Computer-Aided Design and Simulation of Working Fluid Pairs for Absorption Refrigerators

Eman Abdel-Hakim Tora*

Abstract—The performance of real absorption refrigeration systems is influenced by their working fluids. Despite there being many pairs that can act as working fluids, the conventional pairs (ammonia–water and water–lithium bromide) are still the most used. This paper reports an investigation to find an alternative pair via a three-step approach. The first is computer-aided molecular design using ICAS-ProCAMD software to preliminarily find a pair with analogous thermophysical properties. The second step is plotting Dühring curves to display the thermodynamic behaviour of the proposed pair, the required data for which are obtained from Aspen plus. Upon obtaining satisfactory results from the second step, the third step is simulation of an absorption refrigerator operating under different conditions. The results show that n-butane–ethanol can act as a suitable pair, where butane is the refrigerant and ethanol the absorbent. It has an acceptable pressure range (high pressure of approximately 4 atm, low pressure of around 1 atm) and generator temperature (91°C). In addition, there is no crystallisation probability at 0°C. However, the coefficient of performance is up to 0.33, which is low compared to both of the conventional pairs.

Index Terms—alternative working fluid pair, computer aided mixture design, simulation, absorption refrigerator.

1 INTRODUCTION

Absorption refrigerators (ARs) can be driven by low-quality heat sources such as process waste heat and solar energy. Replacing the commercially dominant vapour compression refrigerators with ARs can reduce electricity consumption. Furthermore, ARs are environmentally friendly due to their use of green natural materials such as water and ammonia as the refrigerant [1].

An AR has a working fluid that is a pair/solution comprising a refrigerant and an absorbent. Back in the 1970s, water and sulphuric acid were used in the early AR systems. An AR machine dating back to 1859 used NH₃–H₂O as the working pair; after about a century another working fluid, the H₂O–LiBr pair, was introduced for the first time [2],[3]. Owing to the superior tradeoffs of these two pairs, the other developed alternative working fluids have almost no recognised commercial foothold. These tradeoffs are listed in Table 1. Newly developed working fluids for ARs succeeded in providing some of these properties, but failed significantly to meet other requirements. Many substances can act as working fluids for ARs [4],[5],[6]. Thus, this paper tackles the search for a new working fluid for absorption refrigeration with properties analogous to those of the NH₃–H₂O and H₂O–LiBr pairs. Computer-aided molecular design (CAMD) is used successfully to find new compounds such as solvents for many chemical processes [7], and absorbents for the refrigerant (water) in certain absorption refrigeration configurations [8].

Since the ProCAMD software package can be used to design molecules and mixtures, this software is used to find alternative working fluids with thermophysical and thermodynamic properties that correspond to or surpass the most commercially successful working fluid tradeoffs.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ammonia–Water</th>
<th>Water–Lithium Bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refrigerant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High latent heat</td>
<td>Moderate</td>
<td>Superior</td>
</tr>
<tr>
<td>Moderate vapour pressure</td>
<td>Extremely high</td>
<td>Markedly low</td>
</tr>
<tr>
<td>Low freezing temperature</td>
<td>Excellent</td>
<td>Limited application</td>
</tr>
<tr>
<td>Low viscosity</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td>Absorbent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low vapour pressure</td>
<td>Poor</td>
<td>Superb</td>
</tr>
<tr>
<td>Low viscosity</td>
<td>Acceptable</td>
<td></td>
</tr>
<tr>
<td>Mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid phase formation</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Low toxicity</td>
<td>Poor</td>
<td>Fine</td>
</tr>
<tr>
<td>Affinity between</td>
<td></td>
<td>Good</td>
</tr>
<tr>
<td>refrigerant and absorbent</td>
<td></td>
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</tbody>
</table>

This paper considers a three-step approach through the use of CAMD and process simulation software to find an alternative working fluid pair.

2 PROPERTIES OF THE SUBSTITUTE PAIR

NH₃–H₂O is a successful working pair that is used in industrial applications to provide cooling over a wide temperature range.
range since the normal boiling point is –33.34°C and the freezing point is approximately –74°C. Similarly, H₂O–LiBr can work using a low-quality heat source at around 70°C as an average. Finding a substitute refrigerant that replaces NH₃ and still works well with water as the absorbent can be described as follows.

Regarding the pure refrigerant, the following properties are the design target:
- Low boiling point at atmospheric pressure
- High latent heat of vaporisation
- Low heat of mixing with the absorbent
- Low viscosity
- Not toxic
- The normal boiling point and the vapour pressure of the alternative refrigerant should not be close to those of the absorbent (water) to allow easy separation and regeneration by heating. Moreover, ideally, one should have a mixture with separation efficiency that does not require a rectification column, which in turn can reduce the capital cost and the operating cost of the AR – thus enabling its commercial usage.

Regarding the mixture, the properties to be considered are as follows:
- The boiling point of the solution is in a range that can be provided by low-quality heat sources – for this study, it is taken as a temperature less than 150°C
- High miscibility between the refrigerant and the absorbent
- No azeotrope formation

Furthermore, there is a set of properties that both the pure refrigerant and the mixture should have:
- Completely miscible (it is a necessity to have a completely miscible solution to have a homogeneous solution in the vapour and liquid phases under all conditions)
- Low heat of mixing (the absorption process is an exothermic one with negative heat of mixing, thus the mixture should be a real one with negative deviation from Raoult’s law)
- No solid formation under operation conditions
- Not toxic or at least safe in the allowed range

After the desired properties and the constraints have been determined and the problem formulated, ProCAMD is run to generate the designed compounds. A list of the results is given in Table 3.

An Aspen plus simulation has been conducted to check the possibility of separation and the need for a rectifier, which is addressed in detail in the next section.

Therefore, CAMD is used to generate possible molecules/mixtures; process simulation software (Aspen plus) is employed to validate the cycle performance when the suggested pair is used. New substitutes are determined, and their comparative potential is assessed in terms of coefficient of performance (COP), high and low cycle pressure and heat source required.

**2.1 Alternative Pair Design by ProCAMD**

CAMD starts with a certain given user-preselected set of functional groups, then combines them, estimates their properties, filters and eventually selects the candidates with the desired properties. A working fluid to be designed consists of two compounds, one acting as a refrigerant and the other as an absorbent, with the provision that the pair is completely soluble. Here, the design of the working fluid is achieved through three steps: working fluid pair design is conducted using ICAS-ProCAMD through the design of a refrigerant based on physical properties, the absorbent is designed according to solubility, and then the thermodynamics of the solution is checked.

**2.1.1 Design of refrigerant based on physical properties**

Preselecting functional groups allows one to consider alcohol, ketone, aldehyde, ester, ether, amine, amide, acid, and double- and triple-bond acyclic compounds. In contrast, chlorine-, bromine-, iodine-, sulphur-, phenol- and silicon-based compounds are dismissed.

The physical properties affecting the process are predetermined. These are the boiling point, vapour pressure, solubility, latent heat of vaporisation and freezing/melting point.

Constraints are then set for these properties. These constraints result in compounds with the desired characteristics. The values of ammonia–water properties are taken as the average target values. Table 2 lists these vital properties for this case and their constraints, which are upper and lower acceptable values. An information screen from a ProCAMD run is shown in Fig. 1.

**TABLE 2**

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Unit</th>
<th>Constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal boiling point (NBP)</td>
<td>K</td>
<td>0 ≤ NBP ≤ 275</td>
</tr>
<tr>
<td>Freezing point (FP)</td>
<td>K</td>
<td>0 ≤ FB ≤ 200</td>
</tr>
</tbody>
</table>
| Latent heat of vaporisation (λ)   | kJ mol⁻¹ | 5 ≤ λ ≤ 130  
|                                   |      | λ (NH₃) = 23.27      |
|                                   |      | λ (H₂O) = 40.65      |
| Molecular weight (M)              | g mol⁻¹ | M ≤ 265   
|                                   |      | (M = 236.8 for R-110 hexachloroethane) |
| Vapour pressure (VP)              | atm  | 1 ≤ VP ≤ 11          |
| Solubility (S)                    |       | Minimum pressure is 1 atm to avoid vacuum; maximum allowed pressure is 11 atm to be in an acceptable range, as that is the NH₃ average high pressure

By limiting compound design to a molecular weight of less than 265 g mol⁻¹, normal boiling point of around 0°C and
maximum freezing point of −73°C, ProCAMD considered 10 310 compounds, yet selected only seven compounds matching the desired properties. These are listed in Table 3 in ascending order based on normal boiling point.

The ProCAMD results show that n-butane and acetaldehyde have latent heat of vaporisation almost equal to that of ammonia; however, their normal boiling points are higher. Therefore, they are not superior to ammonia as refrigerants, yet are very similar. Dimethyl ether has almost the same latent heat of vaporisation and normal boiling point as ammonia.

### 3.1 Dühring Curve

For n-butane as refrigerant ethanol as the absorbent, Fig. 2 shows Dühring curves, and, based on them, the appropriate operating conditions to provide cooling at 0°C are as follows; condenser at 42.6°C, desorber at 90°C and absorber temperature of 25°C.

This pair provides cooling at a level comparable to that of water–lithium bromide, yet it surpasses the latter based on the following advantages:

1. No vacuum is needed as in the case of water–lithium bromide
2. The low pressure is 1 atm and the high pressure is 4 atm (moderate pressure)
3. Condenser cooling can be carried out using ambient air, as with water
4. No crystallisation risk

### 3.2 Simulation Using Aspen plus

Based on the Dühring curve results, simulation of an AR cycle has been performed under various conditions. Figure 3 shows snapshots of the simulation under three different operating conditions.
Fig. 3. Aspen plus simulation of n-butane–ethanol pair at different cooling temperatures.

4. RESULTS
The results as given in Table 5 are promising and confirm that the proposed n-butane–ethanol pair is comparable to water–lithium bromide in terms of the required heat demand temperature and pressures. However, for the proposed pair to give a cooling range analogous to that of ammonia–water, the COP of the system is low, as listed in Table 5. Regarding the cooling range of H₂O–LiBr, the proposed pair is superior to H₂O–LiBr from the viewpoint of no crystallisation risk, cooling at lower temperature level, no vacuum and both the low and high pressures being acceptable. However, H₂O–LiBr still has a higher COP than the proposed pair.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>OPERATING CONDITIONS AND PERFORMANCE OF N-BUTANE–ETHANOL PAIR COMPARED TO LITHIUM BROMIDE–WATER PAIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tₑᵛp (°C)</td>
<td>Tₐbs (°C)</td>
</tr>
<tr>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>43</td>
</tr>
</tbody>
</table>

5. CONCLUDING REMARKS
The following conclusions can be drawn based on the Dühring curve and simulation results:
- The proposed working pair (n butane–ethanol) can act as a working pair for absorption refrigerator
- When employing the proposed pair, an absorption refrigeration system has the requirements of mild pressure and a low-temperature heat source
- No crystallisation risk
- The proposed pair can provide cooling at temperatures lower than that be provided by H₂O–LiBr, but with a lower COP than if using NH₃–H₂O
- Employing the new pair involves tradeoffs between the preferable operating conditions and COP value.

ACKNOWLEDGMENT
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References


[8] ICAS documentation: CAPEC, Department of Chemical Engineering, Technical University of Denmark.