THE EFFECTS OF GLYCOL ADDITION TO A
STATIC-WATER-COoled THERMAL ENERGY STORAGE SYSTEM

Martin, M.*, Annamalai, K.*, and Claridge, D.

* Currently at Oak Ridge National Lab, Oak Ridge, Tennessee 37831-6070
† ASME Fellow and Corresponding Author
Mechanical Engineering Department, Texas A&M University, College Station, Texas 77843

ABSTRACT

Within the last fifteen years, interest in the development and utilization of cool thermal energy storage has witnessed a dramatic increase. More recently, research has concentrated on the optimization of the storage device. This study looks at the effects of adding glycol to a static, water-ice thermal storage tank, in the pursuit of increasing storage capacity. The results, however, were not as positive as was hoped, as the lowering of the freezing point of water greatly reduces its latent heat of fusion. Second law analysis was also performed in an attempt to illustrate its usefulness in the design of a more efficient cool, thermal energy storage system. Minimum compressor work input is estimated using availability analysis (zero entropy generation). Since the practical units involve irreversibilities, exergetic efficiencies (= minimum work/actual work) are derived in terms of temperatures of operation of refrigeration system, storage tank and ambient.

Key words: storage, tank, glycol, optimum work, exergetic efficiency

INTRODUCTION

Cool thermal storage is rapidly becoming a widely used means of reducing electric demand charges. The latest studies in cool storage are directed towards design of cold-air distribution systems and optimization of the storage device as discussed in Abraham et al. [1998]. This paper investigates a possible means of increasing storage performance by increasing the sensible capacity through the lowering of the normal freezing point of the storage media. The type of cool storage system examined contains a static water ice-on-coil apparatus.

An ice thermal storage system stores energy in two process modes, specifically, sensible and latent energy storage. Sensible cool storage occurs when the storage material, i.e. water, experiences a temperature drop from some initial state to a temperature at which solidification begins. Latent storage of cool energy occurs during the liquid to solid phase change of water. Water temperature remains constant during a latent process, as all of the cooling energy is used in the phase change. The roots of this investigation lie within the two-mode storage process. This study focuses on the possibility of obtaining additional storage capacity by delaying the phase change and allowing more sensible storage to occur.

Delay of a phase change may be easily accomplished through the addition of salt or glycol to the water. The penalties of this action, however, are not quite apparent. Propylene glycol was selected for this study on the basis of its low toxicity, miscibility with water, and minimal environmental concerns. Given the thermodynamic properties of various concentrations of water/glycol solutions, a thermodynamic probe into the actual effects of glycol addition was completed. This theoretical analysis studies the effect of glycol addition on overall storage capacity, and on first and exergy (or relative) efficiency, during the storage process.

ANALYSIS

Propylene Glycol Properties

Phase change delay is achieved through the addition of propylene glycol. Propylene glycol is preferred over ethylene glycol on the basis of lower toxicity. Figures 1-4 show the water freezing points, specific heats and anticipated volume expansions of water solutions up to 30wt% glycol [Dean, 1992]. Glycol addition is limited to 30wt% since freezing points at and below this level were expected to produce unacceptable inefficiencies from the condensing unit. Data below 10wt% were unavailable. Note that as glycol concentration is increased, specific heats are reduced. The anticipated volume expansion of the solution, developed from an ideal solution model, is smaller than that of pure water.

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Similarly the freezing point of water in the solution, predicted using ideal solution model and Raoult’s law is lower than the measured freezing point temperatures (Figure 2a) [Abraham 1993].

**Process Thermodynamics**

While the addition of glycol to the water is expected to increase sensible capacity, its effect on latent capacity must also be examined. Data for latent heats of fusion for the water solutions are not readily available from the manufacturer. While the concept of glycol addition for increased sensible capacity has been suggested in the commercial literature [Dow Chemical, 1990], performance tests, however, were never completed at the laboratory level.

The addition of glycol causes water to become supercooled, as it remains in a liquid phase below its intrinsic solidification temperature. Ideally, the latent heat of fusion of a substance in solution is dependent only on its own characteristics, and not on that of the other substance(s) present. A mathematical model is used to determine the values for the latent heat of fusion (LHF) of supercooled water [Chen, 1988].

\[
L_f = L_v + \int_{T_v}^{T} \Delta C_p \, dT
\]

where:
- \( L_f \) = latent heat of fusion
- \( L_v \) = latent heat of fusion at \( T_v \)
- \( \Delta C_p \) = pure substance freezing temperature
- \( T_v \) = pure substance freezing temperature

Chen also presents an empirical, widely accepted equation for the LHF of supercooled water, developed by M. Randall, for temperatures from -39.85°F to 0.15°F:

\[
L_f = 334.2 \times 2.1190 t_s - 0.00783 t_s^2
\]

It is apparent from Eq. (2) that the latent heat of fusion per kg of H_2O decreases as the freezing temperature decreases. It is mainly due to the specific heat of water (4.217 kJ/kg K) being higher than the specific heat of ice (2.11 kJ/kg K) which suggests a large reduction in liquid enthalpy compared to the reduction in the enthalpy of ice when the freezing temperature is lowered. Thermodynamic tables utilizing glycol properties (Table 1), Randall’s LHF equation and equations of state were developed for the various glycol solutions. These tables contain specific incremental values for enthalpy and entropy, as functions of temperature, at atmospheric pressure.

**Equations of State:**

**Sensible Mode:**
- enthalpy \( h_2-h_1 = c (T_f-T_i) \)
- entropy \( s_2-s_1 = c \ln (T_f/T_i) \)

**Latent Mode:**
- enthalpy \( (h_2-h_1)_f = Q_{sens} \)
- entropy \( (s_2-s_1)_f = (Q_{sens}/T_{f,sens}) \)

The storage system model used in this analysis is shown in Figure 2a. This model consists of a storage tank, acting as an evaporator, coupled with an expansion valve and a condensing unit. From this model, two control volumes are derived. The first (CV1) contains only the refrigerant loop while the second contains both the refrigerant lines and the storage tank.

The coefficient of performance (COP) of a refrigeration device is given as:

\[
COP = \frac{\text{Cooling Energy}}{\text{Work Energy}}
\]

For the first control volume,

\[
[COP]_{CV1} = \frac{Q_{sens}}{W_{comp}}
\]

where \( W_{comp} \) is defined as the compressor work required to transfer \( Q_{sens} \) from the tank. For the second control volume

\[
[COP]_{CV2} = \frac{\Delta U_w}{W_{comp}}
\]

where \( \Delta U_w = Q_{sens} \) (if there is no heat loss), is the change in enthalpy of the water during the storage mode. Note that \( [COP]_{CV2} = [COP]_{CV1} \) for an adiabatic tank. The Carnot COP may be used to estimate the upper limit by assuming the refrigeration cycle is ideal. The Carnot efficiency or COP for an ideal refrigeration cycle is:

\[
COP_{CV1,ideal} = \frac{Q_{sens}}{W_{min,comp}} = \frac{T_{vap}}{(T_{cond} - T_{vap})}
\]

A reduction in Carnot COP should force a reduction in actual COP. The \( COP_{CV2} \) will have a similar expression if \( T_{vap} = T_{comp} \) and \( T_{cond} = T_{sens} \).

In practice many thermodynamic inquiries tend to end after application of the first law and definition of COP. However, as recent literature in thermal storage proposes, entropy production should also be considered. The larger the temperature difference between the tank and evaporator coils, and between the ambient and the condenser coils, the greater the entropy generated and the greater the irreversibility in the system. Recall that while the first law enforces the conservation of energy, i.e., the quantity, the second law deals with the loss in quality of energy. Entropy production arises when there is temperature difference between the tank and evaporator coils, and between the ambient and condenser coils.

The thermodynamic property known as exergy, or availability, is an additive combination of the first and second laws. Availability represents the amount of energy that could...
be transferred as work as the system is brought to equilibrium with the ambience under zero entropy generation. For a work absorbing device like the compressor in a storage tank system, an availability analysis leads to the estimation of minimum compressor work for achieving the desired storage capacity. The actual work input is higher than the minimum work input based on availability analysis. Then energy or relative efficiency is defined as:

\[ \eta_{ex} = \frac{\text{minimum work req'd in storage mode}}{\text{actual work req'd in storage mode}} \]  

(11)

The size of \( \eta_{ex} \) should give some insight into how efficiently the actual input work is utilized in achieving a desired output (i.e. storage capacity). The higher the internal irreversibilities of the system, the smaller the value of \( \eta_{ex} \). The \( \eta_{ex} \) expressions for the two control volumes are shown below:

\[ \eta_{ex,cv1} = \frac{W_{min,comp}}{W_{comp}} = \left[ \frac{\frac{Q_{tank}}{W_{comp}}}{W_{min,comp}} \right] = \left[ \frac{Q_{tank}}{Q_{tank}} \right] \]  

(12)

For the CV1, as long as the evaporator and condenser temperatures are fixed during the cooling process, one can recognize the second term on the right as the inverse of the Carnot COP. Hence using Equation (10),

\[ \eta_{ex} = (\text{COP})_{cv1} \left( \frac{T_{evap}}{T_{cond}} \right) - 1 \]  

(13)

where \((\text{COP})_{cv1}\) is the actual COP of the unit.

Since, typically \( T_{tank} > T_{evap} \) and \( T_{target} < T_{cond} \), additional entropy is generated within CV2. Using Control Volume 2, the integrated work required to remove \( Q_{tank} = \Delta U_{w} \) from the tank is given as

\[ \eta_{ex,cv2} = (\text{COP})_{cv2} \frac{W_{min,comp}}{\Delta U_{w}} \]  

(14a)

where the actual \((\text{COP})_{cv2} = (\text{COP})_{cv1}\) if there is no heat loss from the storage tank. Many times the initial temperature of tank \( T_{A} \) is above the freezing point of ice \( T_{F} \) (Figure 2b) and hence the temperature in the tank first decreases from a given initial temperature \( T_{A} \) to \( T_{F} \) and then freezes to ice at constant temperature as it goes to state C. Hence the entropy changes by \( \Delta S_{w} = S_{A} - S_{C} \) (Figure 2b). Under such a condition the availability analysis yields the minimum compressor work input

\[ W_{min,comp} = \Delta U_{w} - T_{target} \Delta S_{w} \]  

(14b)

For pure water initially at 300 K and ambience at 298 K, the minimum compressor work \( (W_{min,comp} = W_{min,comp}/\text{mass of fluid in tank}) \) is estimated as 38.5 kJ per kg of ice or 16.6 Btu per lb mass (Appendix A). Then Equation (14a) is simplified as

\[ \eta_{ex,cv2} = (\text{COP})_{cv2} \left[ \frac{1}{T_{target}} \right] \frac{T_{target} \Delta S_{w}}{\Delta U_{w}} \]  

(14c)

For a Carnot refrigeration cycle with no external irreversibility, the exergetic efficiency will be unity. However, the heat transfer occurs as a result of finite temperature difference and hence the external irreversibilities are inevitable. Appendix A presents an analysis of the work required and the degree of irreversibilities assuming internal reversibility within the refrigeration cycle and external irreversibilities. Suppose \( T_{CH} \) (ambient temperature) and \( T_{L} \) (tank temperature) are fixed. The R-12 Freon vapor at \( T_{COND} \) loses heat to ambient and the evaporator at \( T_{evap} (\leq T_{L}) \) gains heat from \( T_{L} \). Thus the Carnot refrigeration cycle operates within temperature limits of \( T_{COND} \) and \( T_{evap} \).

\[ W = \bar{W} \left( 1 + \frac{\beta}{\eta_{CH}} \right) \left( \frac{T_{cond}}{T_{CH}} \right) \]  

Where the heat transfer rate \( q_{CH} \) across the condenser of surface area \( A_{CH} \) is given by

\[ \bar{Q} = h_{CH} (T_{COND} - T_{H}) \]  

(16a)

and

\[ \tau = T_{evap}/T_{COND} \]  

(16b)

\[ \beta = \frac{1}{h_{CH} A_{CH}} \]  

(16c)

The irreversibility normalized to work input is given by \( \eta' = \frac{\bar{W}}{\bar{W}} = \frac{1 - \tau}{\tau} \) (Irreversibility rate/\( \bar{W} \))

\[ \bar{W} = \frac{1}{\bar{W} \left( 1 - \tau \right) \left( T_{COND}/T_{H} \right) \left( 1 - \frac{1}{\tau} \right)} \]  

(17)

The exergetic efficiency is given as

\[ \eta_{ex,cv2} = W_{min,cond} / \bar{W} = 1 - \frac{1}{\eta'} = \left[ \frac{T_{H}}{T_{COND}} \right] \frac{1}{1 - \tau} \]  

(18)

**RESULTS OF ANALYSIS**

Figure 3 shows the latent heat of fusion (LHF) of water for each solution, as predicted by Randall's equation. Note that the LHF values are in Btu per unit mass of solution. This implies that the reduction in overall LHF for the solution is a result of the reduction in LHF for the subcooled water and the reduction in the amount of water in the solution as more glycol is added. Propylene glycol has no measurable LHF since solidification has never been observed.

The overall effects of glycol, on capacity, are displayed in Figure 4 as a function of initial solution temperature. The first marker in each curve represents the LHF (Btu/lb of solution) for particular concentration. Consider a tank consisting of water initially at 40°F. The water could be cooled to 32°F and then frozen completely to ice. Then the total storage capacity is about 150 Btu per pound of solution at an initial solution temperature of 40°F. If the water was initially at

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32EF, storage capacity is 143 Btu/lb (which is the same as LHF for pure water). Now, consider a 10wt% solution that freezes at 25.8°F. The LHF is only 125 Btu/lb solution. In order to have the same storage capacity as pure water initially kept at 40EF (i.e. 150 Btu/lb of solution), the 10wt% solution in the tank, the water must be cooled from a higher initial temperature of 52EF (last data point in Figure 4 and \( T_A = 52EF \) in Figure 2b) to the freezing point (\( T_f \)) thus removing the sensible portion of \( \Delta U_s \) (25 Btu/lb solution) and then frozen at 25.8°F (LHF portion of \( \Delta U_s \), 125 Btu/lb solution).

Figure 5 shows the required initial temperatures to store 150 Btu/lb of solution for various glycol concentrations. The penalty of lowering the freezing temperatures is evident. Since the LHF is lowered, the loss in latent storage capacity must be accounted for through an increase in sensible storage. This may be achieved by either increasing the amount of storage material or by increasing the sensible temperature range. Thus, the overall effect of glycol addition on capacity is actually destructive.

As discussed in the analysis, equipment and system efficiencies must also be considered. Figure 6 exhibits the effects on ideal Carnot COP of lower freezing point for rejection temperatures of 80°F, 90°F, and 100°F, assuming \( T_{shp} = T_{cond} \) and \( T_{exp} = T_{freeze} \). Appendix B presents an analysis of the work required when a finite temperature difference exists across the condenser and evaporator but assumes that the refrigeration cycle is based on the Carnot cycle. Thus, it is assumed that the temperature is near the freezing temperature. Figures 9 and 10 plot the work input (Figure 9), degree of irreversibility and exergetic efficiency (Figure 10) as a function of \( T_{exp}/T_{cond} \) with \( T_f/T_i \) as a parameter. For given \( T_f/T_i \) ratio and temperature difference required across condenser and evaporator coils, \( T_{exp}/T_{cond} \) can be determined and hence work \( W \) can be determined (Equation 10b, Appendix A). It is shown that the lower the ratio \( T_{exp}/T_{cond} \), the higher the work input and that exergetic efficiency, \( \eta_{ex} \), increases with decreasing freezing points and increasing rejection temperatures which indicates that the minimum compressor work is either increasing at fixed capacity or the capacity decreases at fixed work input. If data is available for COP, then exergetic efficiency is obtained by multiplying the ordinates in Figures 7 and 8 by the COP of the actual refrigeration equipment.

Given tank capacity \( Q_{tank} \), the initial solution temperature can be determined from Figure 4 at any glycol % and hence \( \Delta S_{el} \) can be estimated. Using the expression for minimum work (Equation 14b), the minimum work (zero entropy generation) and \( Q_{tank} \) can be computed. Thus the ratio \( \left( \frac{W_{min,comp}}{Q_{tank}} \right) = \left( \frac{\eta_{ex}}{\text{COP}} \right) \) can be plotted against tank capacity with glycol % as a parameter. Figures 8a-c show the results at rejection temperatures of 80°F, 90°F, and 100°F. At given glycol %, the lowest capacity in Figure 8 corresponds to initial temperature of the tank being at the freezing point and as such the capacity simply equals LHF. The reduction in the ratio with increasing capacity beyond the LHF signifies that as \( Q_{tank} \) increases, the compressor work increases at a lesser rate due to increased COP, i.e. the system operates more efficiently when operated above the freezing point. As glycol is added, the sensible storage is increased to accommodate the loss in the LHF and \( W_{min,comp} \) is also increased.

In order to understand the irreversibility within the system consider the case where a temperature difference exists between the evaporator and the tank, the condenser and the ambient, and the refrigeration cycle is based on the Carnot cycle. It is assumed that the tank is near the freezing temperature. Figures 9 and 10 plot the work input (Figure 9), degree of irreversibility and exergetic efficiency (Figure 10) as a function of \( T_{exp}/T_{cond} \) with \( T_f/T_i \) as a parameter. For given \( T_f/T_i \) ratio and temperature difference required across condenser and evaporator coils, \( T_{exp}/T_{cond} \) can be determined and hence work \( W \) can be determined (Equation 10b, Appendix A). It is shown that the lower the ratio \( T_{exp}/T_{cond} \), the higher the work input. Particularly when glycol is used, the tank temperature or \( T_f \) decreases and hence for a fixed temperature difference across the coils, \( T_{exp} \) decreases and hence the work input increases. Figure 10 shows the decrease of exergetic efficiency and increase of irreversibility with a decrease in \( T_{exp}/T_{cond} \). As irreversibility approaches zero, the exergetic efficiency tends toward unity. The irreversibility could be reduced and exergetic efficiency improved (i.e. reduction in work input) if a lower temperature is maintained with a larger heat exchanger surface area and a higher heat transfer coefficient.

CONCLUSIONS

As was determined theoretically, addition of glycol to water decreases the latent heat of fusion. LHF. For example, a 10wt% glycol solution, which freezes at 25.8°F, exhibits an LHF of 125.8 Btu/lb of solution. This is a 12.4% reduction in latent capacity below that of pure water. Thus, the penalties of delaying the phase change are much greater than the rewards.

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System COPs were also examined to determine if any system-wise benefits were possible. The idea of using the second law/availability analysis as an optimization technique was introduced and used. The ratio $\frac{W_{\text{min,comp}}}{Q_{\text{in}}}$ increased with lowered freezing temperature.

The availability analysis yields the minimum work input for achieving the desired storage capacity. Finally the exergetic efficiency of the actual units yield information on how close the work input of a unit is to the ideal work input.

If a real interest in this storage method still exists, the following suggestions should be considered. First, laboratory testing to obtain actual values for the LHF for varied concentrations of glycol solutions should be completed. While theoretically the LHF of subcooled water is dependent only on the change in specific heats, the authors feel that more precise values would substantiate the results.

REFERENCES


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Appendix A

Work for Storage Tank With External Irreversibility (With Finite Temperature Difference Across Evaporator and Condenser)

Availability analysis yields the minimum work required for a storage system when there are no internal or external irreversibilities. However the heat transfer occurs as a result of a finite temperature difference and hence external irreversibilities are inevitable. This appendix presents an analysis of the work required and the degree of irreversibility assuming internal reversibility within the refrigeration cycle and external irreversibilities. Suppose $T_h$ (ambient temperature) and $T_L$ (tank temperature) are fixed. The hot Freon vapors at $T_{\text{COND}}$ lose heat to the ambient and the evaporator at $T_{\text{EVAP}}$ ($< T_L$) gain heat from $T_L$. The Carnot cycle operates within the temperature limits of $T_{\text{COND}}$ and $T_{\text{EVAP}}$.

\[ \text{COP} = \frac{1}{1/|T_{\text{COND}} / T_{\text{EVAP}}| - 1} \]

The COP is higher and higher as $T_{\text{EVAP}}$ decreases to $T_L$. However the heat absorption rate

\[ Q_h = \dot{Q}_h = h_\text{L} A_L \left( T_L - T_{\text{EVAP}} \right) \]

declines as $T_{\text{EVAP}}$ increases.

Work input \( \dot{W} = \dot{Q} / \text{COP} = Q_h \left| T_{\text{COND}} / T_{\text{EVAP}} \right| - 1 \)

On the other hand as $T_{\text{EVAP}}$ decreases, $Q_h$ will increase but the COP decreases and again the work input increases. Our goal is to determine $T_{\text{EVAP}}$ at which work input is a minimum for given $T_h$ and $T_L$ if such a minimum exists.

\[ \dot{Q}_h = \dot{h}_\text{L} A_L \left( T_{\text{COND}} - T_h \right) \]

Let

\[ \tau = T_{\text{EVAP}} / T_{\text{COND}} \]

Further

\[ \dot{Q}_h / \dot{Q}_h = T_{\text{EVAP}} / T_{\text{COND}} = \tau \]

Using (4a) and (1) in (2),

\[ \dot{W} = \dot{h}_\text{L} A_L \left( T_L - T_{\text{EVAP}} \right) (1 - \tau) \tau \]

or

\[ \dot{W} = \dot{h}_\text{L} A_L T_L \left( 1 - \frac{T_{\text{EVAP}}}{T_L} \right) (1 - \tau) \tau \]

Using (1) and (3) in (4b)

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\[
\frac{Q_L}{Q_H} = h_L \cdot A_L \cdot (T_L - T_{EVAP}) / h_H \cdot A_H \cdot (T_{COND} - T_H) = \tau \tag{7}
\]

Let
\[
\beta = h_L \cdot A_L / h_H \cdot A_H \tag{8}
\]

Then equation (7) becomes
\[
\beta \cdot (1 - T_{EVAP} / T_L) \cdot (T_{COND} / T_{EVAP}) \cdot (T_{EVAP} / T_L) \cdot (T_H / T_L) = \tau
\]

and using (4b)
\[
\beta \cdot (1 - T_{EVAP} / T_L) \cdot (1 / \beta) \cdot (T_{EVAP} / T_L) \cdot (T_H / T_L) = \tau
\]

Solving for \(T_{EVAP} / T_L\)
\[
T_{EVAP} / T_L = (\beta + 9(T_H / T_L)^{1/2}) / (\beta + 1) \tag{9}
\]

Using (9) in (6b), we obtain
\[
W = (\beta + 1) / (h_L \cdot A_L \cdot T_L) = (1 - \tau) \cdot (1 - \tau(T_H / T_L)) / \tau \tag{10a}
\]

Normalizing with respect to \(T_H\)
\[
W^* = W / (\beta + 1) / (h_L \cdot A_L \cdot T_H) = (1 - \tau) \cdot (T_H / T_L) - \tau / \tau \tag{10b}
\]

Equation (10b) is preferable particularly when the tank fusion temperature is changed with the addition of glycol. Differentiating either of the two equations with \(\beta\) and equating to zero.

\[
\tau = (T_{EVAP} / T_{COND}) = (T_L / T_H)^{(1/2)} \tag{11}
\]

or
\[
(T_L / T_H) = (T_{EVAP} / T_{COND})^{2}
\]

which is similar to the expression obtained for a heat engine [Bojan, 1988]. However, if \(T_L = T_{EVAP} = 273\) K, \(T_H = T_{COND} = 300\) K, then \((T_{EVAP} / T_{COND})^{2} = 0.958\). Thus if \(T_{COND} = 310\) K, then \(T_{EVAP} = 296\) K which is higher than 273 K. Unlike heat engines where a maximum work output exists, no minimum exists for work input with a heat pump or refrigeration cycle.

Figure 9 shows the plot of \(W^*\) vs \(\tau\) with \(T_L / T_H\) as parameter. When \(\tau = T_L / T_H\), the heat transfer rate and hence work input rate falls to zero. The integrated work required to remove \(Q_{cond}\) is given by
\[
W = \int W \, dt
\]

Where \(t = Q_{cond} / \dot{Q}_H\). Hence

\[
W / Q_{cond} = \left( W / Q_L \right) = (T_{COND} - T_{EVAP}) / T_{EVAP} = (1 - \tau) / \tau
\]

The secondary axis represents the work \((W / Q_{cond})\) required to remove unit amount of heat from the storage tank. As \(t \rightarrow T_L / T_H\), the work and heat transfer rates \(\rightarrow 0\) but time \(t \rightarrow \infty\) and hence \(W / Q_L\) is still finite. This work represents the minimum work in the absence of irreversibilities across the heat exchangers. For other cases, and given \(T_H\) and \(T_L\), the operator selects the temperature difference across the condenser and evaporator which fixes \(T_{EVAP}\) and \(T_{COND}\) and hence \(\tau\). Then from known \(\tau\), the work input rate and the total work per kJ of heat removed from the storage tank can be estimated. It is apparent that for the same condenser temperature but lowered \(T_{EVAP}\) (when glycol is added), the total work increases.

Finally the entropy balance equation for the control volume 2 yields the following expression:

\[
[\frac{dS_{sys}}{dt}] = - (Q_L / T_H) + \dot{S}_c.
\]

Integrating and recognizing that \(\Delta S_{sys} = Q_{cond} / T_L\) and with

\[
\begin{align*}
\frac{Q_{cond}}{Q_{evap}} &= \frac{T_{cond}}{T_{evap}} \\
T_{cond} &= T_{evap}
\end{align*}
\]

we can obtain

\[
\Gamma = \frac{\dot{S}_{sys}}{T_H / T_L} = \text{Irreversibility} / Q_{cond}
\]

Finally one can express irreversibility as a fraction of work input.

\[
\frac{T}{W} = \text{Irreversibility} / W = (Q_{cond} / W) \cdot \left(1 / \tau - T_H / T_L \right)
\]

Figure 10 shows the non-dimensional irreversibility vs. \(\tau\) for selected \(T_L / T_H\).

<table>
<thead>
<tr>
<th>Property</th>
<th>H_2O</th>
<th>1, 2 Propylene Glycol, C_6H_{12}O_2</th>
<th>Remarks</th>
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<tr>
<td>Freezing temperature, K [R]</td>
<td>273.15, [491.67]</td>
<td>213.2 [383.8]</td>
<td>Ref: Daubert</td>
</tr>
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<td>Specific heat, kJ/kg K, [Btu/lb R]</td>
<td>2.11 (ice), [0.50]</td>
<td>2.5 [10.6]</td>
<td>Ref: Moran and Shapiro, Daubert</td>
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<td>Latent heat of fusion, kJ/kg (Btu/lb)</td>
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<td>--</td>
<td>--</td>
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<tr>
<td>Density, kg/m³ [lb/ft³]</td>
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<td>Ref: Weast</td>
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<tr>
<td>Molecular weight</td>
<td>18.02</td>
<td>76.10</td>
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</tr>
<tr>
<td>Boiling point, K [R]</td>
<td>373.15, [671.67]</td>
<td>461 [830]</td>
<td>Ref: Daubert</td>
</tr>
</tbody>
</table>

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Figure 1: Water-Glycol Properties: (a) Freezing points of water, in glycol solution, as a function of wt% (Dow Chemical, 1990) (b) Temperature dependence of specific heat for 6-30 wt% glycol-water solutions (Dow Chemical, 1990) (c) Volume change of glycol-water solutions during solidification

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**Figure 2:** (a) Control volumes analyzed (b) T-S diagram: tank (AFC) during cooling, Ambience (DE) during heat rejection from Condenser.

**Figure 3:** Reduction in the latent heat of fusion for glycol/water solutions as a function of weight percent glycol for glycol concentrations of 0-30 wt%.

**Figure 4:** Storage capacities for glycol solutions, Btu/lbₘ of solution.
Figure 5: Required range of solution temperatures for storage of 150 Btu/lbm of solution.

Figure 6: Effects of storage and rejection temperatures on Carnot COP.

Figure 7: Effect of freezing and rejection temperatures on second law cycle efficiency ratios.
Figure 8: Effects of freezing and rejection temperatures on energetic efficiency ratios, \( \eta_e/COP \) (a) Rejection temperature of 80°F (b) Rejection temperature of 90°F (c) Rejection temperature of 100°F.

Figure 9: Non-dimensional work rate and integrated work vs. ratio of evaporator to condenser temperature.

Figure 10: Irreversibility and exergetic efficiency.

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