A detailed second law (excergic) analysis approach of H$_2$O-LiBr vapour absorption cooling system

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Abstract. Vapour absorption technology is generally known as a potential environmental friendly strategy to use solar heat energy reliably for space cooling applications. The thermodynamic analysis is used as an approach for determining efficiency in these systems. Two methods are the first law (FLA) and the second law (SLA) analyses in it. FLA uses the energy conservation of each component and gives the COP of the cycle. Comparing vapour absorption cooling systems on the basis of COPs is not justified. Hence second law is used for a better understanding of the performance. Second law analysis uses exergic method, thereby providing information on the losses in each component of the system which will indirectly influence the COP. During the present work on a single-effect H$_2$O-LiBr vapor absorption cooling system of a ton capacity, a comprehensive SLA has been carried out. Enthalpy, entropy, exergic and dead state values at each state have been found. Exergic values have been compared with the literature values. The reason for the differences in these values has been discussed. The importance of choosing dead state properties of a solution and the proper approach to find it has been provided. Among four key components of a vapour absorption system, an absorber is found to be the component with the largest energy losses.

Keywords: second law analysis, exergy, entropy, irreversibility, dead state.

1. Introduction

Vapour absorption cooling systems utilize low-grade energy, for example, solar heat, as input and operating fluids are eco-friendly materials. Therefore, it has the least global warming and ozone depletion consequences compared to vapour compression systems. H$_2$O-LiBr is found to be the most viable option at moderate temperatures for space cooling applications (Mc Neely 1979, Patterson & Perez Blanco 1988, Lee et al. 1990, Jeter et al. 1992, Lenard et al. 1992), hence more suitable for solar energy-based space cooling applications (Jian Sun et al. 2012, Jaru Wongwittaya & Chen 2010), Hassan & Mohamad 2012). Enhancing COP is the major challenge faced by vapour absorption systems. However, complete performance evaluation is not only to enhance COP but also to overcome the drawbacks of crystallization and corrosion issues associated with H$_2$O-LiBr and thereby influencing the size and cost of the system. Thermodynamic analysis needs to be performed to analyze the above factors (Badarinarayana et al. 1982).

Methods to evaluate performance are are First Law Analysis (FLA) and Second Law Analysis (SLA) for vapour absorption cooling systems. Detailed FLA has been discussed in our previous works (Arshi Banu PS et al. 2018(a-b)). A second law analysis calculates the exergy-based system performance that represents the thermodynamic irreversibility. Exergy testing is defined as the maximum amount of work potential in relation to the environment of a material or a form of energy. The losses thereby represent the
real loss of work in an exergy study. Dissipation (friction), heat transfer under temperature difference is essential to irreversible processes contributing to these losses.

Some of the literary works on SLA have been discussed here. Koehler et al. (1988), Olivia et al. (1994) performed the exergic analysis on a single-effect (single heat source based) vapour absorption refrigeration system. Found enthalpy, entropy and exergy at each state. The authors suggested the different approaches in finding the dead states of the solution state points. Talbi et al. (2000) performed the exergic analysis on single-effect vapour absorption refrigeration system. Found enthalpy, entropy and exergy at each state. Sedighi et al. (2007) considered of single effect vapour absorption refrigeration system with SHX (solution heat exchange), with RHX (refrigerator heat exchanger) and with both RHX and SHX. Variations of COP with generator temperature have been discussed in each cycle. Entropy has not been calculated at all state points of the cycle. Raynaldo et al. (2010) considered the vapour absorption refrigeration, heat pump and heat transfer for his studies. He found physical exergy as well as chemical exergy at each state point of the above cycles. He also clearly represented the properties of the H₂O-LiBr solution, such as enthalpy, entropy and crystallization temperature in both graphical and empirical form. Detailed SLA has been performed in the present study by considering the internal circuit of the single-effect vapour absorption system. Enthalpy, entropy and exergic values of refrigerant and solution have been calculated at each state point of the cycle. The Irreversibilities of each component has been evaluated. Importance of the reference dead state and procedure to find it, for refrigerant and solution has been discussed. Exergic values have been compared with various literature values. The reasons for the differences in these values also discussed.

2. SLA of single-effect H₂O-LiBr vapour absorption cooling system

The system used in the second law analysis is an H₂O-LiBr single-effect absorption cooling system with a capacity of one ton shown in Figure 1. The four key elements are; generator (G), condenser (C), evaporator (E) and absorber (A). The generator (G) comprising a strong salt solution is supplied with heat externally. The steams evaporated from solution flows into the (C) and get condensed. Due to the condensed liquid expansion, (E) has the cooling effect. Eventually, vapour dissolved into (A) and maintains the poor salt solution. The salt solution circulates between (A) and (G) functions as a thermal compressor. LiBr is known as an absorbent solution in this sense. For heat exchanger (SHX), the solution of the absorber is preheated by its recovery before reaching the reactor by using the power from the hot fluid exiting the generator. Details of pressure, temperatures, phases at various state points of the cycle and the assumption made during analysis have been discussed in our previous work (Arshi Banu PS et al. 2018(b)).
To evaluate this system according to the second law, Entropy and enthalpy values are needed at each state of the system. Enthalpy, entropy, exergy and availability values of water (refrigerant) and H$_2$O-LiBr solution (absorbent) have been calculated as follows.

2.1 Enthalpy and Entropies of Refrigerant (water)

Enthalpies and entropies of refrigerant (water) circuit (state point ‘1’ to ‘4’) can be obtained from property empirical equations or in-built functions of EES (Engineering Equation Solver) software of pure water. At state 1, water is at a super-heated steam state from the generator at temperature (T$_g$), enthalpy and entropy of super-heated steam are considered at temperature (T$_g$). Super-heated steam is condensed to liquid water in the condenser. The enthalpy and entropy of liquid water are considered at state 2. Liquid water extracts heat in evaporator and vapour is formed. Hence water vapour enthalpy and entropy considered at evaporator temperature and pressure at condition state 4.

2.2 Enthalpies of H$_2$O-LiBr solutions:

An h-T-X diagram analytical equation gives specific enthalpy values for H$_2$O-LiBr solutions for various concentrates (X) and solutions (T$_s$).

\[
h_n = \sum_{0}^{4} A_n X^n + T_s \sum_{0}^{4} B_n X^n + T_s^2 \sum_{0}^{4} C_n X^n
\] (1)
2.3 Entropies of H$_2$O-LiBr solution:
Empirical equation (2) gives specific entropy values in terms of solution concentrations (X) and solution temperatures (T$_s$) for H$_2$O - LiBr solution (Kaita et al. 2001).

\[
s_n = \sum_{i=0}^{2} \sum_{j=0}^{3} A_{ij} X^i T_s^j
\]  \hspace{1cm} (2)



| n | A$_n$ | B$_n$ | C$_n$ |
|---|---|---|---|
| 0 | -2024 | 18.2829 | -3.7008214E-2 |
| 1 | 163.309 | -1.1691757 | 2.8877666E-3 |
| 2 | -4.88161 | 3.248041E-2 | -8.1313015E-5 |
| 3 | 6.302948E-2 | -4.034184E-4 | 9.9116628E-7 |
| 4 | -2.913705E-4 | 1.8520569E-6 | -4.4441207E-9 |

2.4 Exergy calculation
The exergy of water (refrigerant) circuit (1-2-3-4) is given by:

\[
\psi_n = [h_n - h_o] - T_o [s_n - s_o]
\]  \hspace{1cm} (3)

h$_o$ and s$_o$ are enthalpy and entropies of water at dead state considered at atmospheric pressure (p$_o$) = 1bar and temperature (T$_o$) = 25°C.

The exergy of a binary mixture solution is generally given by:

\[
\psi_n = [h(T_n, X_n) - h_o(T_o, X_{sat})] - T_o [s(T_n, X_n) - s_o(T_o, X_{sat})]
\]  \hspace{1cm} (4)

h$_o$ and s$_o$ are enthalpy and entropies of dead state for the solution is considered at temperature T$_o$ and concentration as X$_{sat}$. Saturated concentration (X$_{sat}$) is the concentration of LiBr in water obtained at pressure (p$_o$) = 1 bar and temperature (T$_o$) = 25°C.

2.5 Availability Loss
The availability loss of a system is calculated by:

\[
\Delta \psi = \sum m_i \psi_i - \sum m_e \psi_e - Q \left(1 - \frac{T_o}{T}\right) - W
\]  \hspace{1cm} (5)

The first word on the right of the equation is the amount of input exergy. The second is the amount output exergy production, whereas the third term is heat exergy Q, transmitted at constant temperature ‘T’. The final term is the transfer of mechanical work to or from the system (Arzu et al. 2005).
2.6 The availability loss in each component is calculated by:

Availability loss in condenser: \( \Delta \psi_c = m_1 \psi_1 - m_2 \psi_2 - Q_c \left(1 - \frac{T_o}{T_c}\right) \)  

(6)

Availability loss in Refrigerant Expansion Valve: \( \Delta \psi_{ev} = m_2 \psi_2 - m_3 \psi_3 \)  

(7)

Availability loss in Evaporator: \( \Delta \psi_e = m_3 \psi_3 - m_4 \psi_4 - Q_e \left(1 - \frac{T_o}{T_e}\right) \)  

(8)

Availability loss in Generator: \( \Delta \psi_g = m_7 \psi_7 - m_8 \psi_8 - m_1 \psi_1 - Q_g \left(1 - \frac{T_o}{T_g}\right) \)  

(9)

Availability loss in Absorber: \( \Delta \psi_a = m_4 \psi_4 - m_5 \psi_5 - m_{10} \psi_{10} - Q_a \left(1 - \frac{T_o}{T_a}\right) \)  

(10)

Availability loss in Solution Heat Exchanger: \( \Delta \psi_{hx} = m_6 \psi_6 - m_7 \psi_7 + m_8 \psi_8 - m_9 \psi_9 \)  

(11)

Availability loss in Solution Expansion Valve: \( \Delta \psi_{sev} = m_9 \psi_9 - m_10 \psi_{10} \)  

(12)

Availability loss in Solution Pump: \( \Delta \psi_{sp} = m_2 \psi_5 - m_4 \psi_6 - W \)  

(13)

Based on these sets of equations, exergetic analysis is performed and heat losses that occurred in each component of VACS have been found. The result obtained from the second law analysis/exergetic analysis has been tabulated in Table 2.

3. Results obtained from SLA

Results obtained from SLA using exergetic method on a single-effect H2O-LiBr vapour absorption system of one ton capacity has been presented here. For the analysis the values of parameters considered are: generator temperature \( (T_g) = 87.8^\circ C \), condenser temperature \( (T_c) = 37.8^\circ C \), absorber temperature \( (T_a) = 37.8^\circ C \), evaporator temperature \( (T_e) = 7.2^\circ C \), ambient temperature \( (T_o) = 25^\circ C \) and effectiveness of solution heat exchanger is assumed as 0.8. The reason for selecting the parameter values are, these are obtained from real experimental values and also similar readings have been considered by various authors, hence it will be convenient in validating and comparing current work with literature. The details are discussing in the next section. Using these parametric values SLA has been performed. At each state point of the cycle, enthalpy, entropy values were calculated and tabulated in Table 1. State 1 to 4 represents pure refrigerant values obtained from water property charts. State 5 to 7 represent weak solution values and state 8 to 10 represent strong solution values. These are obtained from equation (1-2). Entropy values for refrigerant and solution are obtained from equation (3) and equation (4) respectively.

Table 2 results show the irreversibilities contributed by each component of the absorption system calculated from equation (6-13). It also represents the difference between inlet and outlet exergy and the percentage of exergetic losses by each component of the vapour absorption cooling system. They have been given in the higher to lower order in the percentage of contribution. It is found that with a change in flow rates of refrigerant, weak and strong solution, the values of irreversibilities will keep changing. Whereas the percentage of irreversibilities will remains constant for the given set of component temperatures. For external circuit, irreversibilities depend on the real state point data such as inlet & outlet temperatures and mass flow rates occurring in each component. Deciding and comparing the irreversibilities considering the external circuit is not consistent and will vary case to case. Hence in the present work, internal circuit has been considered for finding the irreversibilities occurring in each component.
Table 1 Enthalpy, Entropy and Exergic data obtained from SLA

| State Point | Temperature (°C) | Pressure (kPa) | Concentration (%) | Enthalpy (kJ/kg) | Entropy (kJ/kg.K) | Exergy (kW/kg) |
|-------------|------------------|----------------|-------------------|-----------------|-------------------|----------------|
| 1           | 87.8             | 7.5            | 0                 | 2664            | 8.58              | 112            |
| 2           | 37.8             | 7.5            | 0                 | 158.3           | 0.54              | 1.01           |
| 3           | 7.2              | 0.84           | 0                 | 158.3           | 0.57              | 1.01           |
| 4           | 7.2              | 0.84           | 0                 | 2514            | 8.97              | -154.2         |
| 5           | 37.8             | 0.84           | 55.86             | 92.22           | 0.229             | 26             |
| 6           | 37.8             | 7.5            | 55.86             | 92.22           | 0.229             | 26             |
| 7           | 76.53            | 7.5            | 55.86             | 175.3           | 0.405             | 32.8           |
| 8           | 87.8             | 7.5            | 62.75             | 220             | 0.479             | 81.89          |
| 9           | 47.8             | 7.5            | 62.75             | 146             | 0.29              | 71.92          |
| 10          | 47.8             | 0.84           | 62.75             | 146             | 0.29              | 71.92          |

It is found that the absorber contains the highest availability losses. The reasons are the differences in temperatures accruing between absorber and surroundings. These losses can be avoided by increasing the heat transfer area of the absorber. However, this promotes the cost of absorber. In order to increase the overall performance of the system, care must be taken in designing the components to reduce the irreversibilities that occur in it. The details of absorber design to overcome these losses have been discussed in our work (Arshi Banu PS et al. 2018(c)). The exergic losses of generators are next to the absorber. These losses are due to refrigerant evaporation in the generator from a strong solution. By selecting appropriate working fluids and heat source combination these losses can be avoided.

Table 2 Exergic losses of H2O-LiBr vapour absorption system

| Component       | Exergy Loss(Δψ)(kJ) | % of Exergy Loss |
|-----------------|---------------------|------------------|
| Absorber        | 60.53               | 40.9             |
| Generator       | 50.57               | 34.2             |
| Evaporator      | 7.843               | 5.3              |
| Heat Exchanger  | 21.53               | 14.5             |
| Condenser       | 7.403               | 5                |
| System          | 26.24               | 100              |
### 4. Comparison with literature values and identification of dead state of solution

Exergetic values obtained in the present study have been compared with the literature works of three authors Koehler et al. (1988), Oliveira et al. (1994), Raynaldo et al. (2010) as shown in Table 3. Single effect vapour absorption refrigeration system shown in Figure 1, has been considered with 10 state points for comparison. Common temperature, pressure and flow rates have been maintained at all state points. Input parameters considered for the comparison are generator temperature as 87.8°C, condenser and absorber temperature as 37.8°C and evaporator temperature at 7.2°C. Calculated enthalpy, entropy and exergy values with these inputs have been compared with literature. It is found that there is an enormous difference in the values of exergy by various authors even though there is a similarity in enthalpy and entropy values at all state points. The major reasons identified for the differences in the exergetic values are: Lack of clarity in choosing the dead state reference parameters such as pressure, temperature and concentration of solution; Differences in choosing the methodology for finding the dead state enthalpy and entropy of the solution; Variations in choosing the property values of water as well as H$_2$O-LiBr solution from literature.

According to Koehler et al. (1988), temperature and concentration are the major parameters in deciding the dead state properties whereas pressure is also a vital parameter in defining dead state, which has not been clearly represented in the work. He only considered the reference temperature as 25°C and corresponding concentration to find the dead state enthalpy and entropy of solution. Oliveira et al. (1994) considered pressure as 100 kPa and temperature as 25°C and concentration as 20% to find the dead state enthalpy and entropy for solution circuit. The reason behind considering the 20% concentration and not been discussed. Arzu Sencana et al. found dead state enthalpy and entropy (h$_o$, s$_o$) at temperature 298.5 K. Talbi et al. (2000), Sedighi et al. (2007) & Azhar et al. (2019 & 2020) mentioned environmental condition as the dead state reference properties. Specific pressure, temperature and concentration have not been mentioned in the paper, pressure and concentration details of the solution to find the dead state properties have not been discussed. Reynaldo et al. (2010) considered temperature as 25°C and pressure as one atmosphere. The concentration of the solution has been considered corresponding to the above pressure and temperature. The author mentions the corresponding saturation concentration as 55.4 % for calculations.

In the present study, dead state properties of the solution have been found at the temperature of 25°C and pressure as one atmosphere. Reference concentration has been considered at these pressure and temperature to find the dead state properties h$_o$, s$_o$ for the solution circuit (For state points ‘5’ to ‘10’). Exergetic values obtained from the present study have similar behaviour with the Reynaldo et al. (2010)'s values in solution circuit state points. But the author mentions the saturation concentration as 55.47% whereas for the present study saturation concentration is 13.86 %. Refrigeration circuit (state point ‘1’ to ‘4’) values are matching with the values of Oliveira et al. (1994).
Table 3 Comparison of exergic values of present study with literature at each state point of H₂O-LiBr cycle

| St. Point | Temperature (°C) | Pressure (kPa) | Mass flow rate | Concentration (%) | Enthalpy (kJ/kg) | Entropy (kJ/kgK) | Exergy (kW/kg) (Present Study) | Koehler et al. | Oliveir et al. | Raynaldo et al. |
|-----------|------------------|----------------|---------------|------------------|-----------------|-----------------|------------------------------|---------------|---------------|-----------------|
| 1         | 87.8             | 6.558          | 1             | 0                | 2664            | 8.58            | 112                         | 731.9         | 110.8         | 160.7           |
| 2         | 37.8             | 6.558          | 1             | 0                | 158.3           | 0.54            | 1.01                        | 622.2         | 1.02          | 50.98           |
| 3         | 7.2              | 1.016          | 1             | 0                | 158.3           | 0.57            | 1.01                        | 615.2         | -5.9          | 44.08           |
| 4         | 7.2              | 1.016          | 1             | 0                | 2513.8          | 8.97            | -154.2                      | 465.7         | -155.4        | -105.5          |
| 5         | 37.8             | 1.016          | 9.035         | 55.42            | 91.54           | 0.229           | 26                          | 32.56         | 114.9         | 501.4           |
| 6         | 37.8             | 6.558          | 9.035         | 55.42            | 91.54           | 0.229           | 26                          | 32.57         | 114.9         | 501.4           |
| 7         | 66.2             | 6.558          | 9.035         | 55.42            | 148.95          | 0.405           | 32.8                        | 37.35         | 119.7         | 506.2           |
| 8         | 87.8             | 6.558          | 8.035         | 62.32            | 221.2           | 0.479           | 81.89                       | 10.42         | 180.4         | 608.7           |
| 9         | 53.08            | 1.016          | 8.035         | 62.32            | 156.64          | 0.29            | 71.92                       | 1.88          | 171.8         | 600.2           |
| 10        | 53.08            | 1.016          | 8.035         | 62.32            | 156.64          | 0.29            | 71.92                       | 1.88          | 171.8         | 600.2           |

5. Conclusions

Second law analysis using exergic method of single-effect H₂O-LiBr vapour absorption system of one ton capacity has been performed and conclusions obtained from the analysis have been discussed here.

- Enthalpy, entropy and exergy values of each state point of the vapour absorption system have been calculated.
- Using the exergic values, exergy losses, irreversibilities and the percentage of losses contributed by each component of the VACS have been identified.
- It is found that the absorber contains the highest availability losses followed by the generator. In order to increase the overall performance of the system, care must be taken in designing these components, selecting appropriate working fluids and heat source to reduce the irreversibilities that occur in it.
- Exergic values have been compared with various authors. The reasons for the differences in these values have been discussed.
- The importance of choosing dead state properties of the solution and the clear procedure to find them has been discussed.
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Nomenclature:

- Q: Heat load of components (W)
- T: Temperature (°C)
- h: Enthalpy (kJ/kg)
- s: Entropy (kJ/kgK)
- ψ: Availability (kJ/kg)
- Δψ: Exergic loss /Availability (kJ/kg)
- X: Solution concentration (%)
- FLA: First law Analysis
- SLA: Second Law Analysis
- RHX: Refrigerant Heat Exchanger
- SHX: Solution Heat Exchanger
- COP: Coefficient of Performance

Suffix

- a: Absorber
- c: Condenser / Cooling water
- e: Evaporator
- g: Generator
- r: Refrigerant (Water)
- w: Weak solution
- o: Dead state
- s: Strong solution
- 1 to 10: State points