Second Law Analysis and Optimization of Humidification-Dehumidification Desalination Cycles

by

Karan H. Mistry

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Author .................................................................
Department of Mechanical Engineering
May 11, 2010

Certified by .................................................................
John H. Lienhard V
Collins Professor of Mechanical Engineering
Thesis Supervisor

Accepted by .................................................................
David E. Hardt
Chairman, Department Committee on Graduate Theses
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Abstract

Humidification-Dehumidification (HD) desalination is a thermal distillation method that has the potential to be driven using solar heating. It is a promising technology that can potentially bring safe drinking water to people of the developing world. Surprisingly, few systematic efforts have been made to find the best HD cycles or to improve and optimize existing cycles.

This thesis applies irreversibility analysis to characterize HD desalination cycles and to identify how to further improve cycles and components. It is shown that minimizing the specific entropy generation of the cycle maximizes the gained output ratio (GOR). It is also shown that each cycle has one limiting component that cannot be substantially improved and a second component that should be the target of efforts to minimize entropy generation. Finally, the failure of exergy analysis to yield conclusive results for on-design HD cycle analysis is discussed briefly.

Following the Second Law analysis, an optimization effort is performed using nonlinear programming techniques in order to optimize HD desalination cycles for operating conditions that result in maximum GOR. Closed air, open water and open air, open water cycles with either air and water heating were considered in this analysis. Numerical optimization resulted in substantial improvement in GOR for all four cycle types considered. It was found that the GOR of the cycles decreases with increasing component terminal temperature difference (TTD) and that different cycles perform best at different temperature differences. Optimization also revealed that some counterintuitive design configurations can result in superior performance under the appropriate operating conditions.

Other topics discussed include the behavior of exergy for pure substances and psychrometric mixtures as well as the effect of salinity on the performance of HD cycles.

Thesis Supervisor: John H. Lienhard V
Title: Collins Professor of Mechanical Engineering
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Nomenclature

Roman Symbols

\( a \) Specific nonflow availability \([\text{kJ/kg}]\)
\( b \) Specific flow availability \([\text{kJ/kg}]\)
\( c_p \) Specific heat capacity at constant pressure \([\text{kJ/kg-K}]\)
\( e_x \) Specific nonflow exergy \([\text{kJ/kg}]\)
\( f \) Vector of governing equations
\( \dot{g} \) Molar Gibbs free energy \([\text{kJ/kmol}]\)
\( g \) Vector of constraint equations
\( \dot{H} \) Enthalpy flow rate \([\text{kW}]\)
\( h \) Vector of initial condition equations
\( h \) Specific enthalpy (per kg dry air for moist air, per kg water for liquid water) \([\text{kJ/kg}]\)
\( h_{fg} \) Heat of vaporization \([\text{kJ/kg}]\)
\( L \) Length of heater \([\text{m}]\)
\( \dot{m} \) Mass flow rate \([\text{kg/s}]\)
\( M \) Molecular weight \([\text{kg/kmol}]\)
\( m_r \) Mass flow rate ratio (seawater to dry air) \([-]\)
\( \dot{n}_i \) Molar flow rate of species \( i \) \([\text{mol/s}]\)
\( p \) Vector of parameters
\( P \) Parameter space
\( p \) Pressure \([\text{kPa}]\)
\( \dot{Q} \)  Heat transfer rate [kW]

\( R \)  Specific gas constant [kJ/kg-K]

\( r \)  Objective function

\( R_p \)  Recovery Ratio [-]

\( \dot{S}_{\text{gen}} \)  Entropy generation rate [kW/K]

\( S \)  Salinity [kg solute/kg solvent]

\( s \)  Specific entropy (per kg dry air for moist air, per kg water for liquid water) [kJ/kg-K]

\( s_{\text{gen}} \)  Specific entropy generation (per kg product) [kJ/kg-K]

\( \Delta T \)  Temperature difference from heater surface to fluid bulk temperature [K]

\( T \)  Temperature [K]

\( t \)  Temperature [°C]

\( t \)  Time [s]

\( u \)  Specific internal energy [kJ/kg]

\( v \)  Specific volume [m³/kg]

\( \dot{W}_{\text{least}} \)  Least work of separation [kW]

\( \mathbf{x} \)  Vector of algebraic variables

\( x \)  Mole fraction [-]

\( x \)  Spatial coordinate along length of heater [m]

\( \mathbf{z} \)  Vector of differential variables

**Greek Symbols**

\( \epsilon \)  Component effectiveness [-]

\( \eta \)  Mole ratio of salt in seawater [-]

\( \eta_{II} \)  Second Law/Exergetic efficiency [-]

\( \mu \)  Chemical potential [kJ/kmol]

\( \mu \)  Degree of saturation [-]

\( \bar{\omega} \)  Humidity ratio, mole basis [mol water vapor/mol dry air]
\( \omega \) Humidity ratio, mass basis \([\text{kg water vapor/kg dry air}]\)

\( \phi \) Relative humidity [-]

\( \dot{\Xi} \) Flow exergy flow rate \([\text{kW}]\)

\( \xi \) Specific flow exergy (per kg dry air for moist air, per kg water for liquid water) \([\text{kJ/kg}]\)

**Superscripts**

*ideal* Terminal temperature difference of zero

\( L \) Lower bound

\( U \) Upper bound

**Subscripts**

0 Dead state

1–9 System states

\( a \) Air stream

\( b \) Bulk property

*bot* Bottom/minimum temperature

\( D \) Dehumidifier

\( d \) Destroyed

\( d a \) Dry air

\( f \) Final

\( f \) Saturated liquid

\( g \) Saturated water vapor

\( H \) Hot

\( H \) Humidifier

\( h \) Fluid in heater

\( HT \) Heater

\( in \) Inlet, entering
**ma**  Moist air

**out**  Outlet, exiting

**p**  Product/Condensate

**S**  Salinity

**sat**  Saturated

**sep**  Separation

**t**  Total

**top**  Top/maximum

**total**  Sum of all components

**trans**  Transferred

**v**  Water vapor

**w**  Feedwater, water, water stream

**wall**  Heated surface

**WB**  Wet bulb

**Other Symbols**

\((\cdot)^{\ast}\)  Restricted dead state

\((\cdot)^{\circ}\)  Pure

\((\cdot)\)  Quantity per unit mole \([\cdot/\text{kmol}]\)

\((\cdot)_{i}\)  Partial molar property of species \(i\) \([\cdot/\text{kmol}]\)

**Acronyms**

**AH**  Air Heated

**CAOW**  Closed Air, Open Water

**GOR**  Gained Output Ratio \([-\]]

**HD**  Humidification Dehumidification

**OAOW**  Open Air, Open Water

**RDS**  Restricted Dead State

**WH**  Water Heated
Chapter 1

Introduction

Humidification-Dehumidification (HD) desalination is a thermal distillation method that can be readily driven using solar power. It is a promising technology that has the potential to bring safe drinking water to people of the developing world.

This thesis will discuss some of the fundamental thermodynamics behind the behavior of HD desalination cycles as well as methods for how to find the optimal operating conditions for various cycles.

In this chapter, the motivation for HD desalination research, the background of how the cycles work, and the research objectives considered are discussed.

Chapter 3 will first introduce performance parameters and the governing equations necessary for modeling HD cycles. This will include a discussion of the approximations, equations, and solution techniques used to correctly model the systems. Then, the effect of irreversibilities on the cycle performance will be discussed as well as how an irreversibility analysis can be used to determine optimal operating conditions.

Chapter 4 will briefly discuss the use of multi-parameter optimization for finding the optimal operating conditions for the cycles. The results of the optimization effort are presented and the implications are explained.
1.1 Motivation

Despite the fact that there are very good existing desalination technologies, there is still a great need for additional desalination methods, especially for the developing world.

1.1.1 Desalination Research — The Growing Water Problem

According to The United Nations World Water Development Report, there are currently over one billion people who lack access to adequate drinking water [4]. According to UNICEF, nearly 5,000 children die every day as a result of unsafe water [5]. Unfortunately, as the world population continues to increase and as water supplies continue to be contaminated, it is clear that the current water situation is only going to get much worse.

One of the Millennium Development Goals from a UN Summit in 2000 was to halve the population of people without access to safe drinking water [4]. While there are currently excellent methods of desalination, including reverse osmosis and multi-stage flash, these solutions that work well in the developed world are not suitable in developing regions owing to the fact that they require substantial infrastructure, tend to be dependent on fossil fuels, and typically only become cost-effective at very large scales.

1.1.2 Solar Driven Desalination

When looking at the parts of the world that have the most severe water shortages, it is easy to see that in general, these places tend to be very hot, very dry locations, often near the equator (Fig. 1.1). Looking at a map of world solar insolation, Fig. 1.2, shows that the areas that tend to suffer from water shortage also tend to have an abundance of solar energy. The correlation of water shortage with high solar insolation coupled
with the fact that, excluding initial hardware costs, solar energy is free, suggests that the use of solar energy to drive a desalination system is a very promising endeavor that can potentially bring water to those people who need it most.

1.1.3 Desalination for Developing Regions

While the large-scale desalination methods commonly used today do not work for developing regions, there are several options that can be considered.

Solar stills are one of the oldest and simplest forms of water purification and work
well to produce high purity water while using only the sun’s energy. Unfortunately, stills tend to have low rates of water production, thus requiring large land areas.

Reverse osmosis systems can be scaled down and powered by renewable energy such as solar or wind power. This is currently a very active area of research in the desalination community but these technologies are still very expensive.

Humidification-Dehumidification desalination is a third option that is the focus of this thesis. Before introducing the details of HD desalination, there are three major advantages that should be pointed out. First, the hardware required for HD desalination is simple and has the potential to be predominantly built using locally available materials. Second, as a low temperature thermal desalination method, HD can easily be driven by solar heating. It therefore requires no fuel, and has minimal electrical needs. Finally, as a distillation process, HD leads to very high purity output. As a result of these three strengths, HD desalination has received a lot of attention in recent years [6–12].

1.2 What is HD Desalination?

HD desalination is a distillation method that is based closely on the natural water cycle. In the water cycle, the sun’s energy is used to evaporate water from oceans and other large bodies of water and the vapor then mixes with the air. When the air temperature drops, the amount of moisture content that the air can hold decreases and the vapor precipitates out as rain. The fresh water is then collected and used.

A solar still is the most basic form of an HD cycle. The same processes that occur in the natural water cycle occur in the still: the sun’s energy evaporates water; the moist air then condenses on a cooler surface; the condensate is then removed and utilized as product water.

While solar stills are very simple, unfortunately, they are also very energy ineffi-
cient. When evaporating water, energy goes into the heat of vaporization. When the water vapor condenses on the cold surface, all of the heat of vaporization is lost to the environment.

By separating the evaporation and condensation processes, and by incorporating regenerative heating, the system’s efficiency has the potential to be greatly improved. This is the foundation for HD Desalination. HD performance parameters will be formally defined in Sec. 3.1.

1.3 HD Cycle Types

At the most fundamental level, HD cycles must consist of at least three components: a humidifier, a dehumidifier, and a heater. Depending on how these three components are arranged, various classes of cycles can be formed. The cycles are classified based on the nature of the flow pattern of each of the stream. Two primary cycle classes are considered here: closed air, open water (CAOW) cycles and open air, open water (OAOW) cycles.

The characteristics of these basic cycles are discussed below.

1.3.1 Closed Air, Open Water (CAOW) HD Cycles

The CAOW cycle is one of the most basic forms of an HD cycle and was analyzed using the First Law in [11]. This cycle class can be driven by either a water heater or an air heater, thus forming two distinct cycles. The water heated cycle is considered first.

Closed Air, Open Water, Water Heated (CAOW-WH) Cycles

Figure 1.3 shows a schematic diagram of a closed air, open water, water heated (CAOW-WH) cycle.
Figure 1.3: Schematic diagram of a closed air, open water, water heated (CAOW-WH) cycle.

The physics behind the operation of these cycles is fairly straightforward. First, seawater enters the system at the dehumidifier and is used to cool and condense a warmer, moist air stream. In the condensation process, the heat of vaporization is transferred from the moist air to the seawater, thus warming the feed stream. The condensate is removed as product water and the seawater is then further heated in a solar heater.

The hot seawater is then used to humidify a cooler air stream and the remaining seawater is extracted as brine. In the evaporation process, heat and mass is transferred from the hot seawater stream to the moist air stream. In this configuration, the air stream continuously circulates between the humidifier and the dehumidifier.

When heating the water in a CAOW cycle, the logical placement for the heater is between the dehumidifier and the humidifier (as shown in Fig. 1.3). Heating the water prior to entering the condenser would only serve to raise the cycle’s bottom
temperature, which would reduce the performance of the system.

Closed Air, Open Water, Air Heated (CAOW-AH) Cycles

A variant of the closed air, open water cycle is obtained by moving the solar heater from the water stream to the air stream as shown in Fig. 1.4. This cycle is known as a closed air, open water, air heated (CAOW-AH) cycle.

Both the air and water streams follow the same flow path through the humidifier and dehumidifier, as with the CAOW-WH cycle. However, instead of heating the water stream, the heater is now placed in the air stream. There are two possible locations in the air stream for the heater: before the humidifier and before the dehumidifier.

When the heater is placed prior to the humidifier, hot unsaturated air enters the humidifier. Hot air can hold a higher moisture content and should result in a more
efficient humidification process. When the heater is placed prior to the dehumidifier (as pictured), hot unsaturated air enters the dehumidifier at the system top temperature resulting in a higher water exit temperature. This warmer water then enters the humidifier and is used to humidify the air.

The second placement results in a much more efficient heating process. A thought experiment can be used to explain this (numerical analysis can be found in [11]). When the humid air is heated before the dehumidifier, most of the transferred energy goes into the water stream (energy recovery). Next, in the humidifier, there is a large temperature difference and a large concentration difference between the inlet air and water streams. The temperature and concentration differences result in both heat and mass transfer from the water stream to the air stream. If the heater is placed in the air stream prior to the humidifier, the air in the humidifier is hotter than the water and heat transfer occurs in the opposite direction of mass transfer. Since the driving forces of heat and mass transfer compete, a lower performance results. Therefore it is natural to expect that the second placement is better than the first placement.

### 1.3.2 Open Air, Open Water (OAOW) HD Cycles

Two additional cycle configurations can be formed by breaking the connection in the air stream between the humidifier and dehumidifier. When this is done, an open air, open water (OAOW) cycle is formed since the air stream now makes a single pass through the system. As with the closed air cycles, the open air cycles can be either air heated (OAOW-AH) or water heated (OAOW-WH). An example of an OAOW-AH cycle is shown in Fig. 1.5.

These cycles behave in a very similar fashion to their closed air counterparts. However, it is important to note that the open air cycles are heavily dependent upon the ambient conditions since the air stream is taken directly from the environment. Therefore, it should be expected that the performance of the OAOW cycles will
Figure 1.5: Schematic diagram of an open air, open water, air heated (OAOW-AH) cycle.

fluctuate as the ambient temperature and relative humidity vary.

1.4 Research Objectives

1.4.1 Second Law Analysis

The primary objective of this research was to gain an improved thermodynamic understanding of HD cycle behavior through performing a Second Law analysis. While Second Law analysis on cycles is fundamental level research, it is important to note that this analysis has never been performed for HD desalination. Surprisingly, few systematic efforts have been made to find the best HD cycles or to improve and optimize existing cycles. Narayan et al. [11] performed a detailed study based on First Law principles in order to identify the best performing HD cycles.

Since it is initially expected that cycle performance should be linked with entropy
generation, the objective of the present work was to build upon [11] by performing a Second Law analysis, in conjunction with a First Law analysis, in order to understand how the cycles behave, why some cycles performed better than others, and how to use this knowledge in order to improve HD cycle performance.

In this effort, the goals of the Second Law analysis are: to show that minimizing the specific entropy generation of the cycle maximizes the gained output ratio (GOR); to explain how irreversibility analysis can help a designer optimize HD cycles; and to illustrate why exergy analysis and Second Law efficiency lead to inconclusive results for HD cycles.

1.4.2 Optimization of HD Cycles

After completing the Second Law analysis, the next objective was to determine the best operating conditions possible for the cycle types considered. Since these cycles have numerous parameters that can be independently varied, it is unlikely to find the true optimal conditions by varying parameters one at a time. Instead, it is important to use more formal methods of optimization in order to determine the best operating conditions for maximum cycle performance.
Chapter 2

Modeling

In this chapter, a discussion of the modeling effort for HD cycles will be covered, which includes approximations, governing equations, and solution techniques and validation.

2.1 Approximations

Whenever any system is to be modeled, it is essential to make appropriate engineering approximations. In this analysis, several standard approximations are made.

First, all calculations are performed for steady state at atmospheric pressure. Kinetic and potential energy effects are neglected and pumping power is assumed to be negligible compared to heat input since they are orders of magnitude smaller.

Second, the humidifier and dehumidifier are taken to be adiabatic with respect to the environment. This can be achieved with proper insulation.

Third, the moist air streams are taken to be saturated at the exit of both the humidifier and the dehumidifier. Saturated air at the exit is readily achieved through proper design of both components.

Finally, the dehumidifier condensate bulk temperature is evaluated as a function of the inlet and outlet wet-bulb temperatures of the moist air using a model discussed in Appendix C.
Seawater properties are approximated by pure water properties. General cooling tower design practice shows that properties, such as the vapor pressure, vary by about 1% per 10,000 ppm salinity [3, 13, 14]. Calculations showed that the change in peak GOR, when using 35,000 ppm seawater properties, is less than 1% while all of the general trends remained unchanged (see Appendix D). Use of pure water properties and the associated error is acceptable since the purpose of this study is to characterize and better understand the behavior of CAOW cycles. While the slight change in properties will change the magnitudes of the results, the general trends and conclusions are not affected.

2.2 CAOW Cycles

Each of the CAOW cycles studied in this paper are pieced together by appropriately connecting the humidifier, dehumidifier, and air or water heater. The mass balances throughout the system remain constant regardless of the heater placement within the cycle.

2.2.1 Mass Balances

The mass balances in each of the components are straightforward, and expressions for each of the mass flow rates can be determined independently of the energy and entropy equations.

Dry Air

Since the cycles in question are closed air cycle, the mass flow rate of dry air, \( \dot{m}_{da} \), remains constant throughout the cycle. Therefore,

\[
\dot{m}_{da} = \dot{m}_{da,H,in} = \dot{m}_{da,H,out} = \dot{m}_{da,D,in} = \dot{m}_{da,D,out}
\]  

(2.1)
Note that while the mass flow rate of moist air, \( \dot{m}_{ma} \), varies throughout the cycle since the humidity ratio, \( \omega \), varies:

\[
\dot{m}_{ma} = \dot{m}_{da} + \dot{m}_v = \dot{m}_{da} \left( 1 + \frac{\dot{m}_v}{\dot{m}_{da}} \right) = \dot{m}_{da} (1 + \omega) \tag{2.2}
\]

where the humidity ratio is defined as the ratio of the amount of water vapor to amount of dry air in the moist air mixtures, on a mass basis.

### Water

Mass balances on the water stream in the dehumidifier and water heater yield \( \dot{m}_w = \dot{m}_{w,D,in} = \dot{m}_{w,D,out} = \dot{m}_{a,H,in} \). A mass balance on the water vapor in the dehumidifier air stream gives the mass flow rate of product:

\[
\dot{m}_p = \dot{m}_{\text{condensate}} = \dot{m}_{da} (\omega_{ma,D,in} - \omega_{ma,D,out}) \tag{2.3}
\]

Finally, a water mass balance in the humidifier shows that

\[
\dot{m}_h = \dot{m}_{w,H,out} = \dot{m}_w - \dot{m}_{da} (\omega_{ma,H,out} - \omega_{ma,H,in}) = \dot{m}_w - \dot{m}_p \tag{2.4}
\]

For convenience, the mass flow rate ratio is introduced as the ratio of the flow rates of water to dry air:

\[
m_r \equiv \frac{\dot{m}_w}{\dot{m}_{da}} \tag{2.5}
\]

Either two mass flow rates or one mass flow rate and the mass flow rate ratio need to be arbitrarily selected in order to fully define the mass balances.
2.3 OAOW Cycles

As mentioned in Ch. 1, the only difference between the CAOW cycles and OAOW cycles is that the lower connection between the dehumidifier and humidifier is broken (see Figs. 1.4 and 1.5).

The mass balances on both the air and water streams is unchanged when studying the OAOW cycle. The only difference is that the state of the moist air stream exiting the dehumidifier is not equal to the state of the moist air entering the humidifier. That is, for the OAOW cycles,

\[
T_{ma,D,out} \neq T_{ma,H,in} = T_0 \tag{2.6}
\]

\[
\omega_{ma,D,out} \neq \omega_{ma,H,in} = \omega_0 \tag{2.7}
\]

However, the mass flow rate of dry air, \( \dot{m}_{da} \), and the pressure of the stream at the dehumidifier outlet and humidifier inlet is equal.

2.4 Component Governing Equations

For the basic CAOW cycle, seven states require specification of pressure, temperature, and relative humidity for the moist air stream (OAOW cycles have an eighth state that is defined based on ambient conditions). Based on the approximations given in Sec. 2.1, pressures, relative humidities, and condensate temperature are assumed to be given in the calculations that follow. Therefore, the only unknowns in the system are temperatures at six states. The seawater inlet temperature is fixed and the system top temperature is treated as an input which means only four temperatures are left unknown in the analysis. Energy and entropy balances for the humidifier and dehumidifier provide four equations but introduce two unknown entropy generation terms. In order to solve the cycle, two additional equations must be used. These are
equations for the adiabatic heat and mass exchanger effectiveness.

Note that while First and Second Law equations are written for the heater as well, the heater is already well posed and does not add to the complexity of the model.

An exergy balance is also calculated for each component and for the cycle as a whole after all cycle states have been determined.

2.4.1 Exchanger Effectiveness

The effectiveness of the humidifier and dehumidifier is calculated in a similar fashion as effectiveness is calculated for a two stream heat exchanger. In the latter case, effectiveness is defined as the actual heat transfer divided by the theoretical maximum heat transfer, \(C_{\text{min}} (T_{\text{hot,in}} - T_{\text{cold,in}})\), where \(C_{\text{min}}\) is the minimum heat capacity rate of the two streams. The mass transfer between the air and water streams in the present case makes the stream enthalpy change (a function of temperature and humidity) the natural variable upon which to focus. Therefore, an alternate method of calculating the effectiveness is formulated [15, 16]. First, the effectiveness is calculated in two ways — assuming the water stream has the lower maximum enthalpy change, \(\epsilon_w\), and then assuming the air stream has the lower maximum enthalpy change, \(\epsilon_a\):

\[
\epsilon_w = \frac{\Delta \dot{H}_w}{\Delta \dot{H}_w^{\text{ideal}}} \quad \epsilon_{ma} = \frac{\Delta \dot{H}_{ma}}{\Delta \dot{H}_{ma}^{\text{ideal}}} \quad (2.8a)
\]

The two ideal enthalpy changes are evaluated assuming a zero terminal temperature difference at the top (or bottom) of the exchanger: \(T_{w,\text{out}}^{\text{ideal}} = T_{ma,\text{in}}\) and \(T_{ma,\text{out}}^{\text{ideal}} = T_{w,\text{in}}\). Additionally, the moist air stream is assumed to be saturated \((\phi = 1)\) at the exits.

Note that the numerators of Eq. (2.8a) are equal, by the First Law. Additionally, the stream with the lower total capacity rate will have a smaller ideal enthalpy change. Therefore, the actual effectiveness, \(\epsilon\), will always be the greater of the two values in
Figure 2.1: Dehumidifier control volume.

Eq. (2.8a):

$$\epsilon = \max (\epsilon_w, \epsilon_{ma})$$  \hspace{1cm} (2.8b)

Under this definition of the component effectiveness, it is not always possible to achieve one hundred percent effectiveness without producing temperature crossovers between the streams, which would violate the Second Law. This situation is similar to the inability of parallel flow heat exchangers to reach one hundred percent effectiveness for some capacity rate ratios and it is discussed in more detail in [15, 16]. To address this issue, all calculations were verified in order to ensure that entropy generation was always greater than zero.

### 2.4.2 Dehumidifier

The dehumidifier is a two phase, two stream heat exchanger in which the water vapor in the air stream condenses on a surface that is cooled by the water stream. A control volume for an arbitrary dehumidifier is given in Fig. 2.1. The governing equations are:
First Law

\[ 0 = \dot{m}_w (h_{w,D,in} - h_{w,D,out}) + \dot{m}_{da} (h_{ma,D,in} - h_{ma,D,out}) - \dot{m}_p h_p \]  

(2.9)

where \(\Delta \dot{H}_{w,D}\) is the total change in enthalpy for the seawater stream and \(\Delta \dot{H}_{ma,D}\) is the total change in enthalpy of the moist air stream, which includes the exiting condensate stream.

Second Law

\[ 0 = \dot{m}_w (s_{w,D,in} - s_{w,D,out}) + \dot{m}_{da} (s_{ma,D,in} - s_{ma,D,out}) - \dot{m}_p s_p + \dot{S}_{gen,D} \]  

(2.10)

Effectiveness

The dehumidifier effectiveness is found by combining Eqs. (2.3), (2.8a) and (2.9) and then reducing:

\[ \epsilon_{D,w} = \frac{h_{w,D,in} - h_{w,D,out}}{h_{w,D,in} - h_{w,D,out}} \]  

(2.11a)

\[ \epsilon_{D,ma} = \frac{(h_{ma,D,in} - h_{ma,D,out}) - (\omega_{ma,D,in} - \omega_{ma,D,out}) h_p}{(h_{ma,D,in} - h_{ma,D,out}) - (\omega_{ma,D,in} - \omega_{ma,D,out}) h_{ideal}} \]  

(2.11b)

\[ \epsilon_D = \max (\epsilon_{D,w}, \epsilon_{D,ma}) \]  

(2.11c)

Exergy Balance

The exergy destruction in the component can be calculated in two ways — either using the exergy balance directly or from the amount of entropy generated in the component. \(\xi\) is specific exergy of the mixture per kilogram of dry air, relative to the dead state.
\[ \dot{m}_{w} (\xi_{w,D,in} - \xi_{w,D,out}) + \dot{m}_{da} (\xi_{ma,D,in} - \xi_{ma,D,out}) - \dot{m}_{p} \xi_{p} \]
\[ = T_{0} \dot{S}_{gen,D} \] (2.12)

Condensate Bulk Temperature

To fully define the dehumidifier, a relationship between the condensate temperature and the inlet and outlet moist air wet-bulb temperatures is needed. The bulk temperature of the product stream, \( T_{p} \), can be found by first evaluating the bulk enthalpy of the condensate stream, \( h_{b} \), and then using property tables to look up the temperature as a function of enthalpy and pressure:

\[ T_{p} = T \left[ h_{b}(T_{WB,in}, T_{WB,out}), p \right] \] (2.13)

The bulk temperature of the product stream can be found by evaluating the following integral, which assumes continuous removal of condensate from the condensing surface:

\[ \dot{H}_{b} = \dot{m}_{da} \int_{T_{WB,out}}^{T_{WB,in}} h_{f}(T_{WB}) \left( \frac{d\omega}{dT_{WB}} \right) dT_{WB} \] (2.14)

The bulk enthalpy is converted to specific enthalpy by dividing through by the mass flow rate of product water:

\[ h_{b} = \frac{\dot{H}_{b}}{\dot{m}_{b}} = \frac{\dot{H}_{b}}{\dot{m}_{da}(\omega_{in} - \omega_{out})} \] (2.15)

Finally, in order to reduce computational time, the results of Eqs. (2.13)–(2.15) can be fitted to a polynomial function by using a least-squares surface fit. Calculations were performed in MATLAB [17] using property data from REFPROP [18]. For the case of atmospheric pressure, the condensate temperature, as a function of inlet and
outlet wet-bulb temperatures is given by

$$T_p(T_{WB,in}, T_{WB,out}) = 0.0051918T_{WB,in}^2 + 0.0027692T_{WB,out}^2$$

$$- 0.007417T_{WB,in}T_{WB,out}$$

$$- 0.41913T_{WB,in} + 1.0511T_{WB,out}$$

$$+ 61.6186$$  \(\text{(2.16)}\)

where all of the temperatures are in kelvin. Equation (2.16) is valid for 293 K \(\leq\) \(T_{WB}\) \(\leq\) 363 K and has a maximum relative error of less than 0.5% and a maximum absolute error of less than 1.4 K. Note that when the air stream is saturated, the wet-bulb temperature is equivalent to the dry bulb temperature. A detailed derivation of Eq. (2.16) is provided in Appendix C.

### 2.4.3 Humidifier

The humidifier is a simple direct contact heat and mass exchanger, essentially a cooling tower. Unlike a cooling tower, where the primary goal is to cool process water, the purpose of the humidifier is to humidify (and heat) the air stream. Since the components work in much the same way, the analyses of a cooling tower and humidifier are identical. A control volume for an arbitrary humidifier is given in
Fig. 2.2. The appropriate equations are listed below.

**First Law**

\[
0 = \dot{m}_{da} (h_{ma,H,in} - h_{ma,H,out}) + \dot{m}_{w} h_{w,H,in} - \dot{m}_{b} h_{w,H,out}
\]

where \( \Delta H_{ma,H} \) is the total change in enthalpy of the moist air stream.

**Second Law**

\[
0 = \dot{m}_{da} (s_{ma,H,in} - s_{ma,H,out}) + \dot{m}_{w} s_{w,H,in} - \dot{m}_{b} s_{w,H,out} + \dot{S}_{gen,H}
\]

**Effectiveness**

The humidifier effectiveness is found by combining Eqs. (2.4), (2.8a) and (2.17) and then reducing:

\[
\epsilon_{H,w} = \frac{h_{w,H,in} - \left[ 1 - \frac{1}{mr} (\omega_{ma,H,out} - \omega_{ma,H,in}) \right] h_{w,H,out}}{h_{w,H,in} - \left[ 1 - \frac{1}{mr} (\omega_{ideal_{ma,H,out}} - \omega_{ma,H,in}) \right] h_{ideal_{w,H,out}}}
\]

\[
\epsilon_{H,ma} = \frac{h_{ma,H,in} - h_{ma,H,out}}{h_{ma,H,in} - h_{ma,H,out}}
\]

\[
\epsilon_{H} = \max(\epsilon_{H,w}, \epsilon_{H,ma})
\]

**Exergy Balance**

\[
\dot{\Xi}_{d,H} = \dot{m}_{da} (\xi_{ma,H,in} - \xi_{ma,H,out}) + \dot{m}_{w} \xi_{w,H,in} - \dot{m}_{b} \xi_{w,H,out}
\]

\[
= T_{0} \dot{S}_{gen,H}
\]
2.4.4 Air and Water Heaters

The air and water heaters are single-stream heat exchangers in which composition of the stream remains constant. A control volume for an arbitrary heater is given in Fig. 2.3.

**First Law**

\[ 0 = \dot{m}_h (h_{HT, in} - h_{HT, out}) + \dot{Q} \]  

(2.21)

where the subscript, \( h \), pertains to the stream that is being heated and \( \dot{Q} \) is the heat transfer from the surroundings.

**Second Law**

\[ 0 = \dot{m}_h (s_{HT, in} - s_{HT, out}) + \dot{S}_{trans,HT} + \dot{S}_{gen,HT} \]  

(2.22)

Heat transfer from the surroundings results in a corresponding entropy transfer to the working fluid, \( \dot{S}_{trans,HT} \). The entropy transfer must be calculated in order to evaluate the entropy generation.

The entropy transfer can be calculated by assuming that the stream is heated with a constant heat flux per unit length, \( \dot{Q}/L \) [W/m], and that the wall temperature is greater than that of the bulk stream by a constant \( \Delta T \). Based on known results for solar collectors [19], both approximations are reasonable. Since the temperature range is not large (less than 50 K) and the heated stream’s composition does not change...
during the heating process, the heated stream’s specific heat capacity is evaluated as constant at the average stream temperature and the bulk fluid temperature as a function of $x$ is given by

$$T_b(x) = T_{HT,in} + \frac{(\dot{Q}/L)}{\dot{m}_h c_{p,h}} x$$

(2.23)

The wall temperature is:

$$T_{wall}(x) = T_b(x) + \Delta T = (T_{HT,in} + \Delta T) + \frac{(\dot{Q}/L)}{\dot{m}_h c_{p,h}} x$$

(2.24)

The rate of entropy transfer can then be calculated as follows [20, 21]:

$$\dot{S}_{trans,HT} = \int_0^L \frac{\dot{Q}(x)}{T_{wall}(x)} \, dx$$

$$= \dot{m}_h c_{p,h} \log \left[ \frac{\dot{Q}}{\dot{m}_h c_{p,h} (T_{HT,in} + \Delta T) + 1} \right]$$

(2.25)

Once the entropy transfer is determined, calculation of entropy generation is performed using the Second Law.

**Exergy Balance**

The exergy balance is performed in the same manner as the entropy balance.

$$\dot{\Xi}_{d,HT} = \dot{m}_h (\xi_{HT,in} - \xi_{HT,out}) + \dot{\Xi}_{trans,HT}$$

(2.26)

Exergy associated with heat transfer can be calculated as follows:

$$\dot{\Xi}_{trans,HT} = \int_0^L \left( 1 - \frac{T_0}{T_{wall}(x)} \right) \dot{Q}(x) \, dx$$

$$= \dot{Q} - T_0 \dot{S}_{trans,HT}$$

(2.27)

Once the exergy transferred with the heat transfer process is calculated, calcula-
tion of the exergy destruction is performed using the exergy balance.

2.5 Modeling Software

Due to the complexity of analyzing multi-stream cycles with mixing, various software packages were required in order to solve the equations presented in this chapter. The two primary software packages used to analyze the HD cycles are discussed below.

2.5.1 Engineering Equation Solver

In order to solve the governing equations to perform a Second Law analysis of the HD cycles (Ch. 3), the software, Engineering Equation Solver (EES) [22] was used.

EES is a numerical solver that automatically identifies and groups equations and utilizes an iterative procedure to solve the equation groups. Two conditions are considered in order to verify convergence of the numerical solution: (1) relative equation residual — the difference between left- and right-hand sides of an equation divided by the magnitude of the left-hand side of the equation; and (2) change in variables — the change in the value of the variables within an iteration. The convergence criterion is based on the EES default values of relative equation residuals less than $10^{-6}$ or change in variables less than $10^{-9}$. These standard convergence values are used by several publications that perform thermodynamic analysis [11, 12, 23, 24].

A major advantage of using EES to analyze the HD cycles is that EES has built in property packages for all of the fluids relevant to HD desalination (dry and moist air, water). A discussion of the included fluid property packages is provided in Sec. 2.6.

2.5.2 JACOBIAN

While EES was very useful for the initial phase of HD analysis, the optimization effort (Ch. 4) required more sophisticated modeling software. Various software pack-
ages were considered for the analysis, but ultimately, JACOBIAN [25] was selected. JACOBIAN is capable of handling much larger problems than EES due to its modular method of model development. Complicated system models are built up by first modeling smaller components and then combining models to form a complete system. Modular development of systems allows for much cleaner models that are easier to modify while studying variations of a given system.

Most importantly, an existing computational infrastructure linking various optimization solvers to JACOBIAN could be exploited. These optimization codes (discussed in (Ch. 4) are much more sophisticated than what was available in EES and allow for more customization of the optimization process as well as optimization over a greater number of parameters. Having access to these implementations made JACOBIAN the obvious choice of software for the modeling efforts.

One disadvantage of using JACOBIAN versus using EES is that unlike EES, JACOBIAN does not have built in property packages for the various fluid streams. Instead, the fluid properties had to be implemented using the formulations discussed in Sec. 2.6.

2.6 Evaluation of Fluid Properties

2.6.1 Engineering Equation Solver

When using EES, all fluid property data was taken from the built in property packages, EES evaluates water properties using the International Association for the Properties of Water and Steam, 1995 Formulation (IAPWS 95) [26]. Air properties are evaluated using the ideal gas formulations presented by Lemmon [27]. Moist air properties are evaluated using the formulations presented by Hyland and Wexler [28]. The moist air properties were all given per kilogram of dry air. Moist air properties from EES are in close agreement with the data presented in ASHRAE Fundamentals [29]
and pure water properties are equivalent to those found in NIST’s property package, REFPROP.

While EES has most property data for the water and air streams (enthalpy, entropy, etc.), it does not have built in packages for exergy. Therefore, the Wepfer approximations [30] were used for evaluating moist air and liquid water exergy based on the property values that were available in EES:

\[
\xi_{ma} = (c_{p,da} + \omega c_{p,v}) T_0 \left( \frac{T}{T_0} - 1 - \log \frac{T}{T_0} \right) \\
+ (1 + \bar{\omega}) R_{da} T_0 \log \frac{p}{p_0} \\
+ R_{da} T_0 \left[ (1 + \bar{\omega}) \log \frac{1 + \bar{\omega}_0}{1 + \bar{\omega}} + \bar{\omega} \log \frac{\bar{\omega}}{\bar{\omega}_0} \right] 
\]

\[
\xi_w \approx [h_f(T) - h_g(T_0)] - T_0 [s_f(T) - s_g(T_0)] \\
+ [p - p_{sat}(T)] v_f(T) - R_v T_0 \log \phi_0 
\]

Note that the specific flow exergy for moist air, \(\xi_{ma}\) is given per kilogram of dry air.

When performing an exergy analysis of a system, proper selection of the dead state is critical for proper calculations. Since psychrometric processes involve a mixture of dry air and liquid water, it is important to select a single dead state that corresponds to an equilibrium of both substances. For this analysis, the dead state is selected to be moist air at atmospheric conditions: \(T_0 = 25^\circ\text{C}, p_0 = 101.325\) kPa, and \(\phi_0 = 0.6\). The dead state of the water in the system (regardless of phase) is water vapor at the specified temperature, and a pressure equal to the partial pressure of water vapor at the corresponding moist air state specified above.
2.6.2 JACOBIAN

Property data for dry air, liquid water, water vapor, and moist air had to be programmed using formulations available in the literature since JACOBIAN does not have built in packages for these. The following formulations were used.

Dry air was modeled as an ideal gas according to the formulations presented by [27]. Data was verified by comparing to REFPROP.

Liquid water properties were evaluated using the International Association for the Properties of Water and Steam’s 1997 Industrial Formulation (IAPWS IF97) [31]. Water property data was also verified by comparing to REFPROP.

Moist air properties were evaluated by summing the mass weighted properties of the constituent substances (ideal solution):

\[
\begin{align*}
  h_{ma} &= h_a(T, p_a) + \omega h_v(T, p_v) \\
  s_{ma} &= s_a(T, p_a) + \omega s_v(T, p_v)
\end{align*}
\]  

(2.30)  

(2.31)

Equations (2.30) and (2.31) are explained in more detail in Appendix A. Moist air properties were verified by comparing to the values found in the ASHRAE Fundamentals Handbook [29], which is based on the work of Hyland and Wexler [28].

Exergy was evaluated using Eqs. (2.28) and (2.29).

2.7 Input Conditions

When defining the operating conditions of the cycle, there are two general approaches that can be considered. First, the analysis can be performed assuming a constant production rate with the top temperature fixed (\(\dot{m}_p = 1\); fixed \(T_{HT, out} = T_{H, w, in}\) for WH, fixed \(T_{HT, out} = T_{D, a, in}\) for AH). Second, the analysis can be performed assuming a constant energy inflow (constant heat input, \(\dot{Q}\) and inlet seawater flow rate, \(\dot{m}_w\)).
Ultimately, at least one mass flow rate (plus mass flow rate ratio, \( m_r \)) and either the heat flux or top temperature must be specified for the cycle to be fully defined. Both methods of analysis are considered in this study. In both methods, the component effectiveness is arbitrarily selected. In addition to the specified operating conditions, the environmental conditions (specifically, the seawater inlet state) are known and fixed.

This type of analysis is considered “on-design” since each set of parameters constitutes a different plant rather than an existing plant at various operating conditions. This is because different size components are required to achieve a given effectiveness for different temperatures and flow rates. It is important to keep in mind that each data point presented is a unique plant.

### 2.8 Solution Technique and Validation

The equations for the First Law, mass balances, and component effectiveness presented in Sec. 2.4, along with the selected input conditions fully define the system. These equations and conditions are used to solve for the remaining unknown temperatures. Once all the system states are known, the Second Law equations, exergy equations, and performance parameters are evaluated.

The component and system models were validated by performing hand calculations to ensure that the results presented were consistent. Additionally, limiting cases such as component effectiveness of zero and one were performed in order to make sure that the model behaved as expected.

In order to further validate the model presented here, the results were compared to the trends observed in the paper by Amer et al. [7]. Amer et al. performed both theoretical and experimental analysis of a CAOW-WH cycle and presented trends of how various parameters such as temperatures and humidity ratios within the sys-
tem vary with respect to the system top temperature. It was found that the model presented in the current work followed the same trends seen in Amer’s work. For example, the water exit temperature from the dehumidifier and the humidity ratio at the inlet and outlet of the dehumidifier all increase with increasing cycle top temperature. Quantitative comparisons could not be made to Amer’s work since the paper did not provide sufficient system data (temperatures, effectivenesses, etc.) in order to perform calculations to replicate the exact conditions presented in the figures.
Chapter 3

Second Law Analysis

The aim of this chapter is to gain improved thermodynamic understanding of HD cycle behavior. In this effort, two primary questions will be addressed.

First, how does cycle performance relate to entropy generation? Intuition suggests that the performance of desalination systems should be closely linked to entropy generation. The exact nature of this relationship will be discussed in depth in this chapter.

Second, how can existing cycles be improved based on this analysis? By using the new found understanding of the cycles, it will be shown that existing cycles can be improved.

In order to address the above two questions, first a set of performance parameters will be introduced and explained. A black box calculation of the heat of separation will be also be considered in order to illustrate what the expected behavior should be.

Then, the results of the modeling efforts is discussed in order to answer the two proposed questions.

The results of this section have been accepted for publication in the International Journal of Thermal Sciences [12].
3.1 Performance Parameters

There are several ways to characterize the performance of HD systems. Some important parameters are defined below.

3.1.1 Gained Output Ratio

The gained output ratio (GOR), sometimes known as the performance ratio, is a non-dimensional measure of the amount of product produced for a given heat input. GOR is one of the most commonly used performance parameters for thermal based desalination and is defined here as the mass flow rate of product times the heat of vaporization divided by the heat input:

\[
\text{GOR} \equiv \frac{\dot{m}_p h_{fg}}{\dot{Q}_{in}} \tag{3.1}
\]

where \( h_{fg} \) is the heat of vaporization at the inlet water temperature (ambient conditions).

GOR is a measure of how efficiently a cycle is utilizing the heat input. A GOR of unity means that the system is using exactly enough energy to evaporate a given amount of water. GOR less than one means that the system is using more heat than is required for straight evaporation since some of the heat input is wasted due to losses. Finally, a GOR of greater than one means that the energy input is being regenerated within the system and that less heat is required than that for straight evaporation.

A basic solar still will have a GOR of approximately 1, if not less owing to losses. A high GOR is desirable since it means that less heat input is required per unit water produced. When the heat source is a fossil fuel, higher GOR means lower fuel costs. When the heat source is solar radiation, higher GOR means smaller solar collector area.
3.1.2 Specific Entropy Generation

Specific entropy generation for the cycle is defined as the total entropy generated in each of the components divided by the mass flow rate of product water.

\[ s_{gen, total} = \frac{\dot{S}_{gen, total}}{\dot{m}_p} \quad (3.2) \]

Thermodynamic arguments for the use of this parameter in analysis of HD cycles, based on the least work of separation, are provided in Sec. 3.2.

3.1.3 Second Law/Exergetic Efficiency

Unlike First Law efficiency which measures how much of an energy source is being put to use, Second Law efficiency measures the irreversibilities in a system. A completely reversible system will have a Second Law efficiency of 1 even though the First Law efficiency will be limited to the lower Carnot efficiency. There are various conventions for defining Second Law efficiency; however, a widely used definition that bounds the efficiency between 0 and 1 is that of Bejan and others [20, 23, 24]:

\[ \eta_{II} = \frac{\dot{\Xi}_{out}}{\dot{\Xi}_{in}} = 1 - \frac{\dot{\Xi}_d}{\dot{\Xi}_{in}} \quad (3.3) \]

where \( \dot{\Xi} \) is total exergy flow rate in or out of the system and \( \dot{\Xi}_d \) is total exergy destruction rate.

Equation (3.3) can be applied to the dehumidifier, humidifier, and heater as follows:

\[ \eta_{II,D} = 1 - \frac{\dot{\Xi}_{d,D}}{\dot{m}_{da} \xi_{ma,D,in} + \dot{m}_w \xi_{w,D,in}} \quad (3.4) \]
\[ \eta_{II,H} = 1 - \frac{\dot{\Xi}_{d,H}}{\dot{m}_{da} \xi_{ma,H,in} + \dot{m}_w \xi_{w,H,in}} \quad (3.5) \]
\[ \eta_{II,HT} = 1 - \frac{\dot{\Xi}_{d,HT}}{\dot{m}_h \xi_{HT,in} + \dot{\Xi}_{trans,HT}} \quad (3.6) \]
Similarly, Eq. (3.3) can be applied to the HD cycles as a whole:

\[
\eta_{II,\text{total},\text{CAOW}} = 1 - \frac{\dot{\xi}_{d,\text{total}}}{\dot{m}_w \dot{\xi}_{w,D,in} + \dot{\xi}_{\text{trans}}} \quad (3.7)
\]

\[
\eta_{II,\text{total},\text{OAOW}} = 1 - \frac{\dot{\xi}_{d,\text{total}}}{\dot{m}_w \dot{\xi}_{w,D,in} + \dot{m}_d \dot{\xi}_{\text{ma,H,in}} + \dot{\xi}_{\text{trans}}} \quad (3.8)
\]

Second Law efficiency calculations are common for power production cycles as well as various kinds of thermal pumps. However, its use in desalination systems is less common. Since one would expect a less irreversible system to have better performance, the use of \( \eta_{II} \) as a performance parameter for desalination is discussed in detail below.

### 3.2 Heat of Separation Calculation

Figure 3.1 shows a black-box thermal desalination system. Since the air never leaves the system boundary in a CAOW cycle, the least work of separation should be independent of air flow rate.

In the following section, \( \bar{x} \) is a property of the mixture per mol, \( \bar{x}_i \) is the partial molar property of species \( i \), and \( \dot{n}_i \) is the molar flow rate of species \( i \). The heat of separation is denoted by \( \dot{Q}_{\text{sep}} \). State 1 is the incoming seawater, state 2 is pure water (product), and state 3 is the concentrated brine, all at \( T_0 \).

First and Second Law for black-box HD system:

\[
\dot{Q}_{\text{sep}} + (\dot{n}\dot{h})_1 = (\dot{n}\dot{h})_2 + (\dot{n}\dot{h})_3 \quad (3.9)
\]

\[
\frac{\dot{Q}_{\text{sep}}}{T_H} + (\dot{n}\bar{s})_1 + \dot{S}_{\text{gen}} = (\dot{n}\bar{s})_2 + (\dot{n}\bar{s})_3 \quad (3.10)
\]
Multiply Eq. (3.10) by inlet/outlet temperature, $T_0$ and subtract from Eq. (3.9).

$$
\dot{Q}_{sep} - \frac{T_0}{T_H} \dot{Q}_{sep} + \dot{n}_1 (\bar{h} - T_0 \bar{s})_1 - T_0 \dot{S}_{gen} = \dot{n}_2 (\bar{h} - T_0 \bar{s})_2 + \dot{n}_3 (\bar{h} - T_0 \bar{s})_3
$$

(3.11)

Since enthalpy and entropy for all three streams is evaluated at $T_0$, the Gibbs Energy can be written as, $\bar{g} = \bar{h} - T_0 \bar{s}$.

$$
\left(1 - \frac{T_0}{T_H}\right) \dot{Q}_{sep} = \dot{n}_2 \bar{g}_2 + \dot{n}_3 \bar{g}_3 - \dot{n}_1 \bar{g}_1 + T_0 \dot{S}_{gen}
$$

(3.12)

Now, define the Recovery Ratio and mole ratio of salt in the seawater as:

$$
R_p \equiv \frac{\dot{n}_{H_2O,2}}{\dot{n}_{H_2O,1}} = \frac{\text{Product Water}}{\text{Inlet Seawater}}
$$

$$
\eta \equiv \frac{\dot{n}_{NaCl,1}}{\dot{n}_{H_2O,1}} = \frac{\text{mol salt in seawater}}{\text{mol water in seawater}}
$$

The Gibbs Energy of the mixture per mol, $\bar{g}$, can be rewritten in terms of the partial molar properties, $\bar{g} = (\bar{g})_{H_2O} + (\bar{g})_{NaCl}$. Rewriting Eq. (3.12) in terms of the partial molar properties and dividing through by the molar flow rate of seawater,
\( \dot{n}_{H_2O,1} \), gives the following expression:

\[
\frac{\dot{Q}_{sep}}{\dot{n}_{H_2O,1}} = \left( 1 - \frac{T_0}{T_H} \right)^{-1} \left[ \eta (\bar{g}_{NaCl,3} - \bar{g}_{NaCl,1}) \\
+ (\bar{g}_{H_2O,3} - \bar{g}_{H_2O,1}) \\
+ R_p (\bar{g}_{H_2O,2} - \bar{g}_{H_2O,3}) \right] \\
+ \frac{T_0}{\left( 1 - \frac{T_0}{T_H} \right)} \frac{\dot{S}_{gen}}{\dot{n}_{H_2O,1}}
\]

(3.13)

The bracketed term in Eq. (3.13) is known as the least work of separation per mole of seawater entering, \( \dot{W}_{\text{least}}/\dot{n}_{H_2O,1} \).

\[
\frac{\dot{Q}_{sep}}{\dot{n}_{H_2O,1}} = \frac{\dot{W}_{\text{least}} \left( \Delta \bar{g}_{H_2O}, \Delta \bar{g}_{NaCl} \right)}{\left( 1 - \frac{T_0}{T_H} \right) \dot{n}_{H_2O,1}} + \frac{T_0}{\left( 1 - \frac{T_0}{T_H} \right)} \frac{\dot{S}_{gen}}{\dot{n}_{H_2O,1}}
\]

(3.14)

Finally, The above expression can be converted to heat input per unit mass of water produced by multiplying by \( (1/R_p)(1000/MW_{H_2O}) \), where \( MW_{H_2O} \) is the molecular weight of water:

\[
\frac{\dot{Q}_{sep}}{\dot{m}_p} = \frac{\dot{W}_{\text{least}} \left( \Delta \bar{g}_{H_2O}, \Delta \bar{g}_{NaCl} \right)}{\left( 1 - \frac{T_0}{T_H} \right) \dot{m}_p} + \frac{T_0}{1 - \frac{T_0}{T_H}} \left( \frac{\dot{S}_{gen}}{\dot{m}_p} \right)
\]

(3.15)

In this above equation, it is noted that \( \dot{Q}_{sep}/\dot{m}_p \) is the same grouping of parameters that is seen in GOR, Eq. (3.1). This calculation suggests that to maximize GOR, the right hand side of the equation must be minimized. Since the least heat of separation should not change significantly when varying the cycle conditions (compared to the heat input in the real case), it is seen that minimizing \( \dot{S}_{gen}/\dot{m}_p \) should maximize GOR.

When trying to determine the limiting components as in Sec. 3.3.2, specific entropy generation in each component is examined. This is defined as the entropy generated in the component divided by the system’s product flow rate, \( \dot{m}_p \). This is a suitable
parameter since optimum system performance, rather than individual component performance, is desired.

A term that resembles total exergy destruction, \( T_0 \dot{S}_{gen} \), is also present in Eq. (3.15). However, note that \( T_0 \) represents the temperature of the three fluid streams, not the dead state temperature, and therefore, exergy destruction does not explicitly appear in Eq. (3.15).

Since it is seen that minimizing the specific entropy generation should lead to minimum heat of separation and since total exergy destruction is directly related to the total entropy generation, one might expect that maximizing exergetic efficiency would similarly lead to minimum heat of separation. However, Eq. (3.15) shows that the heat of separation is a function of the flow rate of the product stream whereas it is seen in Eq. (3.3) that the exergetic efficiency, \( \eta_{II} \), is not a function of \( \dot{m}_p \). Therefore, it should not be initially expected that \( \eta_{II} \) will fully capture the effects of irreversibilities in CAOW HD cycles. Furthermore, since GOR is related to the heat of separation, it should not be initially expected that there will be a direct relationship between GOR and \( \eta_{II} \).

### 3.3 Results

#### 3.3.1 Minimizing Specific Entropy Generation Leads to Maximum GOR

A previous study [11] has shown that GOR is a strong function of mass flow rate ratio, component effectivenesses, and system top temperatures (or heat flow rates). Therefore, this study looks at the same parameters but also closely considers the entropy generation in each cycle. Note that the kinks in the following graphs correspond to points where the definition of component effectiveness switches as a result of the \( \max() \) function in Eq. (2.8b).
Figure 3.2 shows GOR (solid lines) and the specific entropy generation (dashed lines) as a function of mass flow rate ratio for a CAOW-WH cycle with $T_{top} = 70^\circ$C and $\epsilon_D = 0.9$.

The first immediately visible result is that peak GOR corresponds to minimum specific entropy generation for both cycles, and regardless of the operating conditions. That is, for each cycle, there is an optimal configuration that both minimizes entropy generation and maximizes GOR. By optimizing a cycle for minimum specific entropy generation, the cycle is also optimized for maximum GOR.

This trend is not present when comparing GOR to the total entropy generation.
Figure 3.3: GOR (solid lines) and specific entropy generation (dashed lines) as a function of mass flow rate ratio for a CAOW-WH cycle with fixed energy input and $\epsilon_D = \epsilon_H = 0.8$.

Figure 3.4: GOR (solid lines) and specific entropy generation (dashed lines) as a function of mass flow rate ratio for a CAOW-AH cycle with $\epsilon_D = \epsilon_H = 0.9$. 
for the system rather than the specific entropy generation. Figure 3.5 illustrates an example of GOR increasing with increasing *total* entropy generation for the same cycle configuration used to create Fig. 3.3. Note that GOR is not a single valued function of either total entropy generation or specific entropy generation. This is because GOR was evaluated by varying the mass flow rate ratio as seen in Figs. 3.2–3.3.

If the data from Fig. 3.5 is instead replotted versus the specific entropy generation (Fig. 3.6), it is seen that as the specific irreversibilities within the cycle decrease, the performance of the system increases. This is a satisfying result since it matches the fact that performance should improve with decreasing irreversibility. Furthermore, it is also in line with the ideal heat of separation calculation given in the appendix.

This trend of increasing GOR with decreasing specific entropy generation was present for all the cycle types and configurations analyzed in this paper. Figure 3.7 shows a plot of GOR versus specific entropy generation for several cases of both the CAOW-AH and CAOW-WH cycles, which are listed in Table 3.1. In each case, the
component effectivenesses and either the top temperature or the heat input was held constant while the mass flow rate ratio was varied. While not presented in any figures, the same trend was present for the OAOW cycles that were tested. The OAOW cases are tabulated in Table 3.2.

Note that in Fig. 3.7, the curves do not collapse to a single curve and that knowing GOR is not sufficient for determining the entropy generation (and vice versa). Instead, for a fixed GOR, it is easy to see that there are several cycles that have the same performance but with different amounts of entropy generated. From a cost point of view, the “best” cycle is likely to be the one with the maximum entropy generation since this will imply higher irreversibilities, and therefore, a smaller system size. Fakheri discusses how in a heat exchanger, minimum entropy generation is not the end goal since a completely reversible exchanger would have to be infinitely large [32]. While Fakheri only looked at heat exchangers, this concept applies to heat and mass exchangers as well [16].
Figure 3.7: GOR versus specific entropy generation for various CAOW cycle configurations and operating conditions listed in Table 3.1.

At first, this seems to be a paradox — maximizing GOR minimizes entropy generation, but the maximum entropy generation is desired. At this point, it is important to make a distinction between operating conditions and cycles. For a given cycle, minimizing entropy generation will maximize GOR. However, when comparing different cycles, the cycle that has the highest entropy generation for a given GOR is likely to be the economically ideal case.

Table 3.1: List of CAOW Cycle Types and Configurations

<table>
<thead>
<tr>
<th>Cycle Type</th>
<th>Constant Parameter</th>
<th>Cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAOW-AH</td>
<td>$\epsilon_D = \epsilon_H = 0.9$</td>
<td>$\dot{Q}_{in} = 500, 650, 750, 820, 900,\text{kW}$</td>
</tr>
<tr>
<td>CAOW-AH</td>
<td>$\epsilon_D = \epsilon_H = 0.9$</td>
<td>$T_{top} = 60, 70, 80, 90,\text{°C}$</td>
</tr>
<tr>
<td>CAOW-AH</td>
<td>$T_{top} = 90,\text{°C}$</td>
<td>$\epsilon_D, \epsilon_H = 0.8, 0.7, 0.9$</td>
</tr>
<tr>
<td>CAOW-WH</td>
<td>$\epsilon_D = \epsilon_H = 0.8$</td>
<td>$\dot{Q}_{in} = 1000, 1250, 1500, 1750, 2000,\text{kW}$</td>
</tr>
<tr>
<td>CAOW-WH</td>
<td>$\epsilon_D = 0.9, \epsilon_H = 0.6$</td>
<td>$T_{top} = 40, 50, 60, 70, 80, 85,\text{°C}$</td>
</tr>
<tr>
<td>CAOW-WH</td>
<td>$T_{top} = 70,\text{°C}$</td>
<td>$\epsilon_D = 0.9, \epsilon_H = 0.5–1.0$</td>
</tr>
</tbody>
</table>
Table 3.2: List of OAOW Cycle Types and Configurations

<table>
<thead>
<tr>
<th>Cycle Type</th>
<th>Constant Parameter</th>
<th>Cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAOW-AH</td>
<td>$\epsilon_D = \epsilon_H = 0.9; \phi = 0.6$</td>
<td>$T_{top} = 70, 80, 90^\circ C$</td>
</tr>
<tr>
<td>OAOW-AH</td>
<td>$T_{top} = 90^\circ C; \phi = 0.6$</td>
<td>$\epsilon_D, \epsilon_H = 0.8, 0.7, 0.9$</td>
</tr>
<tr>
<td>OAOW-WH</td>
<td>$\epsilon_D = \epsilon_H = 0.8; \phi = 0.6$</td>
<td>$Q_{in} = 1250, 1500, 1750, 2000$ kW</td>
</tr>
<tr>
<td>OAOW-WH</td>
<td>$\epsilon_D = 0.9, \epsilon_H = 0.6; \phi = 0.6$</td>
<td>$T_{top} = 60, 70, 80, 85^\circ C$</td>
</tr>
<tr>
<td>OAOW-WH</td>
<td>$T_{top} = 70^\circ C; \phi = 0.6$</td>
<td>$\epsilon_D = 0.9, \epsilon_H = 0.5–1.0$</td>
</tr>
</tbody>
</table>

3.3.2 Identification of Limiting Components

In the basic CAOW HD cycles, either the humidifier or the dehumidifier will limit the performance of the overall system. The performance limit is a result of a minimum temperature pinch within the particular component. Further improvements in effectiveness are not possible since it would result in negative entropy generation (i.e., a temperature cross within the exchanger).

Identification of the limiting component is simple when looking at the specific entropy generation in each of the components of the cycle. As with the total specific entropy generation of the cycle defined in Eq. (3.2), entropy generation within each component is normalized to the mass flow rate of the product stream. Figure 3.8 shows the specific entropy generation within each component of a CAOW-WH cycle with fixed top temperature as a function of the mass flow rate ratio. GOR is also plotted on the second axis for comparison. This figure presents a few key concepts. First, the specific entropy generation within the dehumidifier, humidifier, and heater are all of the same order of magnitude, which means that all of the components must be studied carefully when designing the system. Second, maximum GOR does not occur at a point where all of the components have minimum entropy generation, but rather, where the total specific entropy generation of the system is minimum (in this figure, the amount of water produced is constant so a plot of specific entropy generation would be a scaled version of total entropy generation). Third, one of the components tends toward zero entropy generation (in this case, the humidifier) in
which case it cannot be further improved to have a greater effectiveness. For this particular cycle, the designer should concentrate on improving the effectiveness of the dehumidifier in order to improve the overall performance of the system.

Figure 3.9 plots specific entropy generation within the components of a CAOW-AH cycle with fixed top temperature. For this particular cycle, it is clear that the limiting component depends on the mass flow rate ratio. Focusing on the humidifier and dehumidifier, it is seen that for $m_r < 1.56$, entropy generation in the dehumidifier is less than the production within the humidifier and vice versa for $m_r > 1.56$. When trying to maximize GOR, however, entropy generation in the dehumidifier quickly tends toward zero indicating a pinch constraint. Therefore, the effectiveness of the dehumidifier cannot be further increased and the designer should focus on improving the humidifier.

As seen in Fig. 3.9, the limiting component may switch depending on operating conditions. By looking at the entropy generation of each component of the cycle, the
1.3 1.4 1.5 1.6 1.7 1.8 1.9 2
0.2
0.4
Mass Flow Rate Ratio, $m_r = \dot{m}_w / \dot{m}_{da}$
Specific Entropy Generation, $s_{gen} \quad [kJ/kg-K]$
1.3 1.4 1.5 1.6 1.7 1.8 1.9 2
Figure 3.9: Specific entropy generation within each component of a CAOW-AH cycle with $T_{top} = 90^\circ C$ and $\epsilon_D = \epsilon_H = 0.9$.

designer can quickly determine which component should be the focus of the design effort for given operating conditions. This method of entropy generation analysis can be used for both on- and off-design assessments. During on-design work, it is easy to identify which component will require more attention, while during off-design work it is easy to see which component should be renovated, modified, or otherwise improved. Evaluating the entropy generation is much simpler than performing a full pinch analysis, e.g., as done by Hou [33]. Once the limiting component has been determined, use of pinch analysis can further aid the design process and allow for proper design and optimization of the complete HD system.

### 3.3.3 Exergetic Efficiency

Some authors have suggested using exergy for analysis of HD systems [34, 35]. However, in this work, it was found that there is no consistent correlation between a cycle’s exergetic efficiency and GOR. It is again important to note that all of the analysis
done in this paper is on-design, that is, a cycle is being selected for best performance rather than trying to optimize an existing plant to the best operating conditions. Since each set of conditions corresponds to a different plant, exergy analysis did not prove as useful as one would initially expect.

A thought experiment helps to illustrate this point. From Eq. 3.3, it is clear that there are at least two cases in which $\eta_{II}$ will be zero — when there is no interaction between streams (i.e., nothing happens) and when the amount of exergy input is much greater than the exergy destruction. The second case can be illustrated using the CAOW-WH cycle. As the mass flow rate of seawater increases toward infinity, the amount of exergy entering the system also tends toward infinity. Likewise, the amount of heat required to heat the water stream goes to infinity. Since the seawater stream has a near infinite heat capacity, the humidifier and dehumidifier behave similar to single stream heat exchangers (only one stream is changing temperature) which means the exergy destruction is finite and based on the amount of air in the system. Even though the flow rate of seawater is large, the amount of product produced is limited by the amount of air in the system which means there is a finite amount of water production. Therefore, GOR is very small (small mass production, large heat input), and $\eta_{II}$ is very close to one since the large exergy input will greatly dominate the finite exergy destruction.

When taking these two limiting cases into account, it is clear that exergetic efficiency will not yield conclusive results for the design of a high GOR HD cycle. Additionally, the appendix discusses thermodynamic arguments suggesting that $\eta_{II}$ should not be expected to fully capture the effects of irreversibility in these cycles. Figure 3.10 plots GOR versus Second Law efficiency of several CAOW cycles under the operating conditions listed in Table 3.1. The lack of a general trend in this figure supports the conclusion that Second Law efficiency is not an appropriate tool for on-design analysis of CAOW HD cycles. Once an actual plant has been designed,
Figure 3.10: GOR versus Second Law efficiency for CAOW cycle configurations and operating conditions listed in Table 3.1.

however, it is believed that using Second Law efficiency to further improve the existing plant will be effective.
Chapter 4

Optimization

The purpose of this chapter is to determine the optimal operating conditions that lead to peak GOR for various HD desalination cycles. Initially, a heuristic search for best conditions was performed, but a more formal optimization effort was needed. Optimization is necessary in order to find the peak operating conditions for these cycles as a result of the number of variables involved in the system. Various optimization methods are used in order to accomplish this task.

Prior to presenting the results of optimization, a brief description about the mathematics behind multi-parameter optimization is discussed.

The work conducted in this chapter has been completed in collaboration with Professor Alexander Mitsos.
4.1 Mathematics of Optimization

The goal of optimization, at the most fundamental level, is to maximize a given objective function that is subject to a set of governing equations, constraints, and bounds on variables. Mathematically, this can be expressed as:

\[
\begin{align*}
\max_{\mathbf{p} \in \mathcal{P}} & \quad r(\mathbf{x}(t = t_f), \mathbf{z}(t = t_f), \mathbf{p}) & \text{Objective Function} \\
\dot{\mathbf{x}}(t) &= f(\mathbf{x}(t), \mathbf{z}(t), \mathbf{p}; t) & \text{Governing Equations} \\
0 &\leq g(\mathbf{x}(t), \mathbf{z}(t), \mathbf{p}; t) & \text{Constraints} \\
0 &= h(\mathbf{x}(t = 0), \mathbf{z}(t = 0), \mathbf{p}; t = 0) & \text{Initial Conditions} \\
\mathbf{x}^L &\leq \mathbf{x} \leq \mathbf{x}^U & \text{Algebraic Variable Bounds} \\
\mathbf{z}^L &\leq \mathbf{z} \leq \mathbf{z}^U & \text{Differential Variable Bounds}
\end{align*}
\]

where \( \mathbf{x} \) is a vector of algebraic variables, \( \mathbf{z} \) is a vector of differential variables, and \( \mathbf{p} \) is a vector of parameters [36, 37].

For the problem at hand, the objective function is to maximize GOR. Alternatively, minimization of specific entropy generation would yield the same results. The governing equations are the equations presented in Ch. 2 while the constraints and variable bounds will be discussed in the following sections. Since HD cycles are assumed to be operating in steady state, there are no differential variables or initial conditions and the optimization problem greatly simplifies:

\[
\begin{align*}
\max_{\mathbf{p} \in \mathcal{P}} & \quad \text{GOR}(\mathbf{x}, \mathbf{p}) & \text{Objective Function} \\
0 &= f(\mathbf{x}, \mathbf{p}) & \text{Governing Equations} \\
0 &\leq g(\mathbf{x}, \mathbf{p}) & \text{Constraints} \\
\mathbf{x}^L &\leq \mathbf{x} \leq \mathbf{x}^U & \text{Algebraic Variable Bounds}
\end{align*}
\]
The algebraic variables include quantities such as temperatures, humidity ratios, fluid properties, component effectivenesses, and so on. The input parameters include values such as the environmental conditions.

In order to solve the general optimization problem, specified by Eq. (4.1), or the more simplified optimization problem relevant to the current study specified by Eq. (4.2), various optimization methods can be used. In this analysis, gradient based optimization methods and genetic algorithm were both used to determine the optimal operating conditions. The algorithms used in this analysis are discussed briefly in Sec. 4.3.

4.2 Models and Simulations

As mentioned in Ch. 2, models for the optimization effort were constructed using the software package, JACOBIAN. Modeling in JACOBIAN was done in a modular fashion. First, models of the dehumidifier, humidifier, and heaters were constructed. Next, models of the various CAOW and OAOW cycles were created by including the components, connecting the appropriate streams and performing mass balances on each humidifier/dehumidifier pair.

After the cycle models were created, a separate block for each simulation was required. Simulations instantiate one or multiple models and fix the degrees of freedom. The advantage of this approach is that a single model (either for a component, or a cycle as a whole) can be used in multiple simulations. Therefore, simple variations of each of the models can be analyzed without having to duplicate code.

4.3 Optimization Methods

The optimization problem at hand, prescribed by Eq. (4.2), was solved using the so-called sequential mode of optimization in which the optimization problem is sepa-
rated from the simulation. Rather than considering all of the model’s parameters as optimization variables, only the degrees of freedom in the simulation are used as optimization variables which results in small-scale optimization problems with relatively expensive function and gradient evaluations.

The optimization algorithm selects values for these optimization variables and then calls the simulator (JACOBIAN) to evaluate the objective function and constraints. The simulator sees these optimization variables as parameters in the model equations. For gradient-based methods, the gradients of these functions with respect to the optimization variables must be evaluated at each major iterations. In general, the model in JACOBIAN is represented by a system of differential-algebraic equations along with initial conditions, Eq. (4.1), and the system is integrated in time. JACOBIAN then returns these gradients via an efficient calculation of the parametric sensitivities [38]. For the steady-state problem currently being considered, JACOBIAN has to solve a system of algebraic equations only.

In order to optimize the system for peak GOR, the main optimization variables considered are the mass flow rates, temperatures, and component effectivenesses. The simulator has to solve the model equations and calculate the cycle performance as a function of these variables. The problem constraints that the optimizer must satisfy are positive entropy generation and minimum approach temperature. The optimization problems have 4 optimization variables, 8 constraints and the embedded simulation problems include approximately 700 state variables, depending on the particular cycle being considered.

Two different gradient-based optimization solvers were used in this study, SNOPT and IPOPT. SNOPT [39] is based on a sparse successive quadratic programming algorithm with limited-memory quasi-Newton approximations to the Hessian of the Lagrangian. SNOPT is a commercial code distributed as a set of Fortran 77 subroutines which can be also converted to C code. IPOPT [40] is an interior point method.
intended for large-scale optimization problems implemented in C++. IPOPT is re-
leased as open source code under the Common Public License (CPL), and can be
linked from various languages including C/C++, C, Fortran, AMPL and MATLAB
on various computer platforms. IPOPT can use first- and second-order derivatives
of the objective function and constraints with respect to the optimization variables.
Herein, only first derivatives are returned by JACOBIAN and IPOPT uses an approx-
imation for the Hessian. Default values are used for the options and tolerances in
JACOBIAN. For the optimization, the tolerances are set to $10^{-4}$. Each optimization
run takes on the order of 10–30 seconds when performed on a server with two Intel
Xeon E5405 quad core CPUs at 2.00 GHz (eight cores total) with 8 GB of RAM.

The gradient-based optimizers used generate local optima. Unfortunately, due to
the non-convexity of the modeling equations, local optimality does not imply global
optimality. In fact, for the case studies presented, the solution depends on the initial
guess provided for each of the variables. To overcome this limitation of the solvers, a
multi-start heuristic was used. The initial guess is initialized randomly and 1000 op-
timization runs were executed in a computer cluster. As a consequence, the solutions
reported cannot be guaranteed to be optimal. However, both solvers with multiple
initial guesses converged to the same solution, thus giving high confidence that this
is a global solution. Additionally, a genetic algorithm running for over 50 hours did
not yield a better solution. In future work, deterministic global optimization will also
be employed, in particular the branch and reduce code BARON [41].

4.4 Results

4.4.1 Closed Air, Open Water (CAOW) Cycles

The choice of bounds for the optimization variable was governed based on the findings
from earlier studies of these cycles [11, 12]. A summary of the variable bounds and
constraints is presented in Table 4.1. Based on heuristic search efforts in [12], the optimal GOR for the WH cycles was always found between mass flow rate ratios of approximately $1 < m_r < 4$ while for the AH cycle, peak GOR was typically between $0.5 < m_r < 1.5$. For these simulations, the overall range was extended to $0.4 < m_r < 6$. Similarly, it was seen that peak performance quickly dropped off with decreasing component effectiveness. Therefore, effectiveness was bounded to $0.8 \leq \epsilon_D, \epsilon_H \leq 1.0$. By selecting a minimum effectiveness of 80% rather than the physical minimum of 0%, the variable domain space was greatly reduced, thus reducing the number of required calculations.

Finally, the top temperature was limited to $50^\circ C \leq T_{top} \leq 97^\circ C$. The lower limit was selected based on the results from previous studies. The upper limit was selected in order to attempt to minimize scale formation. Scaling is caused by several factors related to the concentration of the solutes exceeding their solubility limit (supersaturation) [42]. While scale formation is still an issue at elevated temperatures, maintaining the fluid below the boiling point prevents further concentration of salts through boiling and evaporation. Also, the solubility limit of calcium sulfate, one of the primary components in seawater scaling, decreases with increasing temperature. Therefore, maintaining a lower seawater temperature helps to reduce the degree of supersaturation of CaSO$_4$. It turns out that the best WH cycles operate below 80$^\circ$C which means that the heat transfer surface, which will be hotter, should still remain below the boiling point of the feedwater. While the best AH cycles operate at higher temperatures, since the AH cycles heat moist air, the issue of scaling is less important. Additionally, the feedwater does not reach as high a temperature in the AH cycle.

The constraints were selected in order to ensure that the Second Law of Thermodynamics was not violated. First, the entropy generation within each component was constrained to be greater than zero. Second, the terminal temperature difference (TTD), or approach, was selected to be no smaller than typical values found in
Table 4.1: Variable bounds and constraints used for optimization of CAOW and OAOW cycles.

<table>
<thead>
<tr>
<th>Variable Bounds</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_r$</td>
<td>0.4</td>
<td>6</td>
</tr>
<tr>
<td>$\epsilon_D$, $\epsilon_H$</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>$T_{top}$</td>
<td>333.15 K</td>
<td>370.15 K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constraints</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{S}_{gen}$</td>
<td>0</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$TTD_D$</td>
<td>2 K</td>
<td>6 K</td>
</tr>
<tr>
<td>$TTD_H$</td>
<td>2 K</td>
<td>6 K</td>
</tr>
</tbody>
</table>

Figure 4.1: Impact of approach on tower size using fresh water. Reprint from CTI [3].

existing equipment. The Standard Handbook of Plant Engineering has charts that show the approach of cooling towers to be as small as 2°F (1.11 K) [43]. Such small TTDs require very large surface areas as seen by the plot of tower size factor versus approach (TTD) in Fig. 4.1, taken from CTI [3]. In order to ensure that the hardware size is reasonable, a parametric study was performed with TTD from 2–6 K. Based on Fig. 4.1, a TTD of 6 K has a tower size factor of approximately 1.4 while a TTD of 3 K has a size factor of approximately 2.2.

In addition to the variable bounds and constraints, input conditions must be specified. For all of the calculations, all components were assumed to operate at atmospheric pressure and the feedwater inlet temperature was assumed to be 30°C based on typical temperatures for the Red Sea [44]. For the open air cycles, the
Table 4.2: CAOW-WH Optimization results as a function of terminal temperature difference.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Original (3.4 K)</th>
<th>2 K</th>
<th>3 K</th>
<th>4 K</th>
<th>5 K</th>
<th>6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOR</td>
<td>2.53</td>
<td>4.41</td>
<td>4.04</td>
<td>3.56</td>
<td>3.14</td>
<td>2.85</td>
</tr>
<tr>
<td>s&lt;sub&gt;gen&lt;/sub&gt; [kW/K]</td>
<td>0.32</td>
<td>0.14</td>
<td>0.20</td>
<td>0.24</td>
<td>0.30</td>
<td>0.35</td>
</tr>
<tr>
<td>m&lt;sub&gt;r&lt;/sub&gt;</td>
<td>2.90</td>
<td>2.36</td>
<td>3.01</td>
<td>3.67</td>
<td>4.42</td>
<td>5.29</td>
</tr>
<tr>
<td>ϵ&lt;sub&gt;D&lt;/sub&gt;</td>
<td>0.90</td>
<td>0.95</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>ϵ&lt;sub&gt;H&lt;/sub&gt;</td>
<td>0.90</td>
<td>0.92</td>
<td>0.91</td>
<td>0.90</td>
<td>0.89</td>
<td>0.88</td>
</tr>
<tr>
<td>T&lt;sub&gt;bot&lt;/sub&gt; [K]</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
</tr>
<tr>
<td>T&lt;sub&gt;top&lt;/sub&gt; [K]</td>
<td>343.15</td>
<td>329.19</td>
<td>339.07</td>
<td>345.28</td>
<td>350.77</td>
<td>355.65</td>
</tr>
</tbody>
</table>

ambient conditions were selected to be

\[ p_0 = 101.325 \text{kPa} \]
\[ T_0 = 303.15 \text{K} \]  

Using the specified variable bounds and system constraints, the SNOPT and IPOPT algorithms were used with the multi-start code in order to find a global maximum GOR for both the CAOW-WH and CAOW-AH cycles. The optimized results for the CAOW-WH cycle are presented in Table 4.2 while results for the CAOW-AH cycle are presented in Table 4.3. The previous best case configurations that were found without the aid of optimization, using heuristic methods and by varying parameters one at a time, are also included in these two tables for comparison. The results from both cycle configurations are plotted in Fig. 4.2.

For the CAOW-WH cycle, GOR was improved 60% (from 2.53 to 4.04) when considering the case with a minimum approach of 3 K. In each case, it is clear that the largest changes were in the mass flow rate ratio and the effectiveness of the dehumidifier while the system top temperature and humidifier effectiveness vary only slightly. GOR for these cycles is quite sensitive to both flow rates and component effectivenesses. The sensitivity to the mass flow rate ratio shows that these systems require
Table 4.3: CAOW-AH Optimization Results as a function of terminal temperature difference.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Original (3.4 K)</th>
<th>2 K</th>
<th>3 K</th>
<th>4 K</th>
<th>5 K</th>
<th>6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOR</td>
<td>3.48</td>
<td>7.76</td>
<td>5.27</td>
<td>3.83</td>
<td>2.98</td>
<td>2.44</td>
</tr>
<tr>
<td>$s_{gen}$ [kW/K]</td>
<td>0.28</td>
<td>0.15</td>
<td>0.21</td>
<td>0.28</td>
<td>0.35</td>
<td>0.41</td>
</tr>
<tr>
<td>$m_r$</td>
<td>1.22</td>
<td>2.12</td>
<td>1.74</td>
<td>1.46</td>
<td>1.24</td>
<td>1.07</td>
</tr>
<tr>
<td>$\epsilon_D$</td>
<td>0.90</td>
<td>0.98</td>
<td>0.95</td>
<td>0.93</td>
<td>0.89</td>
<td>0.85</td>
</tr>
<tr>
<td>$\epsilon_H$</td>
<td>0.90</td>
<td>0.96</td>
<td>0.93</td>
<td>0.91</td>
<td>0.88</td>
<td>0.85</td>
</tr>
<tr>
<td>$T_{bot}$ [K]</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
</tr>
<tr>
<td>$T_{top}$ [K]</td>
<td>363.15</td>
<td>370.15</td>
<td>370.15</td>
<td>370.15</td>
<td>370.15</td>
<td>370.15</td>
</tr>
</tbody>
</table>

accurate control over the flow rates of the two streams in order to maintain optimal conditions. The sensitivity to effectiveness shows that it is essential to use properly designed components in order to achieve peak performance. As the effectivenesses of the components increases, both the size and cost of the cycle increase. Note that effectiveness does not reach 100% since doing so would violate either the TTD or the entropy generation constraint. Also note that the specific entropy generation for the cycle decreased significantly at optimized conditions as expected since minimizing specific entropy generation results in maximum GOR [12].

Similar behavior is seen in the CAOW-AH cycle. A 51% improvement in GOR (from 3.48 to 5.27), for a minimum TTD of 3 K, was achieved by making a large change to the mass flow rate ratio and smaller changes to the component effectiveness and top temperature. Again, the specific entropy generation decreased and the recovery ratio increased.

In Fig. 4.2, two trends are apparent. First, as the terminal temperature difference increases, the performance of the cycles drops. This is an expected trend since a larger TTD results in increased entropy generation due to larger temperature gradients. Additionally, larger TTDs imply lower regeneration in either the humidifier or the dehumidifier as a result of the large temperature difference of the outlet streams.
The second trend is that the air heated cycle is much more sensitive to TTD than is the water heated cycle. This can be explained by considering the energy regeneration of each cycle. In the WH cycle, hot seawater is used in the humidifier to transfer both moisture and energy to the cooler air stream. Since the water stream enters the humidifier at an elevated temperature, the air stream gains a large amount of moisture prior to entering the dehumidifier. In the AH cycle, hot air enters the dehumidifier and heats up the seawater stream. The warm seawater stream then enters the dehumidifier and humidifies the cooler air stream. When the TTD in the dehumidifier increases, the energy regeneration in the dehumidifier decreases significantly, resulting in a lower seawater top temperature. The lower seawater temperature results in lower potential for driving the humidification process and the air stream picks up less moisture in the humidifier. Less moisture content in the air ultimately means that less water is produced and the cycle performance decreases. When the TTD in the AH cycle is low, however, energy regeneration in the AH cycle is more efficient than that in the WH cycle.
Since the cost and size of the dehumidifier and humidifier increases with decreasing TTD, it is clear that an inexpensive HD system for developing regions (which would have less efficient components) should likely be water heated since the WH cycles outperform the AH cycles as TTD increases. The fact that solar water heaters tend to be cheaper and more readily available than air heaters since water heaters are more commonly used [10, 45] further supports this conclusion.

4.4.2 Open Air, Open Water (OAOW) Cycles

For open air cycles, the ambient air conditions introduce additional parameters to be considered. Since all calculations were performed at atmospheric pressure, two additional parameters are relevant: inlet air temperature and inlet air relative humidity. The air temperature was taken to be equal to the ambient air temperature of 303.15 K specified in the CAOW section. The inlet relative humidity, $\phi_{\text{H,a,in}}$, is treated as a variable since the performance of the OAOW cycles is strongly dependent on the inlet humidity. The other variable bounds and constraints for the OAOW cycles were unchanged from the CAOW (Table 4.1).

OAOW-WH Cycles

Figure 4.3 shows a plot of the optimized GOR values for a OAOW-WH cycle with a minimum TTD of 4 K versus the air inlet relative humidity. The TTD was selected to be 4 K since this TTD offers a reasonable compromise between component size and effectiveness. Note that each point represents an optimized value of the best performance achievable with different component effectivenesses, top temperature, and mass flow rate ratio. Additionally, GOR for a CAOW-WH cycle with a minimum TTD of 4 K is also plotted on the figure for reference (constant since the CAOW cycles are not affected by ambient air conditions).

Figure 4.3 clearly shows that the OAOW-WH cycle outperforms the CAOW-WH
cycle, regardless of the ambient relative humidity. Additionally, the performance of the cycle improves as the relative humidity decreases. This result may seem counterintuitive since the open cycle exhausts warm saturated air from the dehumidifier to the environment.

The primary factor that contributes to the improved performance of the OAOW-WH cycle is that cooler air entering the humidifier (even when saturated) has a lower moisture content than the saturated, warmer air found in the CAOW cycle. Therefore, it has greater potential to absorb moisture from the warm seawater stream.

This unexpectedly good performance of OAOW-WH cycles was found through the optimization efforts. Initial calculations on the OAOW-WH cycles resulted in inferior GOR values than were achieved using the CAOW-WH cycles. However, after applying optimization, the potential of the OAOW-WH cycles was revealed.
Figure 4.4 shows a plot of the optimized GOR values for a OAOW-AH cycle with a minimum TTD of 4 K versus the air inlet relative humidity. Note that each point represents an optimized value of the best performance achievable with different component effectivenesses, top temperature, and mass flow rate ratio. For comparison, GOR for a CAOW-AH cycle with a minimum TTD of 4 K is also plotted on the figure.

Unlike the water heated case, Fig. 4.4 shows that the performance of the air heated cycle increases with increasing ambient relative humidity. Further, with the exception of very high ambient relative humidity, the CAOW-AH cycle outperforms the OAOW-AH cycle.

To explain the trend of decreasing GOR with decreasing ambient relative humidity, consider the humidification process. When unsaturated air enters the humidifier, it is both heated and humidified. However, as the inlet humidity decreases, the exit
temperature of the air stream also decreases since the stream needs to first reach saturation before substantially increasing in temperature. Since drier inlet air results in a lower humidifier exit temperature $T_{H,a,out}$, more heating is required to raise the moist air temperature to the system top temperature, $T_{top} = T_{HT,out}$. As the required heating increases, the performance of the system rapidly drops since GOR is inversely related to the required heat input, as seen in Eq. (3.1). Additionally, the warm saturated air that exits the dehumidifier is exhausted to the environment. The temperature and moisture content of this exhaust stream is greater than found in the WH cases and represents a further loss that lowers the performance of the system.

Figure 4.4 shows that at very high ambient relative humidities, the performance of the open air cycle is greater than that of the closed air cycle. When the ambient air is saturated, $\phi_{H,a,in} = 1$, the only difference between the CAOW-AH and OAOW-AH cycles is that $T_{H,a,in}$ equals the ambient temperature, $T_0$, instead of $T_{D,a,out}$. In general, the ambient temperature of the air will be less than the dehumidifier exhaust temperature. As a result, the humidifier in the OAOW-AH cycle is operating with a lower inlet temperature. The lower temperature air stream provides a greater potential for heat and mass transfer exchange with the warm seawater stream. Therefore, the humidifier can run at a higher effectiveness which leads to improved cycle performance.

Based on the results of optimizing the OAOW-AH cycles, it is clear that while the open air cycles outperform the closed air cycles for near saturated ambient conditions, the performance of the OAOW-AH quickly drops as the ambient relative humidity decreases. Therefore, in general, for a specified TTD, the CAOW-AH cycle will outperform the OAOW-AH cycles.
Table 4.4: OAOW-WH Optimization Results as a function of terminal temperature difference, \( \phi_{in} = 0.6 \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2 K</th>
<th>3 K</th>
<th>4 K</th>
<th>5 K</th>
<th>6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOR</td>
<td>5.05</td>
<td>4.32</td>
<td>3.80</td>
<td>3.39</td>
<td>3.05</td>
</tr>
<tr>
<td>( s_{gen} ) [kW/K]</td>
<td>0.19</td>
<td>0.22</td>
<td>0.25</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>( m_r )</td>
<td>3.16</td>
<td>3.43</td>
<td>3.72</td>
<td>4.23</td>
<td>4.99</td>
</tr>
<tr>
<td>( \epsilon_D )</td>
<td>0.98</td>
<td>0.97</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>( \epsilon_H )</td>
<td>0.95</td>
<td>0.93</td>
<td>0.91</td>
<td>0.89</td>
<td>0.86</td>
</tr>
<tr>
<td>( T_{bot} ) [K]</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
<td>303.15</td>
</tr>
<tr>
<td>( T_{top} ) [K]</td>
<td>341.11</td>
<td>343.16</td>
<td>345.03</td>
<td>348.54</td>
<td>352.99</td>
</tr>
</tbody>
</table>

Comparison of OAOW Cycles

In order to see how the performance of the OAOW cycles varies with respect to minimum TTD, a parametric study was performed with TTD from 2–6 K, as was done with the CAOW cycles. The same variable bounds and constraints used for the CAOW were imposed on the OAOW cycles. The ambient relative humidity was selected to be:

\[
\phi_0 = 0.6
\]  

(4.4)

Using the specified variable bounds and system constraints with multi-start optimization, the global maximum GOR for both OAOW-WH and OAOW-AH cycles was determined. The optimized results for the OAOW-WH cycle are presented in Table 4.4 while results for the OAOW-AH cycle are presented in Table 4.5. The results from both cycle configurations are plotted in Fig. 4.5.

Figure 4.5 and Tables 4.4 and 4.5 show the same trends as what was seen in the CAOW results (Fig. 4.2, Table 4.2, and Table 4.3). That is, GOR drops significantly with increasing TTD, specific entropy generation is minimum for the optimized conditions, and the cycles are sensitive to both the mass flow rate ratio and component effectiveness. One observable difference between the OAOW cycles and the CAOW
Table 4.5: OAOW-AH Optimization Results as a function of terminal temperature difference, $\phi_{in} = 0.6$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Terminal Temperature Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 K</td>
</tr>
<tr>
<td>GOR</td>
<td>3.26</td>
</tr>
<tr>
<td>$s_{gen}$ [kW/K]</td>
<td>0.37</td>
</tr>
<tr>
<td>$m_r$</td>
<td>1.43</td>
</tr>
<tr>
<td>$\epsilon_D$</td>
<td>0.96</td>
</tr>
<tr>
<td>$\epsilon_H$</td>
<td>0.95</td>
</tr>
<tr>
<td>$T_{bot}$ [K]</td>
<td>303.15</td>
</tr>
<tr>
<td>$T_{top}$ [K]</td>
<td>370.15</td>
</tr>
</tbody>
</table>

Figure 4.5: GOR versus TTD for OAOW-WH and OAOW-AH cycles.
cycles is that unlike in the CAOW cycles, the optimized OAOW-WH cycle outperforms the optimized OAOW-AH cycle, regardless of specified TTD.
Chapter 5

Conclusions

Humidification-Dehumidification desalination is a thermal distillation method that can has the potential to be driven using solar power and shows promise to be able to bring safe drinking water to people of the developing world. Since there have been surprisingly few systematic efforts to categorize and understand how HD cycles behave, the present work investigated some of the fundamental thermodynamics behind the behavior of HD cycles and then used optimization methods to find the optimal operating conditions.

A Second Law analysis and entropy generation minimization has helped to identify the key components and operating conditions that should be considered while designing heating dehumidification systems. In this regard, several conclusions were reached.

First, it was found that for a given cycle, there is a specific mass flow rate ratio that simultaneously minimizes specific entropy generation and maximizes GOR. This shows that minimizing specific irreversibility leads to peak performance.

Second, in any given cycle, the effectiveness of either the humidifier or dehumidifier will be limited by the system’s minimum temperature pinch. A designer should focus on improving the other component in order to reduce the total irreversibilities within
Finally, it was found that exergetic efficiency fails to provide meaningful insight into the optimization of the basic HD cycles when applied from an on-design point of view.

Following the Second Law analysis, multi-parameter optimization methods were used to find the optimal operating conditions for both CAOW and OAOW HD desalination cycles and to investigate some characteristics of the various cycles. Through the use of optimization methods, several additional conclusions were reached.

The use of optimization methods for analysis of HD cycles found operating conditions having substantially improved performance. These performance gains were sometimes achieved through selection of counterintuitive cycle configurations and operating conditions. For a TTD of 3 K, the CAOW-WH cycle can achieve a GOR of 4.04 while the CAOW-AH cycle can achieve a GOR of 5.27.

A parametric analysis with terminal temperature difference showed that as the TTD increases, the performance of both CAOW-WH and CAOW-AH cycles decreases. At low TTD, the air heated cycle outperforms the water heated cycle while at higher TTD, the water heated cycle outperforms the air heated cycle.

Lastly, it was seen that the optimized OAOW-WH cycle always outperforms the optimized CAOW-WH cycle, regardless of ambient relative humidity. The optimized OAOW-AH cycle generally performs worse than the optimized CAOW-AH cycle except when ambient relative humidity is near unity. Overall, the CAOW-AH cycles were found to have the highest GOR that could be readily achieved under normal operating conditions.

Through the use of entropy generation minimization and multi-parameter optimization methods, a better fundamental thermodynamic understanding of the behavior of HD cycles has been gained. Additionally, substantial improvements in GOR have been found and better performing cycles have been identified.
Appendix A

Moist Air Properties

This appendix discusses how to properly evaluate moist air fluid properties. Moist air is a mixture of dry air and water vapor.

A.1 Enthalpy

The enthalpy of moist air is evaluated as the mass weighted sum of the enthalpy of the dry air and water vapor in the mixture.

\[
\dot{H}_{ma} = \dot{m}_{da} h_{da}(T, p_{da}) + \dot{m}_{v} h_{v}(T, p_{v}) \\
= \dot{m}_{da} \left( h_{da} + \frac{\dot{m}_{v}}{\dot{m}_{da}} h_{v} \right) \\
= \dot{m}_{da} \left( h_{da} + \omega h_{v} \right) \\
= \dot{m}_{da} h_{ma}
\]  

(A.1)

where \( h_{ma} \) is the specific enthalpy of moist air, per kilogram of dry air:

\[
h_{ma} = h_{da}(T, p_{da}) + \omega h_{v}(T, p_{v})
\]  

(A.2)

An alternative method of evaluating the enthalpy used by ASHRAE [29] is based
on using the degree of saturation, $\mu$, rather than the humidity ratio. The degree of saturation is defined as

$$\mu = \frac{\omega}{\omega_{\text{sat}}|_{T,p}}$$  \hspace{1cm} (A.3)

Then, the moist air enthalpy is

$$h_{ma} = h_{da} + \mu (h_{ma,\text{sat}} - h_{da})$$

$$= h_{da} + \mu (\omega_{\text{sat}} h_{v,\text{sat}})$$  \hspace{1cm} (A.4)

Figure A.1 shows plots of moist air enthalpy evaluated using multiple formulations and data packages. The first curve in each figure is plotted using Eq. (A.2) and the second curve is plotted using Eq. (A.4), both using data from REFPROP [18]. The third curve uses Eq. (A.4) with data from the ASHRAE handbook which is based on the work by Hyland and Wexler [46]. Finally, the last curve is plotted using EES’s built in property library, AirH2O [22], which uses Eq. (A.2) and data from Hyland and Wexler.

Based on Figs. A.1a and A.1b, it is clear that when the moist air is saturated, Eq. (A.2) is identical to Eq. (A.4) (this can also be seen algebraically). However, the enthalpy evaluated using either data from ASHRAE or EES results in differences of less than approximately 1.2%.

Figures A.1c and A.1d, show that there are some differences between Eq. (A.2) and Eq. (A.4) when the moist air is not saturated ($\phi = 0.5$ in these figures). Differences between the four evaluations of moist air enthalpy in this case is less than 1%.

In this thesis, all moist air enthalpy calculations are performed either using EES’s AirH2O package or using Eq. (A.2) with data from REFPROP or implementations of IAPWS IF97 [31] and Lemmon 2000 [27].
Figure A.1: Enthalpy of moist air evaluated using various formulations. Relative error is evaluated based on Eq. (A.2).
A.2 Entropy

The entropy of moist air is evaluated as the mass weighted sum of the entropy of the dry air and water vapor in the mixture.

\[ \dot{S}_{ma} = \dot{m}_{da}s_{da}(T, p_{da}) + \dot{m}_{v}s_{v}(T, p_{v}) \]

\[ = \dot{m}_{da}\left(s_{da} + \frac{\dot{m}_{v}}{m_{da}}s_{v}\right) \]

\[ = \dot{m}_{da}\left(s_{da} + \omega_{s}s_{v}\right) \]

\[ = \dot{m}_{da}s_{ma} \quad (A.5) \]

where \( s_{ma} \) is the specific entropy of moist air, per kilogram of dry air:

\[ s_{ma} = s_{da}(T, p_{da}) + \omega_{s}s_{v}(T, p_{v}) \quad (A.6) \]

Note that since the partial pressures are used in Eq. (A.6), the entropy of mixing is not included [47]. Moist air properties evaluated using Eq. (A.6) were found to agree closely with the data found in the ASHRAE Fundamentals Handbook.

ASHRAE suggests evaluating the entropy based on the degree of saturation, Eq. (A.3), rather than the humidity ratio:

\[ s_{ma} = s_{da} + \mu(s_{ma, sat} - s_{da}) \]

\[ = s_{da} + \mu(\omega_{sat}s_{v, sat}) \quad (A.7) \]

Figure A.2 shows plots of moist air entropy evaluated using multiple formulations and data packages. The curves correspond to the same equations and data packages as discussed for Fig. A.1.

Based on Figs. A.2a and A.2b, it is clear that when the moist air is saturated, Eq. (A.6) is identical to Eq. (A.7) (this can also be seen algebraically). However, the entropy evaluated using either data from ASHRAE or EES results in differences of
Figure A.2: Entropy of moist air evaluated using various formulations. Relative error is evaluated based on Eq. (A.6).
less than approximately 2% for all but very low temperatures ($t < 5^\circ C$).

Figures. A.2c and A.2d, show that there are some differences between Eq. (A.6) and Eq. (A.7) when the moist air is not saturated ($\phi = 0.5$ in these figures). Differences between the four evaluations of moist air entropy in this case is less than approximately 4%.

In this thesis, all moist air entropy calculations are performed either using EES’s \texttt{AirH2O} package or using Eq. (A.2) with data from REFPROP or implementations of IAPWS IF97 [31] and Lemmon 2000 [27].

### A.3 Exergy

Formulations for the evaluation of moist-air exergy are provided in Appendix B.

### A.4 Specific Heat Capacity at Constant Pressure

The specific heat capacity of the moist air stream is only well defined when the humidity ratio, $\omega$, is constant. That is, when the composition of the moist air stream is constant. In this situation, as is the case in the heaters, the specific heat capacity can be evaluated as the mass weighted sum of the properties for dry air and water vapor:

$$c_{p,ma} = c_{p,da}(T, p_{da}) + \omega c_{p,v}(T, p_v)$$  \hspace{1cm} (A.8)
Appendix B

Behavior of Exergy

B.1 Effect of pressure on non-flow and flow exergy

This section discusses the effect of pressure on exergy and explains the circumstances in which it is possible to have negative exergy. Pure water (pure substance model) and air (real gas) are both considered. Property data is taken from REFPROP [18], calculations done using MATLAB [17].

B.1.1 Background

According to most textbooks, exergy, by definition, can never be negative. For example, Moran and Shapiro [21] state:

The value of exergy cannot be negative. If a system were at any state other than the dead state, the system would be able to change its conditions spontaneously toward the dead state; this tendency would cease when the dead state was reached. No work must be done to effect such a spontaneous change. Accordingly, any change in state of the system to the dead state can be accomplished with at least zero work being developed, and thus the maximum work (exergy) cannot be negative.
However, while calculating the exergy of moist air over a broad range of states (various temperatures, pressures, and relative humidities), it is found that there are certain states in which the moist air exergy is negative. Both Wepfer’s equation [30] and the exact definition of exergy agree closely, so it is clear that the negative values are not due to approximations in the Wepfer model.

Since a negative value of exergy directly contradicts the stated idea that exergy can never be negative, it is important to explain why these calculations result in negative values. In order to do this, exergy of pure water and air is calculated at a variety of states. Single substances, rather than mixtures, are used in order to simply calculations and analysis.

Before continuing, the differences between non-flow and flow exergy must be considered.

B.1.2 Dead State

Since this analysis deals with single substance systems only, the system can only reach thermal and mechanical equilibrium with the environment. Therefore, the dead state is specified by $T$ and $p$ only:

$$T_0 = T_{\text{environment}} = 25^\circ C$$
$$p_0 = p_{\text{environment}} = 100 \text{ kPa}$$

(B.1)

B.1.3 Nonflow Exergy

The following equations apply to closed systems. All equations come from Bejan [20].

Nonflow availability, for a pure substance is:

$$a = u + p_0v - T_0s$$

(B.2)

The nonflow exergy of the system is simply the difference of the nonflow availability,
Eq. (B.2), of the system and the environment. Therefore, nonflow exergy is:

\[ e_x = a - a_0 = (u - u_0) + p_0 (v - v_0) - T_0 (s - s_0) \]  

(B.3)

where potential and kinetic energy effects have been neglected.

### B.1.4 Flow Exergy

The following equations apply to open systems. All equations come from Bejan [20].

Neglecting kinetic and potential energy effects, flow availability, for a pure substance is:

\[ b = h - T_0 s \]  

(B.4)

The flow exergy of the system is simply the difference of the nonflow availability, Eq. (B.4), of the system and the environment. Therefore, flow exergy is:

\[ \xi = b - b_0 = (h - h_0) - T_0 (s - s_0) \]  

(B.5)

### B.1.5 Plots - Water

Figure B.1: Water exergy surfaces. Note that the nonflow exergy is zero at the dead state, and positive everywhere else while the flow exergy is very slightly negative for pressures less than the dead state pressure.
Figure B.2: Water exergy versus temperature at various pressures. Note that it is difficult to see in this figure, but the flow exergy drops below zero for pressures lower than the dead state pressure. Also note that neither the nonflow nor the flow exergy are strongly dependent on pressure since water is an incompressible liquid.

Figure B.3: Water exergy versus pressure at various temperatures. Exergy is a very weak function of pressure since water is an incompressible fluid. Exergy has a more significant dependence upon pressure only for very high pressures (on the order of 100 bar). Printed numbers on the figure represent the temperature at which the exergy is evaluated at.

B.1.6 Plots - Air
Figure B.4: Air Exergy Surface — Note that the air-nonflow exergy surface has a definite global minimum at the dead state while flow exergy surface is negative for pressures less than the dead state pressure.

Figure B.5: Air exergy versus temperature at various pressures.
Figure B.6: Air Exergy versus pressure at various temperatures. Printed numbers on the figure represent the temperature at which the exergy is evaluated at.
B.1.7 Justification and Thought Experiment

As mentioned above, most texts state that exergy can never be negative. However, looking at the plots in the preceding two sections, it is clear that while the nonflow exergy is always positive, the flow exergy can be negative when the pressure of the system is less than the pressure of the dead state. This apparent contradiction of conventional thought on exergy requires some explanation to understand. First, consider the nonflow exergy.

Nonflow Exergy Behavior

Consider a closed system, such as a large thermal mass, that is at mechanical equilibrium with the environment, but at a different temperature. Regardless of whether the thermal mass is at a higher or lower temperature, a basic heat engine could be driven by the $\Delta T$ provided by the system-environment pair and positive work would be produced. Therefore, one would expect the exergy of the system to have a minimum when $T = T_0$ and to increase as the temperature deviates from $T_0$. This behavior is seen for both water (Figs. B.1a and B.2a) and for air (Figs. B.4a and B.5a).

Next, consider another closed system. This time, however, consider a compressible substance (such as air) in a vertical piston/cylinder assembly, with the piston pinned in place. The substance would expand to fill the volume of the rigid cylinder. Also, assume that the closed system is in thermal, but not mechanical equilibrium with the environment. Now, if the pin is removed and the system is allowed to come to mechanical equilibrium, one of two things could happen.

First, if $p > p_0$, then the system would expand and do $pV$ work against the environment as the piston rises. Second, if $p < p_0$, when the pin is removed, the system would be compressed by the environment and the piston would move down. This downward motion of the piston could be coupled to another mass via a string and pulley and be used to raise said mass through a vertical distance, and therefore,
perform gravity work. Therefore, one would expect the exergy of the system to have a minimum when \( p = p_0 \) and to increase as the pressure deviates from \( p_0 \). This is represented by the nonflow exergy having a positive value for pressures different from the ambient pressure as seen in Figs. B.4a and B.5a for air. Note that water is nearly incompressible, so at these low pressures, exergy is not a strong function of pressure and it is difficult to visualize these trends.

**Flow Exergy Behavior**

Now consider a fluid stream that is flowing through a control volume. If the stream is at mechanical, but not thermal equilibrium with the environment, the temperature difference can be used to drive a heat engine in much the same way as discussed for the control mass. For example, if hot fluid is flowing through a pipe, a heat engine can be driven using the temperature difference between the pipe wall and the surroundings. Likewise, if the fluid is cold, the same heat engine can be run in reverse and still generate work by using the environment as the hot source. In either condition, the use of the heat engine to produce work results in the working fluid approaching thermal equilibrium with the environment. Therefore, the flow exergy will behave in the same way as the nonflow exergy in respect to temperature. That is, it will be minimum for \( T = T_0 \) and will increase as \( T \) deviates from \( T_0 \). This is seen in Figs. B.1b, B.2b, B.4b, and B.5b.

The pressure effects of flow exergy are more complicated. First consider the case where the flowing fluid is in thermal equilibrium with the environment but is at a pressure higher than the environment, \( p > p_0 \). When the fluid is at a higher pressure than the environment, the fluid stream can be brought to mechanical equilibrium through an expansion process in a turbine. As the pressurized fluid expands to the ambient pressure, work is generated. Therefore, the high pressure stream has a positive value of exergy since it has the potential to do work with respect to the
environment. This can be seen in b of Figs. B.1–B.6, however, since water is nearly incompressible, the trend is easiest to see in the figures for air, Figs. B.4b, B.5b, and B.6b.

Second, consider the case where the flowing fluid is again in thermal equilibrium with the environment, but is now at a pressure lower than that of the environment, \( p < p_0 \). In this situation, the only way to bring the working fluid to mechanical equilibrium with the environment is to run the stream through a compressor in order to increase the pressure to \( p_0 \). It is not possible to use the lower pressure stream to generate positive work in the equilibration process; work must be provided in order to bring the low pressure fluid stream to atmospheric pressure. Therefore, the exergy of the low pressure stream is negative since the stream has a potential to use work, not produce work.

Thus, unlike the nonflow exergy, the flow exergy of a system can be either positive or negative when dealing with pressures below ambient. This phenomenon is discussed in more detail by Moran [48] and can be seen in b of Figs. B.1–B.6, though is easiest to see in the air figures. Note that the effect is more prominent in air since air is a compressible substance. Also, when the working fluid is not in thermal or mechanical equilibrium with the environment, the temperature effects tend to dominate the pressure effects except when the pressure difference is very large.

### B.1.8 Conclusion

The behavior of both nonflow and flow exergy was discussed in this section. Further, both nonflow and flow exergies were calculated for pure water and dry air in order to illustrate the exergetic behaviors. After analyzing both, it is clear that while the nonflow exergy of a system can never be negative, the flow exergy can be negative if the system pressure is sufficiently lower than the dead state pressure.
B.2 Evaluation of exergy for psychrometric processes

This section discusses the correct method for evaluating exergy of mixtures of liquid water and air when dealing with psychrometric processes. The error between exact and approximate formulations is discussed. For brevity, theory is not included and can be found in [20] or [48].

B.2.1 Selection of Dead State

Proper selection of the dead state is critical for accurate calculations when performing an exergy analysis of a system. Since psychrometric processes involve a mixture of dry air and liquid water, the dead state must correspond to an equilibrium of both substances. A single dead state is necessary since exergy analysis involves taking differences of exergies at various states — if the dead state is not consistent, then the exergy differences will not yield meaningful values.

For this analysis, the dead state is selected to be moist air at the environmental conditions given in Eq. (B.1) and at a relative humidity of

$$\phi_0 = \phi_{\text{environment}} = 0.5$$  \hspace{1cm} (B.6)

The conditions provided in Eqns. (B.1) and (B.6) define the dead state for both moist air and liquid water. The dead state of the water in the system (regardless of phase) is water vapor at the specified temperature, and a pressure equal to the partial pressure of water vapor at the corresponding moist air state specified above.
B.2.2 Exergy for Mixtures

The total flow availability of a mixture (mole basis) is:

$$\bar{b}_t = \bar{h} - T_0 \bar{s} - \sum_{i=1}^{n} \mu_{0,i} x_i$$  \hspace{1cm} (B.7)

The total flow exergy is the difference between Eq. (B.7) evaluated at the present and dead states.

$$\bar{\xi}_t = (b_t - b_{t,0}) = \left( \bar{h} - \bar{h}^* \right) - T_0 \left( \bar{s} - \bar{s}^* \right) - \left( \sum_{i=1}^{n} \mu_{0,i} x_i - \sum_{i=1}^{n} \mu_{i}^* x_i \right)$$ \hspace{1cm} (B.8)

The properties denoted with * are evaluated at the restricted dead state (RDS) in which the system is in thermal and mechanical (but not chemical) equilibrium with the environment only.

Discussion of how to evaluate the exergy for moist air is presented below. Sharqawy et al. discussed how to evaluate exergy for seawater in [49].

B.2.3 Exergy of Moist Air

Moist air is typically considered to be an ideal mixture of water vapor and air.

**Exact Moist Air Exergy**

The exact moist air exergy is simply the exergy of the dry air plus the exergy of the water vapor, or simply, the sum of Eq. (B.8) multiplied by the mole fraction of each component:

$$\bar{\xi}_t = x_a \left[ (\bar{h}_a - \bar{h}_a^*) - T_0 \left( \bar{s}_a - \bar{s}_a^* \right) + (\mu_a^* - \mu_{0,a}) \right]$$

$$+ x_v \left[ (\bar{h}_v - \bar{h}_v^*) - T_0 \left( \bar{s}_v - \bar{s}_v^* \right) + (\mu_v^* - \mu_{0,v}) \right]$$ \hspace{1cm} (B.9)

For convenience, the above expression is converted to exergy per unit mass of dry
\[
\xi_t = \frac{\bar{\xi}_t}{x_a M_a} \quad (B.10)
\]

\[
\xi_t = [(h_a - h_{a}^*) - T_0 (s - s_{a}^*) + (\mu_{a}^* - \mu_{0,a})] + \frac{x_v M_v}{x_a M_a} [(h_v - h_{v}^*) - T_0 (s_v - s_{v}^*) + (\mu_{v}^* - \mu_{0,v})] \quad (B.11)
\]

Since chemical potential data is often not readily available, it can be calculated as follows:

\[
\mu_{i}^* = h_{i}^* - T_0 s_{i}^* \]
\[
\mu_{0,i} = h_{0,i} - T_0 s_{0,i} \quad (B.12)
\]

where \(i\) is either \(a\) or \(v\).

**Approximate Moist Air Exergy**

Making use of ideal gas and slightly superheated vapor assumptions, Wepfer derived an approximate expression for Eq. (B.11) that is much easier to evaluate [30].

\[
\xi_t = (c_{p,a} + \omega c_{p,v}) T_0 \left( \frac{T}{T_0} - 1 - \log \frac{T}{T_0} \right) + (1 + \bar{\omega}) R_a T_0 \log \frac{p}{p_0} + R_a T_0 \left[ (1 + \bar{\omega}) \log \frac{1 + \bar{\omega}}{1 + \bar{\omega}} + \bar{\omega} \log \frac{\bar{\omega}}{\bar{\omega}_0} \right] \quad (B.13)
\]

where

\[
\bar{\omega} = \frac{M_a}{M_v} \omega
\]

**Error Between Exact and Approximate**

Equations (B.11) and (B.13) were used to calculate the exergy of moist air at a variety of temperatures and pressures using EES. The results of these calculations are presented in Figs. B.7 to B.9.
Figure B.7: Moist air exergy — $p = 40$ kPa

Figure B.8: Moist air exergy — $p = 100$ kPa
With exception to the exergy minimums, the maximum error between the two equations is typically much less than 1%. Since Wepfer’s equation is much simpler to evaluate and produces very accurate results, it is typically used in evaluating the moist air exergy.

### B.2.4 Exergy of Liquid Water

**Exact Liquid Water Exergy**

When dealing with pure water, the chemical potential term at both the present and dead states are equal, and therefore, cancel out. Further, when considering a pure substance, the RDS and the total dead state are identical and the \(*\) notation can be dropped. Converting Eq. (B.8) to a kilogram basis, the exact total flow exergy of liquid water is:

\[
\xi_{lw} = [h(T, p) - h_0(T_0, p_{v,0})] - T_0 [s(T, p) - s_0(T_0, p_{v,0})] \quad \text{(B.14)}
\]

Where \(p_{v,0}\) is equal to the partial pressure of the water vapor in the moist air dead state, i.e., \(p_{v,0} = x_{v,0}p_0\), and \(x_{v,0}\) is the mole fraction of water vapor.
Approximate Liquid Water Exergy

Bejan [20], Moran [48], and Wepfer [30] all introduce approximate methods of evaluating the liquid water exergy. Bejan’s derivation is the most straightforward and is summarized here.

In order to calculate the total flow exergy of liquid water, Bejan begins with Eq. (B.8) and takes the mole fraction to be unity since a pure stream of liquid water is being considered. Equation (B.8) reduces to:

$$\bar{\xi}_t = (b_t - b_{t,0}) = (\bar{h}_w - \bar{h}_{w,0}) - T_0 (\bar{s}_w - \bar{s}_{w,0}) - (\mu_{0,w,0} - \mu_{0,w}) \quad (B.15)$$

Since the outflowing mixture is at the dead state (in thermal, mechanical, and chemical equilibrium),

$$\bar{h}_{w,0} = T_0 \bar{s}_{w,0} = \mu_{0,w,0} \quad (B.16)$$

and Eq. (B.15) reduces to

$$\bar{\xi}_{t,w} = \bar{h}_w(T, p) - T_0 \bar{s}_w(T, p) - \mu_{0,w} \quad (B.17)$$

where

$$\mu_{0,w} = \bar{h}_0(T_0, p_{0,w}) - T_0 \bar{s}_0(T_0, p_{0,w}) \quad (B.18)$$

Bejan next combines these two equations and converts to a per-unit-mass basis. Note that the barred properties in the chemical potential term are partial molar properties $$[(\partial X/\partial N_i)_{T,p}]$$ whereas the barred properties in the availability terms are specific molar properties ($$X/N$$). For the range of humidities relevant to HD, it is appropriate to make the ideal mixture assumption. Therefore, the partial molar properties are equal to the specific molar properties. Thus,

$$\xi_{t,w} = h_w(T, p) - h_0(T_0, p_{0,w}) - T_0 [s_w(T, p) - s_0(T_0, p_{0,w})] \quad (B.19)$$
Each of the properties in the preceding equation can be evaluated by relating them to the properties of the respective neighboring states on the two-phase dome:

\[
h_w(T, p) \approx h_f(T) + [p - p_{sat}(T)]v_f(T) \quad \text{(B.20)}
\]

\[
h_0(T_0, p_{0,w}) \approx h_g(T_0) \quad \text{(B.21)}
\]

\[
s_w(T, p) \approx s_f(T) \quad \text{(B.22)}
\]

\[
s_0(T_0, p_{0,w}) \approx s_g(T_0) - R_v T_0 \log \left( \frac{p_{0,w}}{p_{sat}(T_0)} \right) \quad \text{(B.23)}
\]

By applying the moderately compressed-liquid and slightly superheated-vapor approximations, the final equation becomes:

\[
\xi_{t,w} \approx [h_f(T) - h_g(T_0)] - T_0 [s_f(T) - s_g(T_0)] \\
+ [p - p_{sat}(T)]v_f(T) - R_v T_0 \log \phi_0 \quad \text{(B.24)}
\]

The subscripts \( f \) and \( g \) correspond to the liquid and vapor saturation states, respectively.

**Error Between Exact and Approximate**

Equation (B.24), rather than Eq. (B.14) is commonly used for psychrometric analysis since the terms are easier to evaluate [20, 48]. In order to verify that the two equations yield equal results, the exergy of liquid water was evaluated for various temperatures of liquid water using both equations. The results are plotted in Figs. B.10a to B.10c. Note that the exergy is not plotted as a function of \( \phi \) since liquid water is not a function of relative humidity. Based on the calculated results of Eqs. (B.14) and (B.24), it is clear that either expression is suitable for calculating liquid water exergy.
Figure B.10: Liquid water exergy for various pressures.
Appendix C

Derivation of Condensate Bulk Temperature

As discussed in Sec. 2.1, it is approximated that the dehumidifier condensate bulk temperature can be evaluated as a function of the inlet and outlet wet bulb temperatures of the moist air. A MATLAB script was written in order to determine the appropriate function to approximate the bulk temperature. This appendix discusses both the physics behind the calculation as well as how the script works.

C.1 Summary of Solution Methodology

Several assumptions were made in order to approximate the bulk temperature of the condensate stream:

1. The condensate is continuously removed from the condensate surface as saturated liquid.

2. Condensation only begins once the air stream reaches saturation. That is, when the inlet moist air is saturated, condensation begins immediately. When the inlet moist air stream is not saturated, first it is cooled (at constant humidity
ratio) until it reaches saturation and then condensation begins.

3. The outlet moist air stream is saturated.

4. The total condensate is well mixed.

5. Change in sensible energy of the condensate in the dehumidifier is negligible.

Based on the above approximations, the bulk temperature of the condensate can be determined by locally evaluating the enthalpy of the condensate and then integrating over the length of the dehumidifier. At any point in the dehumidifier, the differential enthalpy of the condensate is given by

\[ d\dot{H}_b = h_f \cdot d\dot{m}_p \]  \hspace{1cm} (C.1)

where the differential condensate mass flow rate is found by taking the derivative of Eq. (2.3).

\[ d\dot{m}_p = \dot{m}_{da} \cdot d\omega \]  \hspace{1cm} (C.2)

The total enthalpy of the condensate stream can be evaluated by substituting Eq. (C.2) into Eq. (C.1) and integrating from the inlet to the outlet of the dehumidifier.

\[ \dot{H}_b = \int_{\dot{m}}^{\text{out}} d\dot{H}_b = \int_{\omega_{\text{in}}}^{\omega_{\text{out}}} h_f \cdot \dot{m}_{da} \cdot d\omega \]  \hspace{1cm} (C.3)

Equation (C.3) can be evaluated more readily by first performing the chain rule to change from integrating over the humidity ratio to integrating over the air stream wet bulb temperature. Since the humidity ratio decreases along the length of the dehumidifier, note that the integration bounds are switched to ensure a positive quantity. The mass flow rate of dry air is constant in the dehumidifier and can be pulled out of
the integral. The required integral that is evaluated in this program then becomes:

\[
\dot{H}_b = \dot{m}_{da} \int_{T_{WB,out}}^{T_{WB,in}} h_f(T_{WB}) \left( \frac{d\omega}{dT_{WB}} \right) dT_{WB} \tag{C.4}
\]

Once this integral is calculated, it is converted to specific enthalpy and by dividing through by the mass flow rate of the condensate

\[
\dot{m}_b = \dot{m}_{da} (\omega_{in} - \omega_{out}) \tag{C.5}
\]

thus giving

\[
h_b = \frac{\dot{H}_b}{\dot{m}_b} \tag{C.6}
\]

Finally, the output temperature is determined by looking up the temperature that corresponds to the given specific enthalpy and pressure of liquid water using REFPROP.

\[
T_b = T(h_b, p) \tag{C.7}
\]

In order to evaluate Eqs. (C.1)–(C.7), four MATLAB files were required:

- **dehumidifier_integral_updated.m** — Primary source file that includes all of the calculations.

- **airH2O.m** — A small function used to evaluate moist air properties using REFPROP.

- **temperature_surface_fit.m** — A polynomial function used to perform a parabolic temperature surface fit to the data.

- **refpropm.m** — Interface file provided by REFPROP in order to look up property data directly from within MATLAB. Note that all property data was evaluated using REFPROP.
The code in `dehumidifier_integral_updated.m` is explained in Sec. C.2. The code for `airH2O.m` and `temperature_surface_fit.m` is provided in Secs. C.3 and C.4 for reference.

### C.2 dehumidifier_integral_updated.m

#### Initialize Program

```matlab
clear all; close all; clc;

%#ok<*NBRAK>

% Font Sizes
font_size_1 = 18;
font_size_2 = 14;
marker_size = 20;

% set(0,'defaultFigure') to get all options
set(0,'defaultFigureColor',[1 1 1]);
set(0,'defaultFigurePosition',[300 100 800 600]);

% set(0,'defaultLine') to get all options
set(0,'defaultLineWidth',2); % 1
set(0,'defaultLineColor','b'); % 1

% set(0,'defaultText') to get all options
set(0,'defaultTextColor','k');
set(0,'defaultTextFontName','FixedWidth'); % Helvetica
set(0,'defaultTextFontSize',font_size_1); % 12
% set(0,'defaultTextInterpreter','latex');

% set(0,'defaultAxes') to get all options
set(0,'defaultAxesColor','none');
set(0,'defaultAxesFontName','FixedWidth'); % Helvetica
set(0,'defaultAxesFontSize',font_size_1); % 12
set(0,'defaultAxesGridLineStyle',':');
set(0,'defaultAxesMinorGridLineStyle','none');
set(0,'defaultAxesXGrid','off');
set(0,'defaultAxesYGrid','off');
set(0,'defaultAxesXMinorGrid','off');
set(0,'defaultAxesYMinorGrid','off');
set(0,'defaultAxesXMinorTick','on');
set(0,'defaultAxesYMinorTick','on');
```

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Properties

All necessary properties are called from REFPROP, which requires the temperature to be in kelvin. However, since it is desired to have the condensate temperature as a function of inlet and outlet temperatures in both kelvin and degrees Celsius, both temperature scales are carried throughout the problem. Note that since the Kelvin and Celsius scales are only a constant apart, the differential temperature change is equivalent, regardless of unit.

\[
T_K = T_C + 273.15 \quad \text{(C.8)}
\]

\[
dT_K = dT_C \quad \text{(C.9)}
\]

In this section of code, relevant fluid properties are evaluated for \(T = 5\text{–}95^\circ\text{C}\).
T.WB = [T.crop:dT:100-T.crop]'; % Wet Bulb Temperature, [°C]
T = T.WB+273.15; % Wet Bulb Temperature, [K]

% Initialize Variables
p_v = NaN(size(T.WB));
h = NaN(size(T.WB));
hl = NaN(size(T.WB));

% Calculate Vapor Pressure
% phi = p_v/p_sat(T) = vapor pressure/saturated vapor pressure
for i=1:length(T)
    % Note p_v = p_sat since phi=1
    p_v(i) = phi*refpropm('P','T',T(i),'Q',1,'water');
end

% Calculate Humidity Ratio
w = 0.622*p_v./(p_atm-p_v); % [kg water / kg dry air]

% Look up Enthalpies
for i=1:length(T)
    % Total Moist Air Enthalpy (Not needed for calculations)
    h(i) = airH2O('H',T(i),p_atm,w(i)) / 1000; % kJ/kg

    % Enthalpy of liquid water
    hl(i) = refpropm('H','T',T(i),'P',p_atm,'water') / 1000; % kJ/kg
end

Fit Data

In order to properly perform the required integral, each of the properties must be curve fitted. A Fourier series with \( n = 8 \) is used for each curve fit. This type of fit was selected since it offered the best match to the data while still consisting of a simple form.

% Create fitted models for property data
myfit = fittype('fourier8');
fit_w = fit(T.WB,w,myfit);
fit_h = fit(T.WB,h,myfit);
fit.hl = fit(T.WB,hl,myfit);

% Crop data to avoid edge effects from the curve fit.
crop = T.crop/dT;
T(1:crop) = [];
T(end-crop:end) = [];

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% % Humidity Ratio vs. Temperature
figure()
fig_name{end+1} = 'w_vs_T';
plot(T_WB,w,'.','MarkerSize',marker_size);
hold on;
plot(fit_w);
hold off;
my_title('Humidity Ratio vs. Temperature');
my_xlabel('Wet Bulb Temperature, T_{WB} [\text{C}]');
ylabel('{{\textbf{Humidity Ratio}},'\textbf{\omega} [\text{kg water/kg air}]}');
my_legend('{{\phi=1}','fit_w'},'SE');
axis([0 100 0 1.4]);

% Moist Air Enthalpy vs. Temperature
figure()
fig_name{end+1} = 'h_vs_T';
plot(T_WB,h,'.','MarkerSize',marker_size);
hold on;
plot(fit_h);
hold off;
my_title('Moist Air Enthalpy vs. Temperature');
my_xlabel('Wet Bulb Temperature, T_{WB} [\text{C}]');
ylabel('{{\textbf{Specific Moist Air Enthalpy}},'\textbf{h} [\text{kJ/kg dry air}]}');
my_legend('{{\phi=1}','fit_h'},'SE');
axis([0 100 0 4000]);

% Liquid Water Enthalpy vs. Temperature

Plot Data

Plots of both the actual property data taken from REFPROP as well as the curve-fitted models were created to visualize the goodness of the fit.
Figure C.1: Saturation humidity ratio versus wet bulb temperature.
Figure C.2: Saturated moist air specific enthalpy versus wet bulb temperature.

Figure C.3: Saturated liquid water enthalpy versus temperature.
Calculate Exit Temperature as a function of T_in and T_out

This section evaluates Eq. (C.4) for varying inlet and outlet wet bulb temperatures.

\[ m_a = 1; \quad \text{% Mass flow rate of air} \]
\[ T_{\text{range}} = [2*{\text{T_crop}}:1:100-2*{\text{T_crop}}]; \quad \text{% Outlet water temperature} \]

% Evaluate the integrand using the data curve fits. Then, create a new
% curve fit for the integrand that will be used when performing the
% integral.
integrand = fit.hl(T_{\text{range}}) .* differentiate(fit.w,T_{\text{range}});
fit.integrand = fit(T_{\text{range}},integrand,myfit);

T_{\text{bulk}} = \text{NaN(length(T_{\text{range}}));} \quad \text{% Square Matrix}
for \( i=1:\text{length(T_{\text{range}})} \)
    \% i = loop over outlet air temperature
    \% Integrate starting from \( T_{\text{range}}(i) \). Evaluate at each point
    \% in \( T_{\text{range}} \)
    \( H_{\text{out}} = \text{integrate(fit.integrand,T_{\text{range}},T_{\text{range}}(i));} \)
% Mass Balance
m_{\text{out}} = m_a*(fit.w(T_{\text{range}})-fit.w(T_{\text{range}}(i)));%
% Specific Bulk Enthalpy
h_{\text{bulk}} = H_{\text{out}} ./ m_{\text{out}};
% Look up temperature based on bulk enthalpy of water.
% Only consider temperatures for which \( T_{\text{in}} > T_{\text{out}} \).
for \( j=i:\text{length(T_{\text{range}})} \)
    \% j = loop over inlet air temperature
    \% Look up water temperature
    \( T_{\text{bulk}}(i,j) = \ldots \)
    \text{refpropm('T','H',h_{\text{bulk}}(j)*1000,'P',p_{\text{atm}},'water')-273.15;}
% i = row = outlet
% j = column = inlet
end

[T_{\text{in}} T_{\text{out}}] = \text{meshgrid(T_{\text{range}})};
figure()
\text{fname{\text{end+1}}} = 'ExitTempSurface';
\text{surf(T_{\text{in}},T_{\text{out}},T_{\text{bulk}})}
\text{my.title('Exit Temperature vs Inlet/Outlet Temperature');}
\text{my.xlabel('T_{\{WB,\text{in}\}} [\text{C}]);} \quad \text{% column of T_{\text{bulk}} = inlet (see help surf)}
\text{my.ylabel('T_{\{WB,\text{out}\}} [\text{C}]);} \quad \text{% row of T_{\text{bulk}} = outlet}
\text{my.zlabel('Exit Bulk Temperature [\text{C}]);}
\text{hold on;}
Fit a surface to calculated data from above

In this section, a second order surface is fit to the temperature data evaluated in the previous section. The desired function is of the form:

\[ T_b = a_1 T_{WB,in}^2 + a_2 T_{WB,out}^2 + a_3 T_{WB,in} T_{WB,out} + a_4 T_{WB,in} + a_5 T_{WB,out} + a_6 \]  \hspace{1cm} (C.10)

A least squares curve fit is used in order to fit the temperature surface to a function of the form given in Eq. (C.10). The calculations are performed in both degrees Celsius and kelvin.

This portion of the script calls the file, `temperature_surface_fit.m`.

```plaintext
% Loop through meshgrid data in order to form (x,y,z) vectors
k=1;
x = NaN([1,length(T_range)]);
y = NaN([1,length(T_range)]);
z = NaN([1,length(T_range)]);
for i = 1:length(T_range)
```

Figure C.4: Condensate bulk temperature versus inlet and outlet wet bulb temperatures.
for j = 1:length(T_range)
    x(k) = T_in(i,j);
    y(k) = T_out(i,j);
    z(k) = T_bulk(i,j);
    k = k + 1;
end
end

% Filter out NaN points
filter = find(isnan(z)); % Points where T_in < T_out % (not physically possible)
x(filter)=[];
y(filter)=[];
z(filter)=[];

xK = x + 273.15;
yK = y + 273.15;
zK = z + 273.15;

%%%%%%%%%%%%%%%% NOTE − I converted to C on line 209

% Curve fit parabolic surface
% In degrees Celsius
a0 = ones([1,6]); % Starting guess
[a, resnorm_a] = lsqcurvefit(@temperature_surface_fit, ...
    a0,[x;y;z]);

% In kelvin
b0 = ones([1,6]); % Starting guess
[b, resnorm_b] = lsqcurvefit(@temperature_surface_fit, ...
    b0,[xK;yK;zK]);

% Create surface function using found coefficients
TempSurface = @(x,y) a(1)*x.^2 + a(2)*y.^2 + a(3)*x.*y ...
    + a(4)*x + a(5)*y + a(6);
TempSurfaceK = @(x,y) b(1)*x.^2 + b(2)*y.^2 + b(3)*x.*y ...
    + b(4)*x + b(5)*y + b(6);

% Calculate exit bulk temperature using model
T_bulk_model = TempSurface(x,y);
T_bulk_modelK = TempSurfaceK(xK,yK);

% Output
disp('');
disp('For Temperatures in degrees Celsius:');
disp(['T_bulk(T_in,T_out) = ']);
disp(['''', num2str(a(1)), '*' T_in ** 2 + ', ' num2str(a(2)), ' ... ''
    + ' T_out ** 2 + ', num2str(a(3)), '*' T_in*T_out']);
disp([''' + ', num2str(a(4)), ' T_in + ', num2str(a(5)), ' ... ''
    + ' T_out + ', num2str(a(6))]);
disp(' ');
disp(['Max Relative Error = ', ' ...
    num2str(100*max(abs(z−T_bulk_model)./z)), '%']);
disp(' ');

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disp(' ');
disp('For Temperatures in kelvin:');
disp('T_{bulk}(T_{in},T_{out}) = ');
disp(['0.0051918*T_{in}^2 + 0.0027692*T_{out}^2 - 0.007417*T_{in}*T_{out} + 0.39123*T_{in} + 0.53801*T_{out} + 1.6946']);
disp('Max Relative Error = 0.42912%');
plot3(x,y,T_{bulk}\_model,'.')
hold off;

Output from above code:

Optimization terminated: norm of the current step is less
than OPTIONS.TolX.
Optimization terminated: relative function value
changing by less than OPTIONS.TolFun.

For Temperatures in degrees Celsius:
T_{bulk}(T_{in},T_{out}) =
\begin{align*}
&0.0051918*T_{in}^2 + 0.0027692*T_{out}^2 - 0.007417*T_{in}*T_{out} \\
&+ 0.39123*T_{in} + 0.53801*T_{out} + 1.6946
\end{align*}
Max Relative Error = 9.3069%

For Temperatures in kelvin:
T_{bulk}(T_{in},T_{out}) =
\begin{align*}
&0.0051918*T_{in}^2 + 0.0027692*T_{out}^2 - 0.007417*T_{in}*T_{out} \\
&+ -0.41913*T_{in} + 1.0511*T_{out} + 61.6186
\end{align*}
Max Relative Error = 0.42912%
Figure C.5: Surface fit and integral evaluation of condensate bulk temperature versus inlet and outlet wet bulb temperatures.

**Figures**

This section generates several plots to compare the temperature values predicted using the surface fits to those temperatures values determined by evaluating the enthalpy integral. For reference, the average of the inlet and outlet wet bulb temperatures is also plotted.

All plots are for fixed outlet temperature, $T_{WB, out}$.

```matlab
for i=[30:10:80]
    foo = find(y==i); 
    figure()
    figname{end+1} = ['ExitTemp.', num2str(i)]; %#ok<AGROW>
    plot(x(foo),z(foo),'b.','MarkerSize',marker_size);
    hold on;
    plot(x(foo),T_bulk_model(foo),'r-');
    plot(x(foo),(x(foo)+i)/2,'k--');
    hold off;
    my_title(['Exit Water Bulk Temperature, T_{WB,out}=', ...
              num2str(i), ' C']);
```

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my_xlabel('Inlet Wet Bulb Temperature, T_{WB,in} [^\circ C]');
my_ylabel('T_{bulk,out} [^\circ C]');
my_legend({'Integral','Surface Fit','(T_{in}+T_{out})/2'},'SE');
end

%% Print figures
%% for k = 1:length(figname)
%%    figure(k)
%%    print('-dpng',figname{k})
%% end

Figure C.6: Condensate bulk temperature versus inlet wet bulb temperature for exit
wet bulb temperature equal to 30°C
Figure C.7: Condensate bulk temperature versus inlet wet bulb temperature for exit wet bulb temperature equal to 40°C

Figure C.8: Condensate bulk temperature versus inlet wet bulb temperature for exit wet bulb temperature equal to 50°C
Figure C.9: Condensate bulk temperature versus inlet wet bulb temperature for exit wet bulb temperature equal to 60°C

Figure C.10: Condensate bulk temperature versus inlet wet bulb temperature for exit wet bulb temperature equal to 70°C
Figure C.11: Condensate bulk temperature versus inlet wet bulb temperature for exit wet bulb temperature equal to 80°C

C.3 airH20.m

```matlab
function b = airH20(prop,T,P,w)
% Calculates PROP of moist air based on given temperature (K),
% pressure (kPa), and humidity ratio.

ba = refpropm(prop,'T',T,'P',P,...
    'nitrogen','argon','oxygen',[0.78120 0.00920 0.20960]);
 bv = refpropm(prop,'T',T,'Q',1,'water');
 b = ba + w*bv;
end
```

C.4 temperature_surface_fit.m

```matlab
function F = temperature_surface_fit(a, data)
% See the following website for instructions on how this works
% http://www.mathworks.com/support/solutions/data/1-17YMU.html
```
\begin{verbatim}
x = data(1, :);
y = data(2, :);
F = a(1)*x.^2 + a(2)*y.^2 + a(3)*x.*y ... 
    + a(4)*x + a(5)*y + a(6);
end
\end{verbatim}

\section*{C.5 Results}

Based on the previous discussion, the bulk condensate temperature can be approximated using Eqs. (C.11) and (C.12)

In kelvin:

\begin{equation}
T_b = 0.0051918T_{WB, in}^2 + 0.0027692T_{WB, out}^2 - 0.007417T_{WB, in}T_{WB, out} \\
    - 0.41913T_{WB, in} + 1.0511T_{WB, out} + 61.6186 \tag{C.11}
\end{equation}

In degrees Celsius:

\begin{equation}
T_b = 0.0051918T_{WB, in}^2 + 0.0027692T_{WB, out}^2 - 0.007417T_{WB, in}T_{WB, out} \\
    - 0.39123T_{WB, in} + 0.53801T_{WB, out} + 1.6946 \tag{C.12}
\end{equation}

The maximum relative relative error between the surface fit provided in Eq. (C.11) and the actual value determined by evaluating Eq. (C.4) is 0.42912\%.
Appendix D

Effect of Salinity on CAOW HD Desalination Cycles

Real desalination systems operate using either brackish water or seawater. Therefore, more complete analysis of HD systems requires the use of seawater properties when considering the water streams. For simplicity, the initial analysis of the cycles was performed using pure water properties. This appendix investigates the error that is introduced into the analysis by using the pure water approximation.

D.1 Seawater Properties

Seawater properties were evaluated using the formulations presented in [13]. Formulations for enthalpy, entropy, and specific heat capacity at constant pressure are provided below.

In this appendix, pure water properties are denoted by °, temperature, \( t \), is measured in degrees Celsius, and salinity, \( S \), is measured in mass of solute per mass of solvent (kg solute/kg water).
D.1.1 Enthalpy

\[
h_w(T, P) = h_w^\circ(T, P) - S [(27.06262 + S) + (4.83568 + S)t] \tag{D.1}
\]

D.1.2 Entropy

\[
s_w(T, P) = s_w^\circ(T, P) - S \left[ a_1 + a_2S + a_3S^2 + a_4S^3 + a_5t + \right.
\]
\[
\left. a_6t^2 + a_7t^3 + a_8St + a_9S^2t + a_{10}St^2 \right] \tag{D.2}
\]

where

\[
\begin{array}{cc|cc}
  i & a_i & i & a_i \\
  \hline
  1 & -4.231 \times 10^{-1} & 6 & -1.443 \times 10^{-4} \\
  2 & 1.463 \times 10^1 & 7 & 5.879 \times 10^{-7} \\
  3 & -9.880 \times 10^1 & 8 & -6.111 \times 10^{-2} \\
  4 & 3.095 \times 10^2 & 9 & 8.041 \times 10^{-2} \\
  5 & 2.562 \times 10^{-2} & 10 & 3.035 \times 10^{-4} \\
\end{array}
\]

D.1.3 Specific Heat Capacity at Constant Pressure

\[
c_1 = 4206.8 - 6.6197(1000S) + 1.2288 \times 10^{-2}(1000S)^2
\]

\[
c_2 = -1.1262 + 5.4178 \times 10^{-2}(1000S) - 2.2719 \times 10^{-4}(1000S)^2
\]

\[
c_3 = 1.2026 \times 10^{-2} - 5.3566 \times 10^{-4}(1000S) + 1.8906 \times 10^{-6}(1000S)^2
\]

\[
c_4 = 6.8777 \times 10^{-7} + 1.517 \times 10^{-6}(1000S) - 4.4268 \times 10^{-9}(1000S)^2
\]

\[
c_p(t) = (c_1 + c_2t + c_3t^2 + c_4t^3)/1000 \tag{D.3}
\]

D.2 Results

Figures D.1 and D.2 show GOR versus mass flow rate ratio for values of salinity varying from \( S = 0.00-0.05 \) for the CAOW-WH and CAOW-AH cycles, respectively.
Calculations were performed for the CAOW-WH cycle with component effectivenesses of 0.9 and 0.8 as seen in Fig. D.1. Calculations were performed for the CAOW-AH cycle for component effectivenesses of 0.9 as seen in Fig. D.2.

When observing these two figures, it is important to note that varying salinity does not change the general trend of GOR versus mass flow rate ratio. Instead, it shifts the value of \( m_r \) that leads to peak GOR. In each of the three cases considered here, the maximum change in peak GOR due to varying the salinity from 0.00 to 0.05 is less than 0.3%. Clearly, the salinity does not change the peak gor substantially for any of the cases considered. However, for a given mass flow rate ratio, GOR can depend strongly on the salinity of the feedwater stream. For the CAOW-WH cycle with component effectivenesses of 0.9 (Fig. D.1), the maximum change in GOR due to salinity varying from 0 to 0.05 at constant mass flow rate ratio is 37.5%. Therefore, it is important to be able to accurately adjust the \( m_r \) when operating systems that have feedwater with variable salinity.
From Figs. D.1 and D.2, it appears that the performance of a CAOW HD cycle operating with saline water can be predicted by appropriately scaling \( \text{GOR}_{0.00}(m_r) \), where \( \text{GOR}_{0.00} \) is the gained output ratio of the CAOW system using pure water properties. Since the figures suggest that the GOR vs. \( m_r \) curve is being stretched as a function of \( m_r \) and salinity, various scaling functions were tested until one was obtained that closely predicts the cycle performance:

\[
\text{GOR}_S(m_{r,S}) \approx \text{GOR}_{0.00}\left((1 + 1.25S)m_{r,0.00}\right)
\]

Equation (D.4) states that in order to get a GOR of \( \text{GOR}_{0.00} \) when operating a cycle with feedwater with salinity, \( S \), the mass flow rate ratio must be increased to \( m_{r,S} = (1 + 1.25S)m_{r,0.00} \). Note that as the salinity of the feedwater increases, the scaling of the mass flow rate ratio also increases. This equation also suggests that if GOR is plotted as a function of a modified mass flow rate ratio based on the salinity,
the curves should collapse down to a single curve. The modified mass flow rate ratio is defined as:

\[ m_{r,\text{modified}} = \frac{m_r}{1 + 1.25S} \]  

In order to show the goodness of the fit of Eq. (D.4) and the effectiveness of using Eq. (D.5) to rescale the GOR for saline feedwater, Figs. D.1 and D.2 are recreated as Figs. D.3 and D.4. In these new figures, GOR is also plotted versus the modified mass flow rate ratio defined by Eq. (D.5).

In both the CAOW-WH and CAOW-AH cases, it is clear that Eq. (D.4) closely predicts the value of GOR for CAOW cycles using seawater properties based on the pure water performance and the salinity of the feedwater stream.
Figure D.4: GOR versus the modified mass flow rate ratio and salinity for a CAOW-AH cycle with saline feedwater with $T_{top} = 90^\circ C$ and $\epsilon_H = \epsilon_D = 0.9$. 
Bibliography


[39] P. E. Gill, W. Murray, M. A. Saunders, SNOPT.


URL http://knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1547&VerticalID=0


