



## Hybrid Membrane-based Ionic Liquid Absorption Cycle for Water Heating, Dehumidification, and Cooling

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### Abstract

To meet the growing energy consumption and mitigate climate concerns, novel energy efficient technologies need to be developed. Water heating, dehumidification and space cooling form a significant percentage (~24%) of a typical U.S. household energy consumption and a total of 2.6 quad of primary energy consumption. In this paper, we present a novel system for combined water heating, dehumidification, and space cooling. The three processes can be achieved by one device using a novel semi-open absorption based system combined with evaporative cooling. The absorption based system absorbs water vapor from an ambient space. The latent heat of absorption, released into the absorbent, is transferred into the process water that cools the absorbent. The water absorbed is later released in the desorber by adding heat from natural gas combustion, and the water vapor generated in the desorber is condensed and its heat of phase change is transferred to the process water in the condenser. The condensed water vapor can either be drained if dehumidification is desired or be used in an evaporative cooling process for space cooling. The major innovations that enable such an absorption based device are demonstrated in this study through a prototype. First, a membrane based absorption system in a compact and scalable platform is used to alleviate the liquid entrainment issue encountered in the conventional packed bed absorbers. Second, architecture reconfigurations, like novel fluid circuits and semi-open absorption system are deployed for higher performance and lower costs. Finally, a novel absorbent called ionic liquid is implemented, which minimizes corrosion and completely eliminates crystallization risks, a major concern with LiBr, one of the most widely used absorbents. The water heating and dehumidification component of the device are experimentally evaluated and the device is characterized for various system parameters. A water heating COP of 1.4 is achieved in this first generation prototype. These innovations pave the way for a compact, efficient, and low cost absorption based system for residential scale applications.

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Keyword: Ionic Liquid, Absorption, Semi-open, Water heating, dehumidification

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## 1. Introduction

Absorption systems have been around for more than 150 years [1]. The inherent advantage of an absorption based heat pump is that they can provide high efficiency with the ability to utilize waste heat available at site. The advent of cheap electricity in mid-20<sup>th</sup> century increased the sales and market capture of residential cooling systems by vapor compression technology. However, in industrial applications, absorption technology continued to be deployed for large capacity systems, in the form of combined cooling, heating, and power ecosystem [2]. In the last decade, climate concern and global warming have driven the energy efficiency standards to higher targets and also led to new regulations to minimize and eliminate the use of high global warming potential (GWP) refrigerants, which are used in vapor compression cooling and heating systems [3]. This has renewed the research and development for alternate residential cooling and heating systems such as absorption systems.

The absorption systems have mostly been commercialized for high capacity applications. The system architecture involved makes it suitable only for large scale applications [4]. Such high capacity systems involve shell and tube kind of architecture, well suited for capacities which are of the order of few hundred tones. One of the major factors for unfavorable economics with the existing absorption system architecture is that the cost of fabricating the shell and tube architecture is insensitive over a large range of system capacity, for example, a reduction in capacity by five times of a 90 kW system reduces the cost only by half in the commercially available product lines.

To make a compact and efficient absorption system for residential scale application, a new architecture of absorber is required which can achieve high absorption capacity in a compact form factor. Recently, Dazhi et al [5] and Nasr Isfahani et al [6], [7] have demonstrated through numerical and experimental investigations that by using membrane based absorbers, 2-3 times higher absorption rates can be achieved. Another study by Mortazavi et al [8] demonstrated even higher absorption rates in plate and frame kind of architecture, which can be combined with membrane, in a scalable and compact form factor. The structures used in the study control the film thickness and enhance the mixing in falling film architecture.

Apart from the architecture, additional factors that are unfavorable for making a small scale application absorption based device, are the cost of the system controls, high performance metals to avoid corrosion and expensive design to maintain sub-atmospheric conditions [4]. Absorbents for the water vapor based absorption systems have not evolved in past 50-60 years, wherein, hygroscopic aqueous salt solutions like lithium bromide, lithium chloride, calcium chloride and similar brines have been used. These salt solutions have limited operating range and have a higher absorption potential at higher salt concentrations, which aggravates the crystallization risk. Slight deviation from set points, may lead to salt solution crystallization and a total shut down of the system which requires expensive clean up and restoration [9]. To avoid such shut downs, sophisticated control strategies are implemented using expensive controls and processors. The cost of control system is almost 25% in a \$25000, 18 kW absorption chiller machine and more importantly, this cost would remain almost the same if a lower capacity system, for example one ton, is manufactured. Additionally, the absorbents, like lithium bromide and chloride are highly corrosive due to the presence of the halide ion. Corrosion is more pronounced in the desorber which operates at a higher temperature. For instance, the corrosion rate of copper in 55% LiBr solution is about fifteen times higher at a temperature of 90°C compared to that at 25°C [10]. To counter this, costly metals like stainless steel is used. To mitigate corrosion and crystallization issues some hybrid absorbents which involve mixing the absorbent with corrosion or crystallization inhibitor have been investigated [11], but have limited success. Therefore, alternate absorbent pairs, which mitigate corrosion and completely eliminate the expensive control system need to be investigated.

Finally, another factor for high cost of existing absorption systems is a thermodynamic constraint to maintain sub-atmospheric conditions in the system. The sub-atmospheric conditions enable the evaporation of water at

lower temperatures (below ambient temperature), so that heat may be recovered from the ambient environment and space cooling be achieved. To maintain such low pressures over long period of operations, requires hermetic, all metal designs and additionally, may require auxiliary vacuum pumps to purge out non-condensable which build up due to formation of gases like H<sub>2</sub>, or small leaks of non-condensable gases over long period of time. This constraint can be eliminated by using a semi-open absorption [12] system wherein, the ambient water vapor is used as refrigerant.

This article discusses absorption cycle with alternate architecture, new absorbent and novel absorption cycle and demonstrates these innovations through deployment in a working prototype of a residential scale heat pump water heater which also has the potential to serve as a home dehumidifier. Both water heating and dehumidification consume significant amount of primary energy in a typical US residential home. For a typical US home, annual water heating bill is approximately in the range of up to \$200 (14-18% of the total utility bills). Overall, annual water heating expenditure for US is around \$32.6 billion as indicated in the Building energy end user data for 2011 [13]. In recent years, new water heating technologies claiming high site energy factors have been introduced to the market [14]. However, the high product and installation cost has contributed to slow market penetration of these technologies.

On the other hand, the latent load of the air is controlled by the conventional air vapor compression cooling systems, consumes significant amount of primary energy as excess water vapor is removed by cooling the air below its saturation point. Dehumidification can also be achieved by solid desiccant wheels or liquid desiccant systems. Solid desiccant systems have relatively poor energy efficiency and may also lead to additional sensible heating load in the conditioned space. Liquid dehumidification [15] systems are currently available only for large-scale applications.

The proposed changes for an absorption cycle based device which are demonstrated in this article pave the path for a cost-effective, compact, highly efficient open absorption system for residential scale application. First, a plate and frame kind of architecture is used as described by Mortazavi et al. [8] with a membrane, which allows a compact and scalable platform using an open absorption concept. This eliminates the need of the hermetic design requirements, allows direct interface between ambient air and solution as it uses ambient water vapor as refrigerant, thereby this can deliver dehumidification and water heating simultaneously. Second, a new class of absorbents called Ionic Liquid(IL) is used. IL are the class of absorbents and have received lot of attention in the past decade [16]. The two major advantages that IL have over existing absorbents is that they do not crystallize and they are far less corrosive [10], [17]. Using IL as absorbent eliminates the use of the expensive control strategy required in the present day absorption systems. This study attempts to demonstrate innovations that can eliminate issues associated with existing absorption systems and bring the absorption systems to the residential scale systems. Such a device can lead to significant primary energy savings, and in this article the water heating and dehumidification are discussed, which can be extended to any other absorption based system for small scale applications.

## 2. Methods:

### 2.1. Absorbent:

In this study a novel class of absorbent called ionic liquid (IL) has been used. As mentioned previously, ILs have gained lot of attention in the past decade. For application to absorption systems, ILs have the following advantages:

- Low water vapor pressure (comparable to existing absorbents)
- Null volatility
- No issue of crystallization (severe problem with LiBr and LiCl)

- Significantly reduced corrosion rates (much lower than LiBr)
- Non flammable
- Thermally stable over high temperature ranges (up to 200°C)

ILs are usually composed of large asymmetric organic cations and inorganic or organic anions. With numerous anion-cation combinations possible, the properties can be tuned for specific applications. The fine tuning of properties is possible by the variation of the length and branching of the alkyl groups incorporated into the cation [18]. Another important property that has contributed to ILs recent interest is their low volatility [19]. This feature eases their manipulation and purification, facilitates their use in multiple reaction and extraction cycles, and has led to their recognition as environmentally friendly (“green”) solvents [20]. Many ILs are completely miscible with water, which has led to investigation of ILs for the application in absorption systems utilizing water vapor as refrigerant. Numerous theoretical studies have been reported in the literature, discussing the use of ILs in absorption based systems [17], [21]–[26].

Most ILs have the drawback of higher viscosity than aqueous LiBr or LiCl. However, the membrane-based architecture used in this work mitigates this drawback.

## 2.2. New Architecture and Semi-Open design:

**Absorber:** The absorber schematic is shown in Figure 1A was a hybrid metal-polymer design. The water side is completely made from metal, with stainless steel sheets and copper fins for high surface area. The solution side fins are fabricated using the high-end additive manufacturing techniques and bonded onto the stainless sheet. Additional support structures were bonded on the edge of the SS sheet for membrane support.

Commercially available superhydrophobic membranes facilitate air-solution interface as it allows water vapor to pass through but does not allow the liquid to pass through. This open absorption cycle architecture utilizes the ambient water vapor as refrigerant, thereby eliminating need of the evaporator. Four such panels were fabricated and assembled as shown in Figure 1B with a gap in between each panel. Such a gap was necessary for airflow pathway and to incorporate the solution distribution manifold for each side of the panel. Air flows across the panels through the gap between the panels.

**Desorber-Condenser module:** The required water heating temperature (52°C) determines the condenser temperature which in turn dictates the desorber vapor pressure and temperature. To achieve the required temperatures, the desorber was an all-metal design. To enhance the desorption rates, similar structures as used in the absorber were used and the whole assembly was brazed. The heat input was provided to the solution in the desorber using an external temperature controlled silicone oil loop. The condenser used was a commercially available 10 plate heat exchanger and is connected to the desorber using a half inch stainless steel tube.

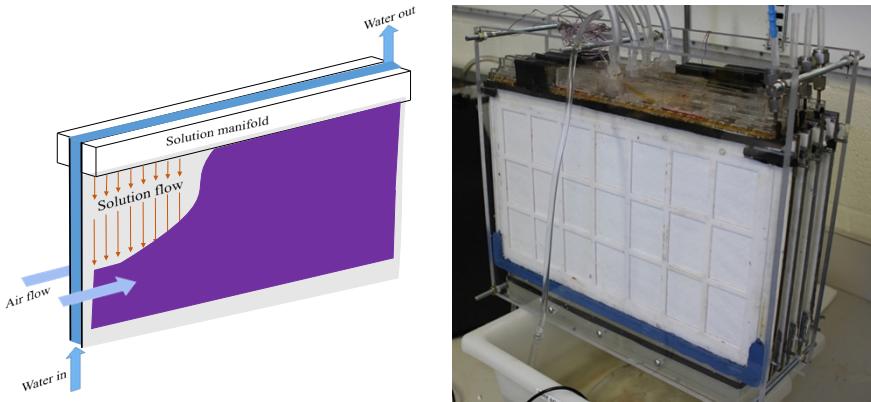


Figure 1 A) Schematic for absorber of one panel. B) Four panels assembled.

**Modified solution flow loop:** The solution flow loop is modified as described in [27], wherein the hot solution flowing out of the desorber exchanges heat with water flowing out of the absorber. The solution heat exchanger was procured as a standard liquid-liquid heat exchanger available in market.

**Concentration measurement:** The concentration of the solution is measured at inlet and outlet of the absorber using inline refractometer index (RI) sensors (Maselli Inc.). RI was used instead of density (as conventionally done in LiBr systems) because the variation in density for ILs is very small over a wide concentration range, making estimation of the concentration infeasible using density measurement. The RI curves at different temperature and concentration were generated for the IL under testing. The concentration was then back-calculated using the measured temperature and RI at inlet and outlet of the absorber.

### 2.3. Experimental test loop:

A fully instrumented test loop was designed and fabricated to be able to test the heat pump at different climate conditions. To achieve that objective, an air loop was incorporated. The duct was designed in-house and fabricated from a local vendor (Rays Sheet Metal, FL). The air duct had a heating/cooling coil connected to a chiller circulator (Thermo Fisher Scientific, MA) to control the temperature of the air. Additionally, to control the humidity level, a steam generator (SteamSpa, NY) is connected to a steam distribution manifold (designed and fabricated in house) installed in the duct. A fan (Orion Fans, TX) provides the air at the required flow rate. An air velocity measuring element (Paragon controls, CA) measures the velocity of the air. Relative humidity and temperature are measured capacitive sensors (Sensirion, CA) and recorded using their proprietary kit. The solution is pumped to the desorber by a solution circulation pump (Iwaki America, MA). The inlet and outlet temperatures are monitored using thermocouples (Omega Engineering, CT). The condenser pressure is monitored through pressure sensor (American Sensor Technologies, NJ). A positive displacement gear flow meter (Omega Engineering, CT) monitors the solution volumetric flow rate at the desorber inlet. The heat of desorption is supplied by synthetic heating oil SIL 180 (Clearco, PA). A heated oil bath (Thermo Fisher Scientific, MA) is used to supply hot oil to the desorber. Another positive displacement gear flow meter (AW-Lake, MI) monitors the oil volumetric flow rate at the desorber exit. The desorbed vapor condenses on the condenser plate heat exchanger (DudaDiesel, AL) facing the desorber. A chiller circulator (Thermo Fisher Scientific, MA) is used to provide the process water at the required flow rate and inlet temperature. A turbine flow meter (Omega Engineering, CT) measure the water flow rate. Absorber inlet and outlet concentration is monitored using the inline refractometers (Maselli Inc, CA) installed at inlet and outlet of the absorber. The data were recorded by a data acquisition system (Agilent Technologies, CA). Figure 2 and Figure 3 show the schematic and an actual picture of the experimental test loop.

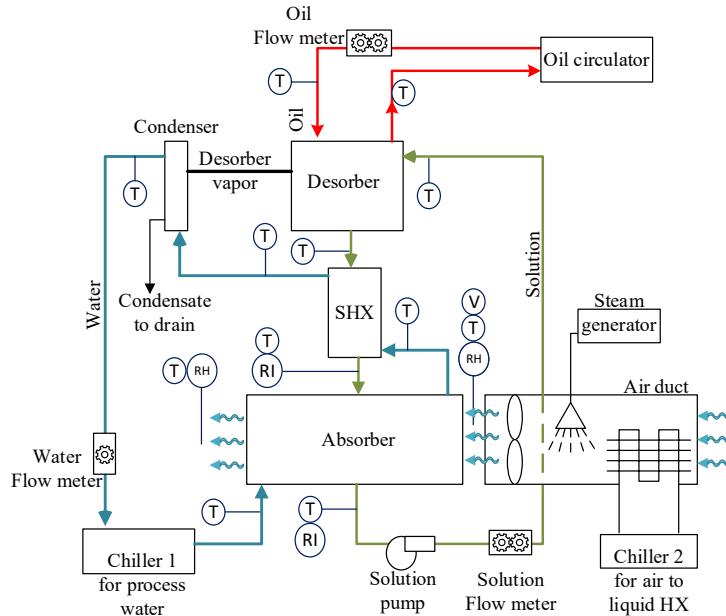


Figure 2. Schematic for the experimental test set up.

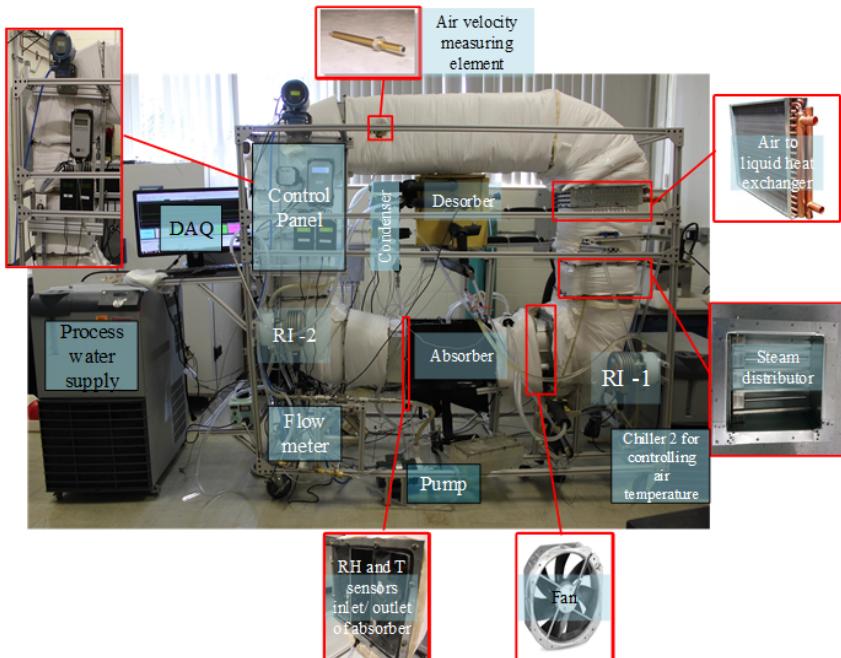


Figure 3. Photograph of experimental test loop with all the auxiliary components. (RI-Inline refractometer , DAQ-Data acquisition system)

## 2.4. Data reduction and Uncertainty

Thermocouples were installed at inlet and outlet of each component and the respective heat capacities were calculated.

### 2.4.1. Absorption rate:

For deducing the absorption rate, the mass flow rate of the vapor is to be estimated. This can be deduced by performing mass and species balance on the absorber as shown in equations 2-6.

$$j = \frac{\text{Mass flow rate of vapor (absorbed)}}{\text{Area}} = \frac{\dot{m}_v}{A} \quad \text{Equation 1}$$

Using species balance in the absorber:

$$\dot{m}_{soln_{in}} * X_{soln_{in}} = \dot{m}_{soln_{out}} * X_{soln_{out}} \quad \text{Equation 2}$$

Mass balance in the absorber:

$$\dot{m}_{soln_{in}} + \dot{m}_v = \dot{m}_{soln_{out}} \quad \text{Equation 3}$$

Substituting in Equation 2,

$$\dot{m}_{soln_{in}} * X_{soln_{in}} = (\dot{m}_{soln_{in}} + \dot{m}_v) * X_{soln_{out}} \quad \text{Equation 4}$$

$$\Rightarrow \dot{m}_v = \dot{m}_{soln_{in}} * \frac{X_{soln_{in}} - X_{soln_{out}}}{X_{soln_{out}}} \quad \text{Equation 5}$$

Flow ratio is calculated as the ratio of the flow rate of the solution to ratio of the mass flow rate of the vapor

$$FR = \frac{\dot{m}_{soln_{out}}}{\dot{m}_v}$$

### 2.4.2. Uncertainty:

The uncertainty was calculated using EES subroutine for propagation of uncertainty. Table 1 and 2 below lists all the relevant uncertainties in this study.

Table 1. Measurement error of the sensors used

Variable	Uncertainty
Temperatures -All T-type TC	1°C
Solution volumetric flow rate	0.5%
Solution RI	0.5%
Water volumetric flow rate	1%
Oil volumetric flow rate	0.5%
Air Relative humidity	3%

## 3. Results and discussion

The performance of the system was studied experimentally in response to variation of various parameters. One major indicator of performance in any absorption based device is the absorption rate, which was strongly dependent upon the design parameters like air-solution interface, solution fin design, and various membrane parameters (thickness, porosity etc.). The results reported in this study are for the first generation of IL based device, based on the analysis designs parameters can be optimized to yield higher absorption rates and efficiency in future generations. The ambient conditions selected was a typical humid condition of 30°C,

70%RH. Other parameters like flow rates of solution, water, oil etc. were based on the results of the thermodynamic cycle analysis performed using MATLAB.

### 3.1. Absorption rate vs solution inlet concentration:

The absorption rate was first studied as a function of the solution concentration. The higher the concentration required for the absorption system, the higher the desorption temperature required. In the water heating application, the condenser temperature predominantly determines the desorber heating temperature. The experimentally measured absorption rate for two different solution concentrations can be seen in Figure 4. It is shown that 90% (w/w) IL has higher absorption rate than at 80%. Temperature also plays an important part as a lower water inlet temperature would lower the vapor pressure to enhance the absorption rate, as can be seen that absorption rate for 21.5°C is slightly higher than for 25°C.

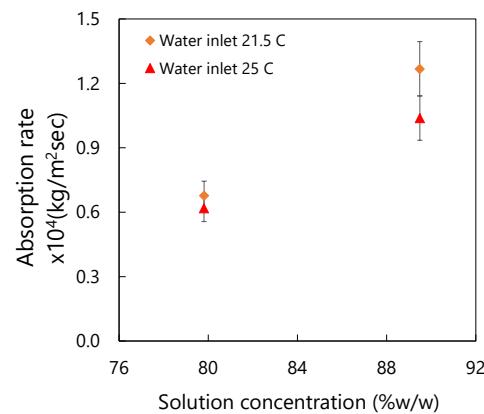


Figure 4. Absorption rate as function of solution concentration. (Ambient T and RH:  $30 \pm 1^\circ\text{C}$ ,  $70 \pm 5\%$ , Solution flow rate:  $2 \pm 0.1 \text{ g/sec}$ )

### 3.2. Absorption rate vs water inlet temperature:

The effect of inlet water temperature on absorption rate was studied. The US DOE water heating standard dictates the water inlet temperature to the tank at  $14.4^\circ\text{C}$  – this is not necessarily the temperature entering the heat pump. The water inlet temperature to the heat pump is dependent upon the hot water storage tank temperature conditions, draw rates from the tank and water flow rate between the hot water storage tank and heat pump. Therefore, it is important to study the absorption rate as a function of the water inlet temperature. Lower inlet water temperatures enhance the absorption rates due to lowering of the absorbent vapor pressure as shown in the experimental measurements of Figure 5. A stratified tank might supply a temperature in the range of  $15\text{--}35^\circ\text{C}$  depending upon above mentioned factors like water heating load and inlet water temperatures.

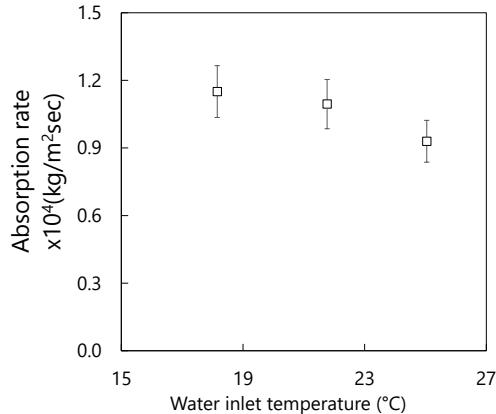


Figure 5. Absorption rate as a function of water inlet temperature. (Ambient T and RH:  $30 \pm 1^\circ\text{C}$ ,  $70 \pm 5\%$ , Solution flow rate:  $2.1 \pm 0.05 \text{ g/sec}$ , Solution inlet X:  $89.7 \pm 0.1 \text{ g/sec}$ )

### 3.3. Absorption rate vs vapor pressure differential:

The main driving force in an absorption system is the vapor pressure differential. A holistic plot can be created between the driving potential (i.e. net vapor pressure difference) and the absorption rate using the above discussed data. Considering the solution vapor pressure from the pressure-temperature-concentration (PTX) data and the partial water vapor pressure of the ambient conditions, the net driving force for absorption rate can be estimated. The major tradeoff of using an open absorption architecture is the significant reduction in the absorption rate due to the presence of the non-condensable gases. This can be seen by comparing the absorption rates of the closed system as reported in Nasr Isfahani [6] and Mortazavi et al [8]. Although the absorbent used in these studies is LiBr, in the same experimental set up Nasr Isfahani reported same order of absorption rate for an IL [26].

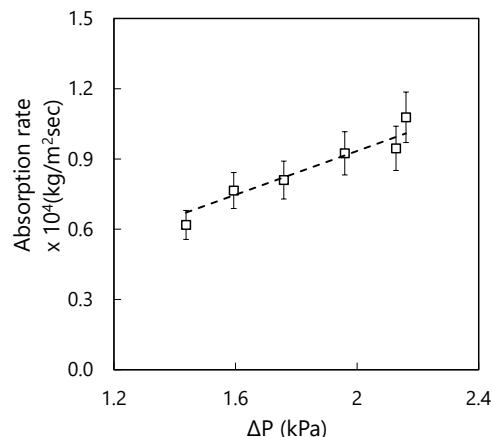


Figure 6. Absorption rate in an open system as a function of the differential vapor pressure.  $\Delta P$  = average water vapor pressure in air side – average solution water vapor pressure.

### 3.4. Absorption rate vs air flow rate:

The absorption rate is also dependent upon the mass transfer resistance, which is strongly influenced by the presence of non-condensable gases like  $\text{O}_2$ ,  $\text{N}_2$  in an open absorption cycle. This is summarized in Figure 7 below as a function of the air flow velocity.

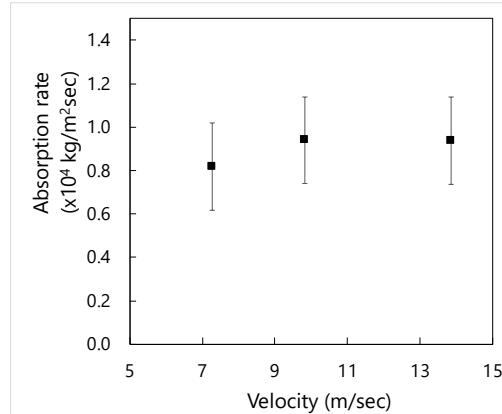


Figure 7. Absorption rate as a function of the air velocity. (Ambient T and RH:  $30 \pm 1^\circ\text{C}$ ,  $70 \pm 5\%$ , Solution flow rate:  $2.2 \pm 0.19 \text{ g/sec}$ , Solution inlet X:  $89.6 \pm 0.16 \%$ , water inlet temperature  $25.1 \pm 0.03^\circ\text{C}$ )

### 3.5. COP and capacity:

Using the prototype, the system water heating capacity and the COP were also experimentally characterized, as shown in Figure 8. The maximum COP achieved by the prototype is 1.4 and the maximum capacity recorded is 1.05 kW. The design is a scalable design and can easily be scaled up by adding panels to the absorber and increasing the desorber and condenser surface areas, thereby increasing the absorber capacity and efficiency.

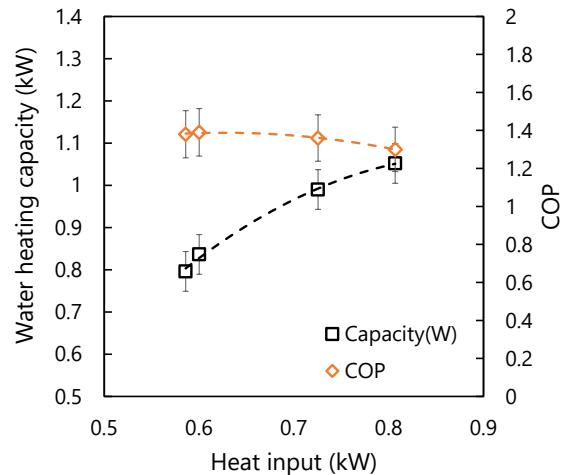


Figure 8. COP and capacity of the experimental prototype. (Ambient T and RH:  $30 \pm 1^\circ\text{C}$ ,  $70 \pm 5\%$ , Solution inlet X:  $89.5 \pm 0.2 \text{ g/sec}$ )

### 3.6. Comparison of COP with theoretical model:

The COP can be compared with a theoretical model described in Gluesenkamp et al. [12]. That model needs modification to accommodate the change in solution flow loop that was described in section 2.2. The modified equation obtained is:

$$COP = 1 + \frac{(L_{\text{cond}} + \alpha)}{FR * Cp * \Delta T_{D-A} * \varepsilon + L_{\text{des}}} \quad \text{Equation 6}$$

Where COP is the coefficient of performance, FR is the flow ratio (mass flow rate of solution/mass flow rate of vapor), Cp is the specific heat of solution (kJ/kg-K),  $\Delta T_{D-A}$  is the temperature difference from desorber to absorber,  $L_{\text{cond}}$  is the heat of condensation of water in the condenser,  $L_{\text{des}}$  is the heat of desorption for the water vapor from solution in the desorber (taken equal to  $\sim L_{\text{abs}}$  here), and  $\alpha$  is the fraction of the heat of sorption that flows through the solution and into the process fluid

All the variables can be measured in the experimental setup to predict the theoretical COP using Equation 8. The experimentally measured COP and the theoretical COP are plotted in Figure 9. As can be seen, the two values agree well over a wide range of FR. The theoretical values are slightly higher than experimental values, which can be attributed to the losses in a real system.

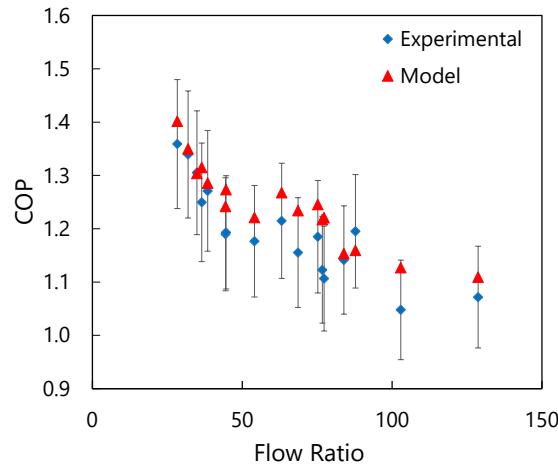


Figure 9. Theoretical and experimental values of the COP

### 3.7. Future improvements:

The nature of the air side mass transfer is purely diffusion in nature. Methods of improving the mass transfer, such as reducing the gap between the panels, would enhance the absorption rate significantly. This suppresses the mass boundary layer and may lead to enhancement of the absorption rate, and thereby more compact designs.

## 4. Conclusion

Three major innovations that can help make a compact, low-cost, scalable absorption based device have been discussed. The innovations are membrane-based open-absorption cycle, novel absorbents, and modified architecture. The membrane-based open-absorption cycle eliminates the need of hermetic and expensive designs. Novel absorbents used are the ionic liquids, which do not crystallize and have minimal corrosion issues. The modified architecture offers a scalable platform to fabricate the device in a compact form factor. These innovations are demonstrated through a working prototype for water heating application which can also serve as dehumidifier and cooler. The prototype is characterized for various system parameters and a thermal COP of 1.4 is achieved for water heating. This demonstration breaks the ground for economical absorption

system based devices for small scale applications. Further improvement in absorption rates can result in higher COPs and capacities.

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