, it can be seen that the required desorber temperatures for maximum COP in heating mode are higher than those in cooling mode for the same working pair. This behavior is due to the lower refrigerant concentration in the absorber in heating mode due to the lower evaporator temperature, which requires that the desorber be at a higher temperature to remove a significant quantity of refrigerant from solution. For example, in cooling mode, $\text{NH}_3\text{-H}_2\text{O}$ exhibits a maximum in COP at a temperature of 115°C , while in heating mode, the maximum occurs around 160°C . Similarly, for $\text{MeOH-}[\text{mmim}][\text{DMP}]^\dagger$ in cooling mode, the maximum in COP occurs near 135°C , but in heating mode, its maximum occurs at or above 215°C . The maximum desorber temperature for the working fluid pairs was limited to temperatures below 230°C in an effort to stay near the range of experimentally-measured data.

The maximum COPs for working pairs operating in heating mode are shown in Figure 5. The thermodynamics of working pairs with an IL absorbent are, as in cooling mode operation, quite favorable when compared with those that use a molecular liquid as the absorbent. The working pairs using methanol as the refrigerant show the best performance, although there are also ethanol-based working pairs that show reasonable performance as well. The best-performing working pair with NH_3 as a refrigerant is $\text{NH}_3\text{-LiNO}_3$, with a COP of 1.46.

Figure 5: Maximum heating COP of evaluated working pairs

Combining the results from Figure 3 and Figure 5, a single working pair can be selected that shows good performance in both heating and cooling mode. This would allow a single heat pump to be constructed and operated in both modes to provide climate control throughout the year. The best candidate based on thermodynamics alone is MeOH-[emim][DEP], with a cooling COP of 0.79 and a heating COP of 1.63 under the selected operating conditions.

6.3. Cooling Mode Heat Transfer Analysis

The focus of this work is on small-capacity systems; thus, as a first approximation, during the calculation of terms proportional to the heat transfer for the comparison of working pairs, the laminar falling-film correlations are used to calculate the total heat transfer area required for each working pair. The terms that are proportional to the component heat exchange areas are presented in tabular form for all working pairs in Appendix B. All working pairs for which a thermodynamic analysis is completed for which transport property data are also available are subjected to a heat transfer analysis to determine the required size of the component heat exchangers. This analysis is carried out at the maximum COP for all working pairs. First, the sizes of the heat exchangers for the individual components are compared using the methodology developed above. In this comparison, all heat exchangers are compared to the size of the same heat exchanger in an $\text{NH}_3\text{-H}_2\text{O}$ system. Subsequently, the physical heat exchanger sizes are calculated for a given heat load and geometric parameters for an $\text{NH}_3\text{-H}_2\text{O}$ cycle and the relative sizes of the heat exchangers are used to calculate the total heat transfer area required for each working pair. These results can then be combined with the results of the thermodynamic analysis to provide a more complete picture of the appropriate working pairs for an absorption heat pump cycle.

To allow the results to be presented in a reasonable amount of space, only the 12 working pairs with the smallest required heat exchangers are presented here. The terms that are

proportional to area are presented in tabular form for all working pairs in Tables B1 and B2 of the Appendices. The relative absorber sizes when operating in cooling mode are shown in Figure 6. The most important factor governing absorber size, and the primary reason why the $\text{NH}_3\text{-H}_2\text{O}$ working pair shows the smallest absorber, is the viscosity of the

working pair. Many of the working pairs (in fact, all of them shown in Figure 6 except $\text{NH}_3\text{-H}_2\text{O}$ and TFE-NMP) use a highly viscous IL or a solid salt as the absorbent; thus, at low temperature and low refrigerant concentration (as outlined in the development of the heat transfer analysis, the refrigerant concentration in the low-refrigerant-concentration solution is used when calculating thermophysical properties in the absorber), the viscosity of the solution is quite high. For example, in the $\text{H}_2\text{O-[mmim][DMP]}^\dagger$ working pair, the absorber viscosity is 15.5 mPa-s, while in the $\text{NH}_3\text{-H}_2\text{O}$ working pair, the absorber viscosity is 0.65 mPa-s. Additionally, the thermal conductivity of the absorbent plays a large role. Even though water has a high thermal conductivity, the lower thermal conductivity of the IL absorbents reduces heat transfer performance substantially.

Figure 7 shows the relative desorber sizes when operating in cooling mode. Out of the 12 working pairs shown, nine use water as a refrigerant. At the high temperatures used for desorption, viscosity is significantly lower than at the temperatures used for absorption, and because the refrigerant concentration is higher, the high-viscosity absorbent has less of an effect on the heat transfer coefficient. In addition, water exhibits the highest thermal conductivity of the refrigerants, and its solutions with salts and ILs show high density, both of which increase the heat transfer coefficient. However, the low thermal conductivity of the ILs reduces this; of the seven working pairs that require the least area, all except one are based on the H₂O-LiBr working pair.

In a cycle operating in cooling mode, the heat transfer areas for the condenser-rectifier and evaporator are almost completely dependent on the refrigerant. The relative heat transfer areas for these components, averaged over all working pairs with the same refrigerant, are shown in Figure 8. There is some small variation in the condenser-rectifier size due to different working pairs experiencing their maximum COP at different desorber temperature, which affects the heat rejected in the condenser-rectifier.

The smallest condenser-rectifier is required for cycles that use water as the refrigerant. This is primarily due to its high thermal conductivity, as well as its high liquid-phase density and relatively

Figure 8: Relative sizes of refrigerant-only components in cooling mode

low viscosity. The smallest evaporator is required for cycles that use ammonia as the refrigerant because it has relatively high thermal conductivity and maintains a low viscosity even at the evaporator temperature.

The relative SHX sizes for cooling mode operation are shown in

Figure 9: Relative SHX sizes in cooling mode

Figure 9. Working pairs with water as

the refrigerant show small required heat transfer areas due to high thermal conductivity.

Additionally, all of the working pairs shown in Figure 9 show reasonable circulation ratios and reasonable enthalpy changes, which serve to reduce the required heat load of the SHX.

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Within a given cycle, all of the components will not be the same size. To allow a more

accurate comparison of the total heat transfer areas required by the different working pairs, a cooling load and geometry are assumed for an $\text{NH}_3\text{-H}_2\text{O}$ working pair, and the required heat transfer areas of each component are calculated. The relative component sizes are then used to calculate the total heat transfer area for the other working pairs. The parameters for the heat transfer area calculation are shown in Table 2. The representative temperature difference for the SHX is set to a different value than for the other components as it transfers heat from a solution entering at the desorber temperature to a solution entering at the absorber temperature.

Figure 10: Heat transfer area and COP in cooling mode. Each stack from bottom to top shows absorber, desorber, condenser-rectifier, evaporator, and SHX area

Table 2: Heat transfer analysis parameters

Cooling Load	3.5 kW
Heating Load	7 kW
Plate Width (<i>L</i>)	30 cm
Representative Temperature Difference	5°C
SHX Representative Temperature Difference	25°C
SHX Plate Spacing	1 mm

Figure 10 shows the total required heat exchanger area for the top 12 working pairs and their COPs based on the geometric and heat load parameters in Table 2. The fluids with the smallest required heat transfer area illustrate the tradeoffs involved in absorption heat pump design. The most compact choice, $\text{NH}_3\text{-H}_2\text{O}$, also has a lower COP. The next three working pairs, which are all $\text{H}_2\text{O-LiBr}$ based, have high COP and are almost as compact but have a limited operating range due to crystallization. The following working pair, $\text{H}_2\text{O-[mmim][DMP]}^\dagger$, requires 38% more heat transfer area than $\text{NH}_3\text{-H}_2\text{O}$, but it has a 55% higher COP. It also has no chance of crystallization. Of the 42 working pairs for which thermodynamic calculations were performed in cooling mode, only five demonstrate a COP above 0.7 and a required heat transfer area below 2.5 m^2 , and all of these use water as the refrigerant. Working pairs with ammonia as the refrigerant suffer from lower COP as seen in Figure 3, while working pairs with methanol as the refrigerant suffer from worse heat transfer performance.

6.4. Heating Mode Heat Transfer Analysis

The relative absorber sizes for operation in heating mode are shown in Figure 11. In general, the same results found in cooling mode operation are found here as well – working fluid pairs with low viscosity, high thermal conductivity, and low circulation ratio require lower heat transfer area than those

Figure 11: Relative absorber sizes in heating mode

with the opposite characteristics. Because of the large temperature difference between the evaporator and the absorber in heating mode operation, circulation ratios tend to be high. Additionally, the high desorber temperature at which the maximum COP occurs tends to result in lower refrigerant concentration in the solution entering the absorber, which in turn, leads to high viscosity. The effect of changes in operating conditions on thermal conductivity is fairly negligible for the alcohols. All three alcohols have thermal conductivities between 0.1 and 0.2 W m⁻¹ K⁻¹, and the ILs considered typically also have thermal conductivities in the same range (Tenney et al., 2014).

Figure 12: Relative desorber sizes in heating mode

Figure 12 shows the relative desorber sizes for heating mode operation. Of the three best-performing

working pairs, each leads to a small required heat transfer area in a different way. $\text{NH}_3\text{-H}_2\text{O}$ has low viscosity and high thermal conductivity, $\text{MeOH-}[\text{mmim}][\text{DMP}]^\dagger$ has high density, and $\text{NH}_3\text{-LiNO}_3$ has high density and low circulation ratio. The normalized heating load also plays an important role in the desorber size.

The exact scaling depends on whether

the flow is laminar or turbulent, but in either case, the required desorber size decreases with normalized load as less refrigerant needs to be generated to provide the same amount of heating.

The relative condenser-rectifier size depends on the working pair for the heating mode because of the aforementioned normalization. In heating mode, heat is delivered to the conditioned space from both the condenser-rectifier and the absorber. Depending on the balance of heat delivered in each component, some working pairs will have a relatively smaller absorber and larger condenser-rectifier or vice versa. The relative condenser-rectifier sizes are shown in Figure 13. Interestingly, the $\text{MeOH-}[\text{emim}][\text{EtSO}_4]$ working pair has the smallest required area for the condenser-rectifier. This working pair has a high circulation ratio, and thus the largest portion of the heat is delivered in the absorber. Because of this, a smaller condenser-rectifier is required.

Figure 14 shows the relative evaporator sizes for heating mode operation. As with the condenser-rectifier sizes, $\text{MeOH-}[\text{emim}][\text{EtSO}_4]$ requires significantly less area than the other

Figure 13: Relative condenser-rectifier sizes in heating mode

working pairs using MeOH as a refrigerant due to the imbalance between heat delivery in the absorber and condenser-rectifier. Comparing Figure 14 and Figure 8, it can be seen there is much more variation in the required evaporator heat transfer area for different working pairs for heating mode operation than for cooling mode operation. This is in part due to the

lower evaporator temperature during heating mode operation, which leads to increased viscosity for all refrigerants, and it is also due to the difference in mass flow rates. NH_3 and MeOH have approximately the same heat of vaporization; therefore, for the same cooling load, the evaporator sizes are based solely on the thermophysical properties. However, $\text{NH}_3\text{-H}_2\text{O}$ has a higher specific heat load than MeOH-[emim][DMP] by a factor of 1.4, which allows a lower ammonia flow rate and thus, less required heat transfer area in the evaporator.

The relative SHX sizes for operation in the heating mode are shown in Figure 15. Due to high thermal conductivity and low viscosity,

Figure 14: Relative evaporator sizes in heating mode

Figure 15: Relative SHX sizes in heating mode

the working pairs with ammonia as the refrigerant require the least heat transfer area, whereas MeOH-[emim][EtSO₄], which has a high circulation ratio and lower thermal conductivity, requires the most heat transfer area.

As with the cooling mode, an analysis is carried out to determine the overall heat transfer area and the

breakdown of the area on a per-component basis. The heating load selected is 7 kW, which is twice the cooling load selected. This is based on a climate like that of Chicago; in a more temperate climate, the heating load might be closer to the cooling load. The other parameters used in this analysis are provided in Table 2.

The results of the analysis are shown in Figure 16. Of the ten working pairs for which a thermodynamic analysis is carried out in the heating mode, only two, NH₃-LiNO₃ and MeOH-[mmim][DMP][†], exhibit a COP above 1.4 and a total heat exchange area less than 3.5 m². As with the results for cooling mode, working pairs with ammonia refrigerants are typically more compact but have worse performance, while working pairs with alcohols suffer from poor heat transfer and require more heat transfer area as a result.

6.5. Further Considerations

The refrigerants investigated fall into two categories on the basis of working pressure: those that operate below atmospheric pressure and those that operate above. The falling-film heat transfer geometry is chosen to minimize pressure drop so that cooling cycles that use water (low-

Figure 16: Heat transfer area and COP in heating mode

side pressure of 0.87 kPa) or heating cycles that use MeOH (low-side pressure of 0.80 kPa) can be included in the comparison. Refrigerants that operate above atmospheric pressure, such as ammonia, can use compact heat exchanger geometries such as microchannels. Because these geometries allow forced flow, the convective heat transfer coefficients are expected to be higher, which will result in less required heat transfer area. In addition, microchannel geometries have a significantly higher surface area-to-volume ratio than falling film geometries, resulting in a system with a smaller footprint for the same heat transfer area.

It should be noted that the analyses developed here do not take mass transfer into account during the absorption and desorption processes, but assume that heat transfer is the limiting factor. For working fluids where mass transfer is the limiting factor, a similar analysis should be conducted to determine the minimum component size on a mass transfer basis.

Finally, the analysis conducted here takes into account only the thermophysical properties of the refrigerants and working pairs when making a recommendation on which working pairs rank better than others. There are, of course, other engineering considerations that should be taken into account as well, such as cost, toxicity, and flammability of working pair components and the purpose of the heat pump. A heat pump designed to be tightly coupled to a conditioned space would have greater need to use a non-toxic working pair, while one designed to be indirectly coupled to the conditioned space could use a refrigerant with higher toxicity. Similarly, a heat pump designed to operate in a location where temperatures remain above 0°C would be able to utilize the H_2O -[mmim][DMP][†] working pair, while one intending to operate in both cooling and heating modes in a colder climate would tend towards an NH_3 - H_2O or NH_3 - LiNO_3 working pair.

7. CONCLUSIONS

Thermodynamic and heat transfer analyses are conducted for an absorption heat pump operating in cooling or heating mode, and closed-form expressions are developed for the COP and for terms that are proportional to the required heat exchange area of each component. The latter can then be used to compare the required heat transfer areas for the same geometry between different working pairs. The analyses are applied to a set of operating conditions chosen based on AHRI standards. In cooling mode, the best working pairs when taking into account both heat transfer and thermodynamics are found to use water as a refrigerant, but ammonia-based cycles are found to be among the more compact. In heating mode, the best working pairs are found to use ammonia as a refrigerant; the penalty to thermodynamic performance is somewhat mitigated by the benefits in heat transfer performance.

Using this general framework and the thermophysical properties of new working pairs determined through experiment or simulation, working pairs can be rapidly compared against those from the literature to allow engineers to select the appropriate working fluid for their application.

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