Suitability of the Kalina Cycle for Power Conversion from Pressurized Water Reactors

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Brigham Young University

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Suitability of the Kalina Cycle for Power Conversion from Pressurized Water Reactors

Jack Ryan Webster

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Master of Science

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ABSTRACT

Suitability of the Kalina Cycle for Power Conversion from Pressurized Water Reactors

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The primary objective of this work is to determine the Kalina cycle's suitability for thermal power conversion from a pressurized water reactor. Several previous papers have examined this application, but these either lack proof of concept or make unfeasible assumptions. This work expands current knowledge by simulating the Kalina cycle and comparing it to current pressurized water reactor Rankine cycles in order to identify which is more efficient.

Prerequisite to the modeling is a simulation tool capable of modeling the thermodynamics of ammonia/water mixtures. Instead of using an existing program, a new one called Clearwater is used. This tool is based on a preexisting Gibbs free energy "super" equation of state. Algorithms for vapor-liquid equilibrium calculations and phase identification are presented. Clearwater will be distributed online as open-source code to aid future developers of ammonia/water power and refrigeration cycles.

A comparison of single-stage Kalina and Rankine cycles driven by heat from PWR core coolant suggests that the Kalina cycle is not well suited to the application. Any benefit from the Kalina cycle's ability to match temperature profiles in the boiling region of the steam generator is outweighed by other drawbacks. These include the cycle's 1) increased turbine exhaust pressure and 2) lower average heat absorption temperature caused by its working fluid's relatively high liquid heat capacity, both of which lower efficiency.

Having concluded this, an attempt is made to quantify the conditions under which the Kalina cycle produces more power than the Rankine cycle. Both cycles are optimized for a range of heat source inlet and outlet temperatures between 350 °C and 525 °C. When both cycles absorb the same amount of heat from the source—i.e., when source outlet temperature is constrained—the Kalina cycle is less effective for small source temperature drops. When outlet temperature is unconstrained, the Kalina cycle outperforms the Rankine cycle for all but the lowest inlet temperature. This is due to the Kalina cycle's non-isothermal boiling profile, which allows it to absorb low temperature heat at relatively high pressure. Because of its isothermal boiling profile, the Rankine cycle cannot capture low temperature heat as effectively, so it performs worse over large, unconstrained source temperature drops.

Keywords: Kalina, Rankine, exergy, efficiency, nuclear
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Nomenclature

$A, B, C, D, E$ ................................................................. empirical vapor pressure coefficients

$A_i, B_i, C_i, D_i, E_i$ ...................................................... Gibbs correlation coefficients

$c_p$ ................................................................................. constant-pressure heat capacity

$f_1, f_2$ or $f$ ................................................................... objective function

$g$ .................................................................................. molar Gibbs free energy

$\tilde{g}$ .............................................................................. partial molar Gibbs free energy

$h$ ................................................................................ molar enthalpy

$J$ ........................................................................................ Jacobian

$P$ .................................................................................... pressure

$\dot{Q}$ ............................................................................... heat flow

$R$ ................................................................................ universal gas constant

$s$ ................................................................................ molar entropy

$T$ ................................................................................ temperature

$v$ ................................................................................... molar volume

$w$ ................................................................................ mass fraction

$\dot{W}_{net}$ ........................................................................ net cycle power

$x$ ................................................................................ liquid mole fraction

$y$ ................................................................................ vapor mole fraction

$z$ ................................................................................ stream mole fraction

$\delta\lambda_1, \delta\lambda_2$ or $\delta\lambda$ ............................................. variable step

$\Delta_{mix}\theta^{IM}$ .............................................................. ideal mixing parameter

$\eta_T$ ............................................................................... turbine efficiency

$\eta_P$ ............................................................................... pump efficiency

$\eta_I$ ............................................................................... energy efficiency

$\eta_{II}$ ........................................................................... exergy efficiency

$\theta$ ................................................................................ generic thermodynamic parameter

$\lambda_1, \lambda_2$ or $\lambda$ ...................................................... unknown parameter
μ ................................................................. chemical potential
χ ................................................................. molar vapor fraction

Subscripts

b ................................................................. reference
B ................................................................. bubble point
c ................................................................. critical point
CW ............................................................. cooling water
D ................................................................. dew point
eq ............................................................. equilibrium
i ................................................................. species i
in ............................................................... inlet
mix ............................................................ mixture
o ............................................................... ideal gas
out ............................................................. outlet
r ................................................................. reduced
S ............................................................... heat source
σ ............................................................... surroundings
1 ............................................................. ammonia
2 ............................................................. water

Superscripts

E ............................................................. excess
L ............................................................. liquid
sat ........................................................... saturated
V ............................................................. vapor
1 INTRODUCTION

1.1 Economic Challenges to Nuclear Energy

Nuclear reactors remain an important means of producing scalable electric power. This is due not only to their negligible atmospheric emissions [1] and reliable operation, but also to the relatively low cost and prevalence of uranium oxide fuel. Despite these advantages, the nuclear industry struggles to compete in the current US power generation market for economic and legislative reasons. Much of the country's grid is now deregulated, meaning supply and demand are not always balanced and consumers buy the cheapest electricity available. Renewables like wind and solar power cost little to operate and so are often utilities' first choices [2]. Also, wind power plants currently have governmental preference. They enjoy both a tax credit and the privilege of selling their electricity first if supply is greater than demand [3].

Since renewables are not always available, other types of plants must be on-hand to fill electricity demand. Gas-turbine plants often play this role because they can load-follow, meaning they increase output based on demand. Gas power also currently has the advantage of cheap fracked fuel, making it attractive to customers [3]. US nuclear plants, on the other hand, generally do not load-follow [4]. Instead, they operate at a single output level (preferably 100%), providing baseload power to the grid.

When there is an excess electricity supply and not all a nuclear plant's power is needed, the plant is asked to carry the burden of load-following. Since these plants are not built to load-
follow, they cannot effectively tune power output to match demand and so must sell electricity at a loss, operate at partial capacity, or ground the electricity they produce until it can be profitably sold again [2, 4]. Other nuclear challenges include stringent government regulations [1], dilemmas over waste management, and the public's fears and negative opinion about nuclear technology in general. Scientific, legislative, and public communities need to resolve these latter issues if nuclear power is to succeed.

This work focuses only on the nuclear industry's need to compete economically with cheaper sources of power like natural gas in regulated and deregulated markets alike. This work attempts to ameliorate the economic challenges outlined above by seeking to improve nuclear power plant efficiencies. Improved efficiencies would increase yearly plant revenues, allowing plants to recoup some of the losses due to deregulation and to offset the high costs required to build and operate nuclear plants. Even small (~1%) gains in plant efficiencies can mean tens of millions of dollars more revenue for their owner utilities [5].

Most industrial-scale nuclear plants in the United States use a power cycle called the Rankine cycle to convert heat from the nuclear core into electricity. The Rankine cycle uses a working fluid of pure water. As a baseline for comparison, the efficiencies of existing nuclear Rankine cycles are between 33% and 37% (from [6], as of 2003).

1.2 The Kalina Cycle

One way to increase nuclear plant efficiencies would be to change the power cycle by which they convert heat to electricity. The Kalina cycle, which uses a zeotropic mixture of ammonia and water as a working fluid, has appeared frequently in the literature over the last three decades as a candidate for high-efficiency power conversion. The specific application of the Kalina cycle to pressurized-water reactors (PWR) is the primary focus of this work.
Figure 1-1 shows a schematic of the simplest single-stage Kalina cycle design [7], which is the one considered in this work.

Because other literature already effectively describes the theory and function of the Kalina cycle [7-9], only a brief description follows. As the working fluid mixture boils between Streams 2 and 3, its concentration of ammonia decreases and its boiling temperature increases. These phenomena slope the temperature profile of the boiling mixture, allowing the profile to parallel that of the heat source and thus maintain a small temperature difference between the two
streams. This property lets the mixture accept heat at a higher average temperature than would be possible if it were a pure chemical and were subject to isothermal boiling. The Kalina cycle's ability to absorb heat at relatively high temperatures allows it, under certain conditions, to achieve better efficiencies than cycles using pure working fluids (e.g. the Rankine cycle). The Kalina cycle's sloped boiling profile also allows it to absorb low-temperature heat at relatively high pressure, which alleviates the trade-off between the energy efficiency of the power cycle and the amount of heat absorbed in the boiler. Under isobaric conditions, pure water boils isothermally, so in some cases the Rankine cycle suffers from larger tradeoffs of this kind than the Kalina cycle does. Mlcak explains these phenomena in detail in "An Introduction to the Kalina Cycle" [9].

The Kalina cycle requires a separation subsystem (Streams 4 through 15 in Figure 1-1) to condense low-pressure turbine exhaust at a feasible absorber temperature. This exhaust pressure must be kept as low as possible to enable a large pressure drop during expansion. This pressure drop is necessary for the cycle to operate with high efficiency. However, there is too much ammonia in the turbine exhaust for it to condense both at 1) low pressure and 2) a realistic absorber temperature (~35 °C). To help the exhaust condense, the Kalina cycle's distillation subsystem siphons off part of the main process flow, separates it into ammonia-rich and ammonia-lean streams, and recycles the ammonia-lean liquid to a point just preceding the absorber. This recycle stream mixes with the relatively ammonia-rich turbine exhaust, which raises the boiling point of the exhaust and allows it to completely condense in the absorber.

1.3 Project Scope

This scope of this work comprises three distinct parts. The first goal is to quantify and compare the efficiencies of Rankine and Kalina cycles based on a typical PWR heat source.
Computer models provide the thermodynamic efficiency values of each cycle. Prerequisite to the modeling is the development of ammonia/water thermodynamics and power cycle simulation tool; its creation and validation are the subject of Chapter 2. The actual comparison of the Kalina and Rankine cycles at PWR conditions then appears in Chapter 3. The comparison's results suggest that the Kalina cycle is not well-suited to PWR power conversion. In light of these results, Chapter 4 compares the same cycles over a range of heat source temperatures to identify the conditions in which the Kalina cycle exhibits superior performance.
2 AMMONIA/WATER THERMODYNAMICS SIMULATOR

Modeling the Kalina cycle requires a simulator that accurately describes the thermodynamic behavior of ammonia/water mixtures. This chapter first describes the need for better documentation of vapor-liquid equilibrium computations in the literature. The chapter then provides this documentation as part of the development of a new ammonia/water thermodynamics simulation tool called Clearwater. Other details regarding this simulator's underlying correlations and algorithms are also given. The chapter concludes by presenting validations of 1) this simulator's thermodynamic computations 2) a Kalina cycle built using the Clearwater simulator.

2.1 Clearwater Simulator

One way to approach simulation of the Kalina cycle would be to buy or request an existing program but doing so has disadvantages. For example, both the National Institute of Standards and Technology (NIST) and F-Chart Software provide packages that calculate ammonia/water properties. Unfortunately, these are proprietary and cost between $300 and $600 [10, 11]. There is a free program following the official International Association for the Properties of Water and Steam (IAPWS) ammonia/water equations available for download on the web, but the program appears to lack procedures for vapor-liquid equilibrium calculations [12]. In relevant literature, other authors present the equations that form the basis of privately developed codes and give flowcharts describing their algorithms [13, 14]. Some of these authors
also offer their code upon request. However, this literature tends to lack descriptions of how iterative ammonia/water vapor-liquid equilibrium calculations are implemented computationally.

In light of these challenges, this work seeks to expand existing knowledge in the area of ammonia/water modeling by developing and documenting a new thermodynamics simulation tool called Clearwater. Both the underlying correlations and their computational implementation are described. Special attention is given to vapor-liquid equilibrium calculation and phase identification algorithms. Clearwater also includes unit operations (e.g., turbine, condenser, flash drum, etc.) necessary for cycle modeling. This simulation tool is written in Python, a modern programming language. The tool will be subsequently published online via Github in open-source format. This easy access will help eliminate the need for future developers of ammonia/water power and refrigeration cycles to buy proprietary programs or create their own.

2.2 Property Calculations

Several authors propose equations of state (EOS) for ammonia/water mixtures, but two seem especially widely known. One appears in the papers of Tillner-Roth and Friend [15, 16] and is based on Helmholtz free energy. This EOS is the current IAPWS standard for ammonia/water mixtures, but its thermodynamic calculations are complex. The second EOS utilizes Gibbs free energy and is easier to implement, so it forms the basis of this work. The primary developers of this second methodology are Schulz [17], Ziegler and Trepp [18], and Ibrahim and Klein [19], but Xu and Goswami [14] and Wang et al. [13] also include its equations in their own work with additions and modifications. The following sections describe how Clearwater uses this Gibbs EOS to compute ammonia/water properties.
2.2.1 Pure-component Properties

Combining the general equation for Gibbs free energy, Equation (2-1), with empirical correlations for fluid volume \( (\nu) \) and heat capacity \( (c_p) \) produces distinct equations for the Gibbs energy of the liquid and vapor phases of ammonia or water, depending on which coefficient set is used. These equations appear below in Equations (2-2) and (2-3), and their corresponding coefficients are listed in Table A-1 of the appendix.

\[
g = h_o - T s_o + \int_{T_o}^{T} c_p dT + \int_{P_o}^{P} \nu dP - T \int_{T_o}^{T} \frac{c_p}{T} dT \quad (2-1)
\]

\[
g^L = RT_b \left[ h^L_{r,o} - s^L_{r,o} T_r + \left( A_1 + A_3 T_r + A_4 T_r^2 \right) (P_r - P_{r,o}) + \frac{A_2}{2} (P_r^2 - P_{r,o}^2) \right. \\
\left. + B_1 (T_r - T_{r,o}) + \frac{B_2}{2} (T_r^2 - T_{r,o}^2) + \frac{B_3}{3} (T_r^3 - T_{r,o}^3) \right] \\
- B_1 T_r \ln \left( \frac{T_r}{T_{r,o}} \right) - B_2 T_r (T_r - T_{r,o}) - \frac{B_3}{2} T_r (T_r^2 - T_{r,o}^2) \quad (2-2)
\]

\[
g^V = RT_b \left[ h^V_{r,o} - T_r s^V_{r,o} + D_1 (T_r - T_{r,o}) + \frac{D_2}{2} (T_r^2 - T_{r,o}^2) + \frac{D_3}{3} (T_r^3 - T_{r,o}^3) \right. \\
\left. - D_1 T_r \ln \left( \frac{T_r}{T_{r,o}} \right) - D_2 T_r (T_r - T_{r,o}) - \frac{D_3}{2} T_r (T_r^2 - T_{r,o}^2) \right] \\
+ T_r \ln \left( \frac{P_r}{P_{r,o}} \right) + C_1 (P_r - P_{r,o}) + C_2 \left( \frac{P_r}{T_r^4} - 4 \frac{P_{r,o}}{T_{r,o}^4} + 3 \frac{P_{r,o} T_r}{T_{r,o}^4} \right) \\
+ C_3 \left( \frac{P_r}{T_r^{11}} - 12 \frac{P_{r,o}}{T_{r,o}^{11}} + 11 \frac{P_{r,o} T_r}{T_{r,o}^{12}} \right) \\
+ \frac{C_4}{3} \left( \frac{P_r^3}{T_r^{11}} - 12 \frac{P_{r,o}^3}{T_{r,o}^{11}} + 11 \frac{P_{r,o}^3 T_r}{T_{r,o}^{12}} \right) \quad (2-3)
\]

In the above expressions, \( T \) is temperature, \( P \) is pressure, \( g \) is Gibbs energy, \( h \) is enthalpy, \( s \) is entropy, \( R \) is the universal gas constant, and the subscripted capital letters \( A_i \)
through $D_i$ are empirical coefficients. The subscript $o$ refers to the reference state, which is different for each chemical. The variables $T_r$ and $P_r$ refer to reduced temperature and pressure and are based on normalization values of $T_b = 100$ K and $P_b = 1$ MPa (e.g., $T_r = T/T_b$).

### 2.2.2 Excess Properties

The Gibbs equation of state assumes that vapor mixtures of ammonia and water are ideal; however, it includes a separate equation for Gibbs excess energy to describe non-ideality in liquid mixtures. The excess Gibbs energy equation, shown in Equation (2-4), has the form $g^E(T, P, x_1)$, in which $x_1$ is the mole fraction ammonia and $E_i$ represent empirical coefficients. This equation's coefficients are given in Table A-2 of the appendix.

\[
g^E = RT_b \left\{ x_1(1 - x_1) \left[ E_1 + E_2 P_r + T_r (E_3 + E_4 P_r) + \frac{E_5}{T_r} + \frac{E_6}{T_r^2} \right. \right.
\]
\[
+ (2x_1 - 1) \left. \left( E_7 + E_8 P_r + T_r (E_9 + E_{10} P_r) + \frac{E_{11}}{T_r} + \frac{E_{12}}{T_r^2} \right) \right. \]
\[
+ (2x_1 - 1)^2 \left( E_{13} + E_{14} P_r + \frac{E_{15}}{T_r} + \frac{E_{16}}{T_r^2} \right) \right\} \quad (2-4)
\]

Equations (2-2) to (2-4) can be differentiated to provide expressions for enthalpies, entropies, and molar volumes via the identities in Equations (2-5), (2-6), and (2-7). These equations give only the pure-component derivatives, but the excess property derivatives are the same except that they also hold composition constant.

\[
h = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{g}{T} \right) \right]_p \quad (2-5)
\]
\[
s = -\left[ \frac{\partial g}{\partial T} \right]_p \quad (2-6)
\]
\[
v = \left[ \frac{\partial g}{\partial P} \right]_T \quad (2-7)
\]
2.2.3 Verification of Symbolic Expressions

As validation that Equations (2-2) to (2-4) and their symbolic derivatives were generated and transcribed correctly, their calculations are compared with those of the same expressions in finite difference (FD) form. Equations (2-8) through (2-10) give the FD expressions for the pure-component properties. This validation's inputs span the following ranges: temperatures are between 240 K and 647 K, pressures are between 7 kPa and 21 MPa, and compositions are between 0.0 and 1.0 (mol frac) ammonia. The number of sample points for each range is 21 and the step size multiplier used in differentiation is $10^{-8}$. The maximum relative errors produced by the comparison appear in Table 2-1.

\[
h \approx -T^2 \frac{g_{T+\Delta T, P} - g_{T, P}}{\Delta T}
\]

(2-8)

\[
s \approx -\frac{g_{T+\Delta T, P} - g_{T, P}}{\Delta T}
\]

(2-9)

\[
v \approx \frac{g_{T, P+\Delta P} - g_{T, P}}{\Delta P}
\]

(2-10)

<table>
<thead>
<tr>
<th></th>
<th>$h$</th>
<th>$s$</th>
<th>$v$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ammonia</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor</td>
<td>3.00 $\cdot 10^{-6}$</td>
<td>9.43 $\cdot 10^{-6}$</td>
<td>3.08 $\cdot 10^{-6}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>2.80 $\cdot 10^{-7}$</td>
<td>4.14 $\cdot 10^{-7}$</td>
<td>1.22 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor</td>
<td>8.20 $\cdot 10^{-6}$</td>
<td>6.57 $\cdot 10^{-6}$</td>
<td>5.74 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>8.84 $\cdot 10^{-7}$</td>
<td>8.26 $\cdot 10^{-7}$</td>
<td>2.98 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td><strong>Excess</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Liquid)</td>
<td>5.01 $\cdot 10^{-8}$</td>
<td>8.13 $\cdot 10^{-8}$</td>
<td>5.71 $\cdot 10^{-5}$</td>
</tr>
</tbody>
</table>
The largest relative error values in Table 2-1 are $9.43 \cdot 10^{-6}$ for $h$ and $s$ and $2.98 \cdot 10^{-3}$ for $v$. Using FD approximations always results in some inherent error. These inherent errors are on the same order of magnitude as the parameter step size with respect to which the derivative is taken. In this case, the magnitudes of the inherent errors are $O(\Delta T) \approx 10^{-5}$ for $h$ and $s$ and $O(\Delta P) \approx 10^{-1}$ for $v$. The fact that the errors from the comparison are on the same or smaller orders of magnitude than these values suggests that the FD approximation is the only source of error and the symbolic expressions are error-free.

### 2.2.4 Mixture and Two-Phase Properties

*Clearwater* combines pure-component properties to describe the behavior of ammonia/water mixtures. Liquid and vapor mixtures are described by Equations (2-11) and (2-12), respectively. In these equations:

- $\theta$ represents any of the four properties of interest: $g$, $h$, $s$, or $v$.
- The superscript "V" refers to vapor, "L" to liquid.
- The subscript "1" refers to ammonia, "2" to water.
- $\Delta_{mix}^{\theta IM}$ is the ideal mixing parameter; it equals zero when calculating $h$ and $v$.

Finally, liquid and vapor properties must be combined to calculate the properties of two-phase mixtures. Assuming the molar vapor fraction, $\chi$, is known, a two-phase mixture property is simply the weighted fraction of its liquid and vapor components as given by Equation (2-13).

\[
\theta_{mix}^L = x_1 \theta_1 + x_2 \theta_2 + \Delta_{mix}^{\theta IM} + \theta^E
\]  

\[
\theta_{mix}^V = y_1 \theta_1 + y_2 \theta_2 + \Delta_{mix}^{\theta IM}
\]  

\[
\theta_{mix} = \chi \theta^V + (1 - \chi) \theta^L
\]
2.3 Vapor-liquid Equilibrium Calculations

The Gibbs energy equations lend themselves to straightforward vapor-liquid equilibrium (VLE) computations by formulating the problem in terms of chemical potential. There are actually multiple ways to define equilibrium. For example, Ibrahim and Klein equate fugacities using the \( \gamma - \phi \) method [19], but this approach only appropriate for systems below the critical points of both components. Therefore, in order to predict equilibria above the critical point of ammonia these authors must introduce an additional equation for the supercritical fugacity of ammonia. Other authors compute VLE behavior using empirical correlations to avoid iterating during computation [13, 14]. The calculations described here, which are also used in Clearwater, eschew the need for additional equations by computing chemical potentials directly from the Gibbs equations via Equations (2-14) and (2-15), which apply to both phases. This is the same approach used by Ziegler and Trepp [18].

\[
\mu_1 \equiv g_1 = g - x_2 \left( \frac{\partial g}{\partial x_2} \right)_{T,P} \tag{2-14}
\]

\[
\mu_2 \equiv g_2 = g - x_1 \left( \frac{\partial g}{\partial x_1} \right)_{T,P} \tag{2-15}
\]

2.3.1 Problem Formulation

Clearwater computes vapor-liquid equilibrium using equations derived directly from the Gibbs EOS's underlying equations. The Gibbs phase rule, Equation (2-16), identifies the number of intrinsic thermodynamic variables needed to define a system's state.

\[
F = 2 + C - P \tag{2-16}
\]

In this equation, \( F \) is the system number of degrees of freedom. \( C \) and \( P \) are the number of components and number of phases present in the system, respectively. Because the mixtures
considered by *Clearwater* have two components, three variables must be specified to fix the state of superheated or subcooled systems and two variables must be specified for saturated systems.

The Gibbs energy equations are functions of temperature, pressure, and liquid and vapor compositions, so *Clearwater* uses these four variables to perform VLE calculations. These calculations have the form, "given two of $T, P, x_1,$ and $y_1$, find values for the other two that satisfy phase equilibrium." Equations (2-17) through (2-20) give the equilibrium conditions.

\[
T^V = T^L = T 	ag{2-17}
\]
\[
p^V = p^L = p 	ag{2-18}
\]
\[
\mu_1^V(T, P, y_1) = \mu_1^L(T, P, x_1) 	ag{2-19}
\]
\[
\mu_2^V(T, P, y_1) = \mu_2^L(T, P, x_1) 	ag{2-20}
\]

These VLE conditions form a system of equations with two equations and two unknowns which can be solved using a multidimensional root finder. *Clearwater's* root finder is based on a Newton-Raphson (NR) solver coupled with boundary enforcement. In general, this solver:

1. Receives two of the four VLE variables ($T, P, x_1,$ or $y_1$).
2. Establishes boundaries and finds reasonable guesses for the unknowns variables.
3. Calls the Newton-Raphson solver, which determines the unknown values by iteration.

The Newton-Raphson algorithm formulates the current values of the objective functions and their Jacobian as a system of equations. For this VLE problem, the objective functions are Equations (2-19) and (2-20) rearranged: $f_1 = \mu_1^V - \mu_1^L$ and $f_2 = \mu_2^V - \mu_2^L$. The NR system of equations is then given by Equation (2-21) or its abbreviated version, Equation (2-22). In these equations $\lambda_1$ and $\lambda_2$ are the unknown VLE variables, collectively denoted by $\lambda$. At each NR iteration, this system of equations is solved for the vector step, $\delta\lambda$, that will drive the objective functions' values toward zero. Adding $\delta\lambda$ to the current value of $\lambda$ gives the evaluation point.
(i.e., the new values of the unknowns) for the next iteration. *Clearwater* evaluates functions and derivatives symbolically instead of with finite differences to avoid roundoff error.

\[
\begin{bmatrix}
\frac{\partial f_1}{\partial \lambda_1} & \frac{\partial f_1}{\partial \lambda_2} \\
\frac{\partial f_2}{\partial \lambda_1} & \frac{\partial f_2}{\partial \lambda_2}
\end{bmatrix}
\begin{bmatrix}
\delta \lambda_1 \\
\delta \lambda_2
\end{bmatrix}
= -\begin{bmatrix}
f_1 \\
f_2
\end{bmatrix}
\]

(2-21)

\[
J \delta \lambda = -f
\]

(2-22)

### 2.3.2 Bounding Unknown Variables

The Newton-Raphson solver described above fails to converge without reasonable guesses and search boundaries for the unknown variables. These unknowns must lie within the global ranges of Table 2-2, in which:

- Mole fraction bounds are the compositions of pure ammonia (1.0) and pure water (0.0); *Clearwater's* programming allows mole fractions to within $10^{-8}$ of these values.
- Temperature bounds correspond to the boiling point of ammonia (240 K) and the critical point of water (647 K).
- Pressure bounds match the extremes of the data of Gillespie et al. [20].

<table>
<thead>
<tr>
<th>Variable</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1, y_1$</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$T$</td>
<td>240 K</td>
<td>647 K</td>
</tr>
<tr>
<td>$P$</td>
<td>7 kPa</td>
<td>21 MPa</td>
</tr>
</tbody>
</table>

Ibrahim and Klein [19] guarantee the Gibbs equations from 240 – 600 K and 2 kPa – 11 MPa. *Clearwater* loosens the upper bounds to perform VLE calculations at higher temperatures and pressures, but users should beware that the results begin to differ significantly from experimental results. This deviance is quantified below in Section 2.7.1. Also, the Gibbs
EOS does used in *Clearwater* does not account for solid phases, so users should verify any VLE calculations in which a solid phase could be present by another method.

The VLE algorithm can establish narrower, more robust search bounds for calculations in which either temperature or pressure is already known. The algorithm does this using a combination of:

1. The pure-component saturation point(s).
2. The mixture critical point.
3. The assumption that the vapor mole fraction of ammonia must always be higher than that of the liquid ($y_1 > x_1$).

The following example, shown in Figure 2-1, illustrates this approach.

![Figure 2-1: The VLE algorithm uses physical limitations to narrow the search region from global (gray) to system-specific (green).](image)

This figure shows a two-phase ammonia-water mixture at a pressure of 10 MPa with a liquid composition of 50 mol % ammonia that must exist between the boiling temperatures of ammonia and water at this pressure (397.6 K and 587.1 K, respectively). Additionally, the vapor...
in this mixture must contain a higher percentage of ammonia than the liquid (i.e. $y_1 > 0.5$).

*Clearwater's* VLE algorithm uses these values as the search boundaries for the unknowns $T$ and $y_1$.

### 2.3.3 Guess Values

Once *Clearwater's* VLE algorithm has bounded the solution region, it makes guesses for the unknown values to provide the solver with place to begin its search. The algorithm first attempts this by combining the Raoult's law fugacity equation, Equation (2-23), with the empirical expression for vapor pressure [21] in Equation (2-24). Using these expressions to generate guess values simplifies and speeds computation since when temperature is known, the Raoult's law equations combine to provide explicit solutions for the unknowns.

\[
y_i P = x_i P_i^{sat}(T) \tag{2-23}
\]

\[
P^{sat} = exp \left[ A + \frac{B}{T} + C ln(T) + DT^E \right] \tag{2-24}
\]

The guessing function described above must inevitably calculate hypothetical "vapor pressures" for ammonia above its critical temperature of 405.65 K. Doing this assumes that the subcritical correlation reasonably approximates the supercritical region. Because of this assumption and other simplifications inherent to Raoult's law, the accuracy of the guess function decreases with increasing temperature (above 405.65 K) and pressure, eventually causing the guess values to fall outside of the previously established bounds on the unknowns. When this happens, the VLE algorithm rejects the Raoult's law guesses and instead uses the unknowns' values at the center of the search region as the starting point for iteration.
2.3.4 Enforcing Bounds

The VLE algorithm also enforces search bounds during iteration. As previously described, the NR solver steps to each new evaluation point based on the current value of the Jacobian—i.e., without any guidance from the user. However, it is essential the objective functions in Equations (2-19) and (2-20) can be evaluated at the new point. Since the objective functions contain natural logarithms, compositions outside the range of 0.0 − 1.0 are unacceptable as are negative values of temperature and pressure. The VLE algorithm conveniently enforces these requirements and keeps the search area small by:

1. Identifying any NR steps that produce negative or out-of-bounds values for the unknowns.
2. Reducing the step length so the new evaluation point is in-bounds while maintaining the original step direction.

2.3.5 Difficult or Unsolvable Problems

On average, VLE computations complete in about twelve hundredths of a second on a 2.7 GHz MacBook Pro. However, if one attempts a VLE calculation with unreasonable inputs, the Newton-Raphson solver may not converge to a solution. Difficult and possibly unsolvable problems include those in which:

1. One or more VLE variables lie outside the ranges given in Table 2-2.
2. The VLE inputs are $T$ and $P$, but the system pressure is less than the vapor pressure of pure water at the system temperature (i.e., $P < P_2^{\text{sat}}(T)$). In this case, the mixture can only exist as a superheated vapor and no VLE calculation is possible.
3. The VLE inputs are $T$ and $P$, but the system pressure is greater than the vapor pressure of pure ammonia at the system temperature (i.e., $P > P_1^{\text{sat}}(T)$). In this case, the mixture
can only exist as a subcooled liquid and no VLE calculation is possible. For ammonia/water mixtures, this only applies when the mixture is at a temperature below the critical temperature of ammonia, \( T_{c,1} = 405.65 \text{ K} \).

4. The VLE inputs suggest that the mixture is above its critical point. This occurs when the input pressure is greater than the mixture critical pressure predicted by the system temperature (i.e., \( P > P_c(T) \)).

5. The VLE inputs are \( x_1 \) and \( y_1 \), and the liquid ammonia composition is greater than that of the vapor (i.e., \( x_1 > y_1 \)).

Inevitably, one must study the VLE behavior of ammonia/water mixtures to determine what VLE input combinations are unlikely to produce solutions. However, Clearwater's VLE algorithm will terminate and alert users to the above problems.

### 2.3.6 Critical Point Estimations

*Clearwater* relies on a polynomial fit of experimental measurements [22-25] to predict mixture critical points. The critical data and fit appear below in Figure 2-2.

![Figure 2-2: Fitting a polynomial to experimental data helps predict mixture critical points.](image)
Since the Gibbs liquid and vapor equations differ from one another in mathematical form and become inaccurate in the vicinity of the critical locus, they cannot predict mixture critical points. Therefore, the experimental data described above is used instead.

2.4 State Calculations

Many unit operations require state calculations in which pressure and either enthalpy or entropy are known, but not temperature. Examples include isentropic pressure change in turbines, isenthalpic expansion in valves, and isobaric heat transfer in condensers and reheaters. In these calculations, the mixture's phase is often unknown \textit{a priori}. For example, it may not be immediately apparent which phases are present following expansion in a turbine. In order to address these challenges, \textit{Clearwater} contains functions that 1) identify phase then 2) calculate state variables for the three input combinations most common to power cycles. These functions are:

I. \( \text{State} = f(T,P,z_1) \)

II. \( \text{State} = f(P,h,z_1) \)

III. \( \text{State} = f(P,s,z_1) \)

Pressure \(P\) and stream composition \(z_1\) are known inputs in all three functions, but the third known variable differs. The following sections describe the algorithms for functions I (temperature is known) and II (enthalpy is known). The algorithm for function III, though not explicitly described, is similar to the algorithm for function II.

2.4.1 State Function: \( f(T,P,z_1) \)

The \( f(T,P,z_1) \) state function identifies phase by comparing the stream composition with the equilibrium liquid and vapor compositions \( (x_{1,eq} \text{ and } y_{1,eq}) \) determined by the mixture.
temperature \( (T) \) and pressure \( (P) \). If \( z_1 = x_{1,\text{eq}} \), the mixture is at its bubble point. If \( z_1 = y_{1,\text{eq}} \), the mixture is at its dew point. If \( x_{1,\text{eq}} < z_1 < y_{1,\text{eq}} \), the mixture is present in two phases; in this case, molar vapor fraction is calculated using the lever rule. The lever rule is given by Equation (2-25), in which \( \chi \) denotes molar vapor fraction. The state function then uses the molar vapor fraction to calculate all other state variables.

\[
\chi = \frac{z_1 - x_1}{y_1 - x_1}
\]  

The phase identification algorithm also handles situations in which the VLE calculator cannot solve for \( x_{1,\text{eq}} \) and \( y_{1,\text{eq}} \). These situations occur when the mixture pressure lies above or below the extent of the phase envelope and are illustrated in Figure 2-3.

The following statements describe the various regions of Figure 2-3:

- \( P < P_{2,\text{sat}}(T) \), the mixture is superheated, shown by the dark red regions.
- For \( P > P_{1,\text{sat}}(T) \), the mixture is subcooled, shaded in dark blue in the left-hand system. This can only occur in systems below the critical point of ammonia.

Figure 2-3: \( Pxy \) plots show the various solution regions for the State\((T, P, z_1)\) algorithm. The left-hand and right-hand plots show subcritical and supercritical cases, respectively.
• For $P > P_c(T)$, the system is above its critical point. The critical pressure is shown by the dotted green line in the right-hand plot. For supercritical systems, the phase identifier compares the overall system composition ($z_1$) with the liquid composition at the empirical critical point ($x_{1,c}$). If $z_1 < x_{1,c}$, it is assumed that the supercritical fluid has properties similar to those of a subcooled liquid. If $z_1 > x_{1,c}$, signified by the dark green region, the phase identifier returns an error. If the cricondentherm were known, a similar assumption would allow the approximation of a supercritical fluid as a superheated vapor for $z_1 > y_{1,c}$. Unfortunately, the cricondentherm is impossible to locate from the Gibbs equations, so no attempt is made to characterize fluids with compositions above $x_{1,c}$.

Figure A-1 in the appendix gives a flowchart of the entire phase identification algorithm.

2.4.2 State Functions: $f(P, h, z_1)$ and $f(P, s, z_1)$

Phase identification is also straightforward for cases II and III. First, Clearwater's VLE algorithm computes bubble and dew point temperatures (see Figure 2-4).

![Figure 2-4: The bubble and dew points occur where $x_1 = z_1$ and $y_1 = z_1$, respectively. Properties at these points help identify the system phase.](image-url)
The state function compares enthalpies to identify the mixture state. The function uses equations (2-11) and (2-12) to evaluate the enthalpies at the bubble and dew points ($h_B$ and $h_D$, respectively). Because enthalpy increases monotonically with temperature for ammonia/water mixtures (see Figure 2-5), the program can then compare the input enthalpy, $h$, with the enthalpies at the bubble and dew points to identify the system phase. There are five possible outcomes for this comparison. These are:

1. $h < h_B$: subcooled liquid
2. $h = h_B$: saturated liquid
3. $h_B < h < h_D$: two-phase
4. $h = h_D$: saturated vapor
5. $h > h_D$: superheated vapor

![Figure 2-5: Enthalpy and entropy increase monotonically with temperature in ammonia water mixtures, as shown by the $T-h$ and $T-s$ curves for a 50 mol % ammonia mixture. Trends are similar for other mixing fractions.](image)

In the saturated cases, 2 and 4, the state is known, but for the other three cases (cases 1, 3, and 5) the system temperature is unknown. To find the system temperature, *Clearwater* uses a root-finding algorithm based on bisection, comparing the calculated and input enthalpies, which converge when the correct temperature is identified. In the two-phase case (case 3), identifying
the system temperature naturally leads to the correct values of $x_1$, $y_1$, and $\chi$. A flowchart of this routine appears in Figure A-2 of the appendix.

2.5 Unit Operations

Descriptions of Clearwater's unit operation algorithms follow. These descriptions are meant to guide future researchers who use this simulation tool. The unit operations are those common to power and refrigeration cycles and are adapted from Wilding's code [26]. They include:

- turbine
- pump
- compressor
- primary heat exchanger (PHX)
- condenser
- re heater
- flash drum
- valve
- mixer
- splitter

The unit operations are constructed as classes—an approach that allows the user to create multiple instances in a single cycle but give them different attributes (for example, high- and low-pressure turbines). The unit operations are solved using only heat and mass balances; transport phenomena taking place inside the unit operations are not considered. The computation times reported for each unit operation are based on a 2.7 GHz MacBook Pro.

2.5.1 Stream

The stream class records the temperature, pressure, molar flow rate, overall stream composition, liquid composition, vapor composition, vapor fraction, enthalpy, entropy, and molar volume of a stream. Streams make it easy to pass attributes from one unit op to another.
Streams also allow the user to inspect a cycle for errors. It is assumed that all streams are perfectly insulated and that they allow fluid to flow with zero pressure drop.

2.5.2 Pressure Changers: Turbine, Pump, and Compressor

The turbine, pump, and compressor unit operations all use a similar calculation method: they first approximates a pressure change as isentropic, then correct the approximate result with an efficiency value. Turbines, which often produce two-phase fluids, achieve results within about 10 seconds. Because compressors and pumps must simulate only a single phase, they generally compute results in less than one second.

2.5.3 Heat Exchangers: Primary Heat Exchanger (PHX), Condenser, and Reheater

The PHX class calculates the molar flow rate of a cycle. The PHX assumes that the heat load is known as well as the inlet and outlet temperatures of the primary and secondary streams. The PHX does not check for pinch points. It normally requires less than a second to compute. The PHX assumes isobaric heat transfer, as do the condenser and reheater.

The condenser class cools an inlet stream to a user-specified outlet condition, which can be either 1) outlet temperature or 2) vapor fraction. The condenser assumes that its heat sink (e.g., cooling water) is isothermal, not sensible. The condenser checks for temperature pinching at its outlet. When outlet temperature is specified, the condenser generally solves in less than a second. When vapor fraction is specified, it requires about three seconds.

The reheater class simulates counterflow heat exchange. The reheater requires the user to specify the outlet temperature of one stream and then calculates the outlet states of both streams. The reheater checks for pinch points throughout the heat exchanger by:
1. Identifying points of phase change for each stream (if any).

2. Approximating the temperature/heat exchange ($TQ$) curves by sampling enthalpy at interior temperature points and then interpolating between them.

3. Applying the interpolation to a fine temperature grid to ensure that $\Delta T_{\text{pinch}}$ is not violated anywhere inside the exchanger.

Users can specify $\Delta T_{\text{pinch}}$, grid resolution, and the type of approximation to use when creating the $TQ$ curves. Linear and spline approximations are available. Which to use depends on the degree of accuracy required and allowable computational expense. Reheaters using the linear $TQ$ approximation are less accurate but a little faster than those using splines (see Figure 2-6).

Computation time depends on the number of phases present in each stream.

![Figure 2-6: Linearly approximating $TQ$ curves (left) is less accurate but slightly faster than using splines (right).](image)

The number of sample points required by a $TQ$ spline depends on the phase it represents. True ammonia/water isobars in the subcooled and superheated phases are slightly curved and have no inflection points. In the two-phase region, isobars can exhibit a single inflection point. Thus the nonlinear interpolation routine approximates single-phase regions as quadratic polynomials and two-phase regions as cubic polynomials. Single-phase regions often exhibit
little curvature, so only one interior sample point is necessary, but two-phase regions require more sample points to better describe nonlinear behavior.

2.5.4 Flash Drum, Valve, Mixer, and Splitter

The flash drum class acts an equilibrium separator with vapor and liquid outlets. Users have the option to specify a drum pressure and/or temperature that are different from those of the incoming stream. If stream temperatures differ, the required heat input is calculated. Flash drums solve in less than a second.

The valve class assumes isenthalpic expansion of a single stream from high to low pressure. The mixer combines two streams into one, computing outlet properties using mass and energy balances. Both the valve and the mixer require several seconds to solve. The splitter simulates a tee valve. The splitter divides one stream into two smaller ones, both of which inherit the intrinsic properties of the inlet. Because it requires no thermodynamic calculations, the splitter computes almost instantaneously.

2.6 Package Structure

The organization of Clearwater is given in Figure A-3 of the appendix. The package has three modules. The props module contains the coefficients and equations required for property calculations. The phase module performs VLE calculations in its primary file, equilibria.py, which depends on several other supporting files for intermediate calculations (e.g. bounds location, vapor pressures, critical points, etc.). The unit_ops module contains all equipment classes and the state calculators.
2.7 Validation of Thermodynamic Calculations

A group of experimental datasets validates the property and VLE computations in Clearwater. In an exhaustive review of available ammonia/water property datasets, Tillner-Roth and Friend [15] identify several datasets as high-quality or important. These include:

- $TPxy$ measurements of Gillespie et al. [20] and Polak and Lu [27].
- Bubble point pressure data of Sassen et al. [25].
- Liquid densities of King et al. [28] and Jennings [29].

Tillner-Roth and Friend do not recommend the enthalpy change data of Macriss et al. [30] due to its high scatter. Despite this caution, this work compares its results with the Macriss data because it is important to validate Clearwater's calculations against many types of thermodynamic data.

Comparing Clearwater's calculations to experimental data produces errors only slightly higher than the "typical" error values reported by Tillner-Roth and Friend while validating their own ammonia/water EOS [16]. Since Tillner-Roth and Friend's EOS functioned for years as the IAPWS standard, it is assumed that their error values are of acceptable magnitudes. These error values are used as a baseline and appear in Table 2-3 alongside the average errors produced by comparisons in this work. The average composition error reported for this work includes only comparisons with the Gillespie et al. data. Polak and Lu's data was measured at very ammonia-lean compositions and, if their data were included, it would make the average composition error appear smaller than it should be.

<table>
<thead>
<tr>
<th>Property</th>
<th>Tillner-Roth and Friend [16]</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compositions (mol frac)</td>
<td>± 0.01</td>
<td>± 0.02</td>
</tr>
<tr>
<td>Saturated Liquid Densities (%)</td>
<td>± 0.3</td>
<td>± 0.9</td>
</tr>
</tbody>
</table>
2.7.1 Vapor-liquid Equilibrium

A comparison of Clearwater VLE computations with the TPxy data of Gillespie et al. [20] follows. Figure 2-7 shows the absolute errors between the compositions predicted by Clearwater and the compositions reported by Gillespie et al. These errors, or residuals, are plotted against pressure and temperature to identify trends in the data. Liquid and vapor residuals appear in the left- and right-hand plots, respectively.

Figure 2-7 demonstrates that Clearwater's predictions become less accurate at high temperature and pressure. These trends qualitatively match the ones reported by Ibrahim and Klein, who performed similar comparisons [19]. Averaging error values from low to high pressure helps quantify the influence of system pressure on prediction error. For instance, the average absolute error between the predicted and measured liquid compositions is less than
0.01 (mol frac) for system pressures below 0.21 MPa. For the vapor compositions, the cutoff is much higher; their average error is less than 0.01 (mol frac) below 6.6 MPa. Table 2-4 gives these and other pressure cutoffs. The mean error for all comparisons is 0.018 (mol frac).

Table 2-4: Error Cutoffs for Comparison with Gillespie Compositions

<table>
<thead>
<tr>
<th>Pressure Cutoffs (MPa)</th>
<th>Average Error (mol frac)</th>
<th>Liquid</th>
<th>Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.21</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>2.93</td>
<td>15.21</td>
<td></td>
</tr>
</tbody>
</table>

Sassen et al.'s bubble point pressure data [25] confirms these trends. The comparison between Clearwater's computations and this dataset suggests that Clearwater's computations are most accurate at low temperature, low pressure, and high ammonia fraction (see Figure 2-8).

Figure 2-8: VLE results under predict the bubble-point pressures of Sassen et al. [25] at high pressures (left) and temperatures (middle) and at low ammonia fractions (right).

Averaging error values from low to high pressure or temperature helps identify error cutoffs. Below 12.9 MPa or 495 °C, the average absolute error is less than 0.5 MPa. The average error for all comparisons with the Sassen et al. data is 1.17 MPa.

Clearwater's VLE computations also compare favorably with the ammonia-lean \( T_P x_y \) measurements of Polak and Lu [27], suggesting that Clearwater's VLE computations can solve
for even very small ammonia compositions. Figure 2-9 compares Clearwater's computations with data measured by Polak and Lu at isobars of 0.1 MPa and 4.5 MPa between 90 °C and 147 °C. The plots exhibit slightly larger errors in the vapor than the liquid, but all errors are very small. For the liquid and vapor phases, the mean absolute errors are 0.0036 and 0.0075, respectively. Clearwater's VLE calculator tends to fail when trying to calculate VLE for nearly pure mixtures; for instance, a calculation including $y_1 = 1 \cdot 10^{-5}$ as a specification is unlikely to produce good results.

![Figure 2-9: Residuals comparing results to Polak and Lu's data [27] suggest that VLE calculator computes reliable results at low ammonia fractions in both the liquid (left) and vapor (right) phases.](image)

2.7.2 Liquid Volumes

Clearwater's volume calculations match the bubble-point volume data measured by King et al. and Jennings [28, 29], which further validates the accuracy of the program's equations. As shown in Figure 2-10, error tends to increase with temperature and decrease with ammonia fraction. The average relative error for all volume comparisons is 0.9%. This amount of error is low in spite of differences up to 0.3 MPa between the system pressures predicted by Clearwater and those reported by King et al. and Jennings, which highlights the weak pressure dependence of liquid volume calculations.
Figure 2-10: Clearwater’s molar volume predictions agree well with the data of King and Jennings [28, 29]. Error tends to increase with increasing temperature (left) and decreasing ammonia fraction (right).

2.7.3 Liquid Enthalpies

Macriss et al. report enthalpy changes of saturated liquid mixtures at four compositions in the ranges of $1 − 6$ MPa and $0 − 250$ °C [30]. Figure 2-11 shows the absolute errors between Macriss et al.’s values and those predicted by Clearwater. The average error for this comparison is small—only 133 J/mol. Error tends to increase somewhat with temperature and pressure.

Figure 2-11: Enthalpy change calculations match the measurements of Macriss et al. [30]. Error tends to increase somewhat with pressure (left) and temperature (right).

2.8 Kalina Cycle Validation

A replication of Marston's simplified cycle in [8] validates both the unit operations and Kalina cycle layout used in this work's comparisons. Marston's design, which incorporates two reheaters and a feedwater heater, is an improved version of the original Kalina cycle proposed in [7] (see Figure 2-12). The Marston cycle uses 550 °C gas as its heat source.
Figure 2-12: The results of this Kalina cycle, presented by Marston [8], validate Clearwater's unit operations and the Kalina cycle convergence procedure.

2.8.1 Specifications

Replicating Marston's cycle using Clearwater is generally straightforward. Table 2-5 presents key cycle specifications—the same originally used by Marston. A workaround at the boiler outlet is required since Clearwater can only identify mixture states below the critical point of water (~647 K). In Marston's cycle, the boiler outlet temperature is 773 K, so this work simply assumes the boiler outlet is superheated vapor and calculates state properties accordingly. Using this assumption, Clearwater calculates the boiler outlet enthalpy to be 2796 kJ/kg. This enthalpy almost exactly matches the value of 2798 kJ/kg reported by Marston for the same stream, which justifies the superheated vapor assumption. The procedure used to converge this cycle is discussed in Chapter 3.
Table 2-5: Validation Parameters and Boundary Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{CW}$</td>
<td>15 °C</td>
</tr>
<tr>
<td>$T_1$</td>
<td>70 °C</td>
</tr>
<tr>
<td>$T_{13}$</td>
<td>500 °C</td>
</tr>
<tr>
<td>$\Delta T_{\text{pinch}}$</td>
<td>5 °C</td>
</tr>
<tr>
<td>$w_{13}$</td>
<td>0.70 (mol frac) NH$_3$</td>
</tr>
<tr>
<td>$p_{13}$</td>
<td>10 MPa</td>
</tr>
<tr>
<td>$\eta_P$</td>
<td>0.60</td>
</tr>
<tr>
<td>$\eta_T$</td>
<td>0.90</td>
</tr>
</tbody>
</table>

2.8.2 Results

The Clearwater simulator's cycle computations agree well with those reported by Marston [8] even though the latter were calculated using a different equation of state. The simulator calculates a first law efficiency of 0.3177. This value differs by less than one efficiency point from the value of 0.3113 reported by Marston.

Table 2-6 shows maximum absolute error values for several stream parameters in terms of the units used by Marston. As the table shows, absolute errors for stream pressures, stream compositions ($w_1$), and relative flow rates ($\dot{m}/\dot{m}_{13}$) are generally small. Temperature errors are generally less than 1 °C; for stream 12, however, Clearwater computes a temperature 10 °C different than the one reported by Marston. It is possible that this anomaly is due to a typographic error in the reference. A complete list of the stream parameters produced by Clearwater appears in Table A-3 of the appendix.

Table 2-6: Maximum Absolute Errors from Marston Cycle Validation

<table>
<thead>
<tr>
<th>$P$</th>
<th>$T$</th>
<th>$w_1$</th>
<th>$h$</th>
<th>$s$</th>
<th>$\dot{m}/\dot{m}_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2 kPa</td>
<td>10 °C</td>
<td>0.012 (mass) NH$_3$</td>
<td>108 kJ/kg</td>
<td>2.3 kJ/kg</td>
<td>0.0980</td>
</tr>
</tbody>
</table>
2.9 Conclusions

The Clearwater simulator is capable of simulating the thermodynamics of ammonia/water mixtures and power and refrigeration cycles that use these mixtures as a working fluid. The simulator is free and will be published online in open-source format to aid future researchers. Two other distinguishing features of the Clearwater tool are 1) its use of a bounded Newton-Raphson root-finding algorithm to execute VLE calculations and 2) its enforcement of mixture critical points.

Validations against experimental data and third party modeling suggests that Clearwater's calculations are sufficiently accurate for research purposes. Comparison with property measurements from literature shows that the simulator's accuracy tends to decrease with increasing temperature and pressure. A Kalina cycle model built with the program generally produces stream conditions similar to those reported by Marston [8] even though his cycle model is based on a different equation of state. The efficiency values of these two cycles are within one percentage point, showing Clearwater's calculations to be of comparable accuracy.
3 KALINA/RANKINE CYCLES COMPARISON AT PWR CONDITIONS

In this chapter the Kalina cycle is applied to direct power conversion from pressurized water reactors (PWR). The chapter first reviews previous studies applying the Kalina cycle in the nuclear space. Many of these studies consider the Kalina cycle for bottoming applications, which is outside the scope of this work. Those studies that do apply the Kalina cycle to direct power conversion from PWRs are either incomplete or make unfeasible assumptions. To provide a more comprehensive analysis, this work uses the Clearwater simulator to model single-stage Kalina and Rankine cycles using heat at PWR conditions. The thermodynamic efficiencies of the two cycles are then compared to determine which is more suited to this application.

3.1 Previous Nuclear Kalina Cycle Studies

3.1.1 Bottoming Applications

With the aim of increasing plant efficiencies, various researchers have investigated the application of the Kalina cycle to nuclear plants. Most of these researchers apply the Kalina cycle as a bottoming cycle, meaning one that produces power using the waste heat of another process. Two specific applications of the Kalina cycle are to 1) the recovery of heat from gas-cooled reactor (GCR) exhaust [31-37] and 2) ocean thermal energy conversion (OTEC) systems driven by plant effluent [38, 39].

Many of the GCR studies report efficiency increases. For instance, Li et al. conclude that adding a Kalina bottoming cycle to a supercritical CO₂ plant raises the plant's baseline exergetic
efficiency by over 8% [31]. Mahmoudi et al. [33, 34] agree with these results, reporting similar efficiency increases.\(^1\) The purpose of bottoming cycles is to raise efficiency, however, so the fact that the combined cycles outperform the gas cycles alone is not surprising. Zare et al. suggest that organic Rankine cycles (ORC) may be a better choice for GCR bottoming; their study concludes that an ORC operating with n-pentane not only exhibits higher efficiencies than the Kalina cycle but also makes for easier operating conditions [35].

ORCs also seem to generate power from nuclear plant effluent more efficiently than Kalina cycles. Kim et al. report in [38] that for OTEC systems with an effluent temperature of 28 °C, an ORC with feedwater heating produces a thermal efficiency about half a percentage point higher than a comparable Kalina cycle configuration. Park et al. [39] find the margin to be higher with a different working fluid.

### 3.1.2 Pressurized Water Reactor Applications

Three studies examine the Kalina cycle as the main power converter for pressurized water reactors (PWR) [13, 40, 41]. Of these studies, the first two lack proof of concept and the third presents models that require unviable operating conditions.

Brodyanskii [40] highlights the low freezing temperatures of ammonia/water mixtures and discusses the Kalina cycle's potential to operate with high efficiency in sub-freezing environments. However, he does not present cycle models to quantify the potential efficiency increase. Zhang et al. [41] state that a Kalina cycle using PWR heat would attain a thermal efficiency at least 10% higher than the steam cycle design. That work also lacks a complete cycle

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\(^1\) Every sensible heat source has a maximum, theoretical amount of power it can produce by changing from its inlet to outlet state via reversible processes. Exergetic efficiency quantifies how much of this theoretical amount a given power cycle converts into usable form.
model, which is a major problem—without a complete model it is easy to overlook some of the Kalina cycle's potential drawbacks, including efficiency loss caused by its relatively high turbine discharge pressure.

In a recent publication, Wang et al. present computational models of three ammonia/water cycles [13]. Two of these cycles do not separate the mixture at any point. As such, these cycles need infeasibly cold cooling water (~5 °C) to completely condense the working fluid, a problem the authors acknowledge. The third cycle does incorporate ammonia/water separation but deviates from more conventional Kalina cycle designs by using less reheating, a different position for the expansion valve, and a compressor. This cycle computes an efficiency of 34.8% but is unlikely to be commercially viable since it appears to compress the working fluid until there is a high amount of liquid present at the compressor outlet. To summarize, there appears to be no complete work comparing the efficiencies of Kalina and Rankine cycles using PWR heat.

3.2 Cycle Specifications

Single-stage Rankine and Kalina cycle designs provide the efficiency values for this work's comparison. To provide an apples-to-apples comparison of cycle efficiencies, both cycles use the same heat source inlet and outlet temperatures, heat load, cooling water temperature, pinch temperature, and equipment efficiencies. Table 3-1 presents these and other key cycle parameters. Additionally, both cycles assume zero pressure drops inside the heat exchangers.

Both the Kalina and Rankine cycles are based on a the same steam generator configuration, which is a Babcock and Wilcox once-through design [42]. The Kalina cycle requires a once-through design [43], which helps to maximize its efficiency, though many PWR Rankine cycles actually use recirculating models. For this comparison, the PWR is considered as
the heat source, thus the hot leg fluid of the steam generator is the reactor core coolant. As required by licensing and design constraints, the coolant must leave and reenter the core at specific temperatures to maintain a steady operation of the nuclear core with minimal reactivity insertions. This means that thermal power transferred inside the steam generator is constant.

### Table 3-1: Steam Generator Parameters and Other Global Constants

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{S,in}$</td>
<td>317.7 °C</td>
</tr>
<tr>
<td>$T_{S,out}$</td>
<td>290.0 °C</td>
</tr>
<tr>
<td>$P_S$</td>
<td>15.17 MPa</td>
</tr>
<tr>
<td>$T_{out, cold}$</td>
<td>307.7 °C</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>1284 MW</td>
</tr>
<tr>
<td>$T_{CW}$</td>
<td>25 °C</td>
</tr>
<tr>
<td>$\Delta T_{pinch}$</td>
<td>10 °C</td>
</tr>
<tr>
<td>$\chi_{condensate}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta_P$</td>
<td>0.85</td>
</tr>
<tr>
<td>$\eta_T$</td>
<td>0.90</td>
</tr>
</tbody>
</table>

### 3.2.1 Rankine Cycle

This work uses a single-stage Rankine cycle design. Figure 3-1 illustrates its flow diagram. Rankine cycles in actual nuclear plants often incorporate several turbine stages, moisture separation and reheating to optimize thermodynamic efficiency. The single-stage design, however, has several advantages: it is simple, requires little optimization, and is of similar complexity as the single-stage Kalina cycle. Therefore, it is the design analyzed in this work. The program used for the in-house Rankine models is called OPTIONS [26]. This program runs in Python and relies on a thermodynamics package for water/steam based on the IAPWS 97 correlation [44].

As seen in Figure 3-1, the single-stage Rankine cycle design comprises four steps. The working fluid receives heat from the reactor coolant in the steam generator at high pressure. The
fluid boils in the process, then flows to the turbine where it expands, producing power. The turbine exhaust pressure is 0.0086 MPa, which is typical of current nuclear steam turbines. After expanding, the working fluid condenses through contact with cooling water. Finally, the fluid pressure increases again via pumping before it reenters the steam generator.

The boiler pressure, $P_2$, is an optimizable parameter in the Rankine cycle. Boiler pressure must be as high as possible for maximum efficiency but low enough to avoid a temperature pinch inside the steam generator. Babcock and Wilcox recommend a conservative boiler pressure of 6.38 MPa, which ensures that Stream 1-2 boils 10 °C below the coolant outlet temperature. In this work, $P_2$ is raised to 7.679 MPa, which just maintains the minimum pinch temperature difference in the boiler. Key Rankine cycle specifications are summarized in Table 3-2.

![Diagram of the single-stage Rankine cycle](image)

**Figure 3-1:** The single-stage Rankine cycle is easy to optimize and is a good standard of comparison.
Table 3-2: Rankine Cycle Specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2$</td>
<td>7.679 MPa</td>
</tr>
<tr>
<td>$P_3$</td>
<td>0.0086 MPa</td>
</tr>
</tbody>
</table>

Originally the scope of this work also included the comparisons of two- and three-stage versions of the Rankine and Kalina cycles at PWR conditions. These comparisons were eventually abandoned due to time constraints and the unfavorable single-stage Kalina cycle results. However, the two- and three-stage Rankine cycle results provide a good jumping-off point for future research. The description of these cycles and their results appear in Section A.5 of the appendix.

3.2.2 Kalina Cycle

Unlike the Rankine cycle, the Kalina cycle has three optimizable parameters. These are 1) the composition of the stream that flows through the steam generator, $z_3$, 2) the separator temperature, $T_{11}$, and 3) the boiler pressure, $P_3$. The method used to specify and converge the Kalina cycle is described in detail by Marston [8]. This work follows his process by choosing values for $z_3$ and $T_{11}$, then evaluating mass and energy balances across each of the cycle unit operations. The optimum value of $z_{11}$ must then be iteratively determined based on the convergence of these balances in the cycle.

The optimum value of $z_{11}$ must be 1) as low as possible to permit a low turbine exhaust pressure and 2) high enough to allow the distiller to raise its cold leg temperature, $T_{\text{DistillerColdOut}}$, to the specified separation temperature, $T_{11}$. Instead of determining $z_{11}$ by hand for each set of $z_3$ and $T_{11}$, this work employs a nonlinear solver to find it. The solver determines the correct value of $z_{11}$ by:
1. Specifying a 10 °C approach at the distiller's cold stream outlet.

2. Guessing values of $z_{11}$.

3. Tracking the error, $err = T_{11} - T_{\text{DistillerColdOut}}$.

This error varies almost linearly with $z_{11}$, so the problem lends itself to the secant method of root finding. The root-finder in this work uses $z_3$ and $0.9(z_3)$ as initial guesses for $z_{11}$ and converges after just a few iterations.

The parameters $z_3$ and $T_{11}$ also control cycle pressures. The highest pressure in the cycle is the steam generator operating pressure, $P_3$. Ideally, $P_3$ would be optimized simultaneously with $z_3$ to produce the highest possible cycle work output. In this comparison a simplification is used instead: $P_3$ is set high as possible while still allowing the steam generator to 1) completely vaporize the mixture and 2) maintain a 10 °C pinch temperature difference. This analysis approximates the boiler's temperature/heat exchange ($TQ$) profiles linearly to reduce calculation time. For the correct mixture composition, this approximation produces parallel heating and cooling curves 10 °C apart inside the boiler. Like Marston [8], this work uses a sensitivity analysis to examine how different combinations of $z_3$ and $T_{11}$ affect cycle efficiency.

3.3 Results/Discussion

3.3.1 Rankine Cycle

The single-stage Rankine cycle model predicts a thermodynamic efficiency of $\eta_I = 33.2\%$, which is the standard of comparison for all Kalina cycle results. The Rankine cycle working fluid absorbs heat in the steam generator at an average temperature of 241.9 °C and leaves with 15.5 °C of superheat. A detailed list the Rankine cycle stream parameters appears in Table A-5 of the appendix.
3.3.2 Kalina Cycle Results

Figure 3-2 displays the data collected from the single-stage Kalina cycle simulations. For each value of $z_3$, this figure shows the following approximate trends:

1. The optimum value of $z_{11}$ increases linearly with increasing $T_{11}$ (top left).
2. $\eta_1$ increases linearly with decreasing $z_{11}$ (bottom left).
3. $\eta_1$ increases linearly with decreasing $T_{11}$ (bottom right).

![Figure 3-2: The relationships among $T_{11}$ and $z_{11}$ (top left), $z_{11}$ and $\eta_1$ (bottom left), and $T_{11}$ and $\eta_1$ (bottom right) exhibit predictable trends.](image)

For a given value of $z_3$, there are upper and lower validity bounds for $T_{11}$. Above the upper bound, the separator liquid outlet contains a higher ammonia fraction than the turbine exhaust. This is counterproductive since the purpose of the separation is to decrease the ammonia
fraction of the turbine exhaust. At the lower bound for $T_{11}$, the boiling/condensing $TQ$ profiles inside the distiller are parallel (see Figure 3-3). Below this lower bound, the boiling portion of the cold leg $TQ$ curve (Stream 10-11) becomes too "flat" and the distiller stream temperatures pinch. For a given value of $z_3$, cycle efficiency reaches a maximum at the lowest possible $T_{11}/z_{11}$ combination. This is because the turbine outlet pressure, $P_4$, decreases with $z_{11}$. Lowering turbine outlet pressure corresponds to more turbine expansion, higher power output, and better thermodynamic efficiency.

![Graph showing $TQ$ profiles inside the distiller become parallel at optimal values of $z_{11}$.](image)

**Figure 3-3:** $TQ$ profiles inside the distiller become parallel at optimal values of $z_{11}$.

The Kalina cycle maximum thermodynamic efficiency increases monotonically with decreasing $z_3$. The left-hand graph of Figure 3-4 shows this trend by plotting the maximum value of $\eta_1$ for each value of $z_3$ tested. This monotonic increase of $\eta_1$ occurs in spite of the match between the steam generator $TQ$ profiles. These profiles become nearly parallel around $z_3 = 0.125$, producing the "best case" heat transfer scenario. For $z_3 < 0.125$, $P_3$ must be specified lower than the stream dew point pressure to avoid pinching and the $TQ$ profiles begin to look like those of the Rankine cycle.
3.3.3 Kalina Cycle Discussion

The lack of an efficiency maximum at $z_3 = 0.125$ implies two possible, non-exclusive conclusions. These conclusions are:

1. The efficiency gains from lower allowable turbine outlet pressures outweigh those from better profile matching.
2. Better profile matching does not actually allow the working fluid to absorb heat at a higher average temperature.

There is strong evidence supporting both conclusions. The strong correlation of increasing $\eta_l$ with decreasing $P_4$, as shown by the opposite trends of the left- and right-hand plots of Figure 3-4, supports Conclusion 1. The average heat transfer temperature of the best case Kalina cycle ($z_3 = 0.125$) supports Conclusion 2. Stream information for this best case cycle appears in Table A-6 of the appendix, and its $TQ$ profiles appear superimposed against those of the Rankine cycle baseline in Figure 3-5. This figure shows that the Kalina cycle working fluid is indeed able to maintain a smaller temperature difference between itself and the heat source fluid than the Rankine cycle during boiling (right-hand portion of the plot). However, the Kalina cycle working fluid's temperature increases from its feedwater temperature more slowly, as exhibited
by the slopes in the left-hand portion of the plot. The overall effect of these phenomena is that the Kalina cycle absorbs heat at an average temperature of 237.5 °C. This absorption temperature is 4.4 °C lower than that of the Rankine cycle, and this difference is one cause of the Kalina cycle's inferior efficiency.

In reality, both Conclusion 1 and Conclusion 2 are correct. The presence of ammonia in the Kalina cycle's working fluid 1) causes the cycle turbine exhaust pressure to be higher than that of the Rankine cycle and 2) increases the working fluid's liquid heat capacity. Both of these phenomena are detrimental to the Kalina cycle's thermodynamic efficiency. In this application of the single-stage Kalina cycle to PWR power conversion the efficiency losses due to these phenomena outweigh the efficiency gain produced by the Kalina cycle's sloped boiling profile.

Applications of the Kalina cycle to other heat sources may produce opposite results to those presented here. The Kalina cycle is not well suited to PWR power conversion because the heat source temperature drop is very small—only 28 °C. For heat sources with larger temperature

Figure 3-5: Steam generator $TQ$ profiles for Rankine and "best case" Kalina cycles show that the Rankine cycle's higher heat absorption temperature is due to its working fluid's low liquid heat capacity.
drops, the efficiency gain due to the Kalina cycle working fluid's ability to boil non-isothermally would be greater than the efficiency losses caused by this cycle's higher turbine exhaust pressure and liquid heat capacity. The ability to easily simulate the Kalina cycle with various heat sources is one benefit of the Clearwater simulation tool; Chapter 4 presents an analysis of this type.

3.3.4 Effect of Feedwater Heating

The single-stage Rankine and Kalina cycle configurations analyzed here suffer from very large temperature differences in the first half of the boiler, but these could be eliminated through the addition of feedwater heating. Practical Rankine cycle designs include feedwater heating, which raises the cold leg fluid's inlet temperature. While the design of a Kalina cycle feedwater heating system is outside of the scope of this work, it is helpful to see how raising the feedwater temperature affects the average heat absorption temperatures of the Kalina and Rankine cycles. For example, the Babcock and Wilcox steam generator discussed above actually operates with a feedwater temperature of 237.8 °C. Re-simulating only the steam generators of the two cycles at this feedwater temperature produces the $TQ$ profiles of Figure 3-6.

Feedwater heating increases the Kalina cycle's average heat absorption temperature. As Figure 3-6 shows, feedwater heating reduces the portion of heat absorbed at low temperature before the onset of boiling. This reduction also eliminates the disadvantage caused by the Kalina cycle working fluid's high liquid heat capacity. The average heat absorption temperature of the Kalina cycle is now 9 °C higher than that of the Rankine cycle (the temperatures are 290.5 °C and 281.5 °C, respectively). The Kalina cycle's increased heat absorption temperature would increase its efficiency relative to the Rankine cycle. However, it is unclear whether this efficiency gain would be enough to offset the efficiency loss due to the Kalina cycle's relatively high turbine exhaust pressure. It is also uncertain whether one could design a Kalina cycle to
operate at this feedwater temperature. More work in this research area would help clarify whether a Kalina cycle with feedwater heating could operate more efficiently than a Rankine cycle of comparable complexity.

![Figure 3-6: Raising the feedwater temperature reduces the fraction of heat absorbed before the onset of boiling and puts the Kalina's average heat absorption temperature above that of the Rankine cycle.](image)

3.4 Conclusions

To review, this comparison of single-stage cycles based on a PWR heat source yields the following conclusions regarding the Kalina cycle:

1. The optimal value of $z_{11}$ decreases approximately linearly with $T_{11}$.
2. Turbine exhaust pressure decreases with $z_3$ and $z_{11}$
3. Cycle efficiency increases with decreasing turbine exhaust pressure.
4. The Kalina cycle's sloped temperature profile in the boiling portion of the steam generator does not provide enough efficiency gain to offset efficiency losses due to the cycle's relatively high turbine exhaust pressure and liquid heat capacity.
As stated by the fourth conclusion, the single-stage Kalina cycle produces an inferior thermodynamic efficiency compared to the Rankine cycle. As such, the Kalina cycle is not recommended for power conversion from pressurized water reactors.
4 CONTINUOUS BOUNDARY COMPARISON

The analysis of Chapter 3 concludes that the Kalina cycle is a poor choice for PWR power conversion, but the analysis gives no insight into this cycle's applicability to other types of heat sources. Other authors have achieved efficiency improvements by substituting the Kalina cycle for the Rankine cycle (see Section 4.1) but there is still a need to quantify the Kalina cycle's region of applicability. The chapter seeks to quantify this region by analyzing how heat source inlet temperature and temperature drop affect the relative performances of the Kalina and Rankine cycles.

4.1 Background

4.1.1 Kalina/Rankine Cycle Comparisons in Literature

A significant body of literature examines the relative performances of Kalina and Rankine cycles using waste heat. The Kalina cycle's creator, Alexander Kalina, reports several studies on this subject. The first of these studies compares the Kalina and Rankine cycles' performances when they are driven by 399 °C diesel engine exhaust. This study concludes that, under the conditions of the study, the Kalina cycle's net power output is 26.5% higher [7]. A slightly improved Kalina cycle configuration performs well as a gas-turbine bottoming cycle. For source inlet temperatures ($T_{S,in}$) between 520 °C and 550 °C, this improved Kalina design produces about 90% more output power than Rankine cycles using single-pressure boilers and 50% more than one incorporating a triple-pressure boiler [45]. A later study finds that a
multistage Kalina cycle designed for gas-turbine bottoming achieves much smaller margins—the power improvements over a triple-pressure Rankine cycle baseline are between 16% and 22% [46]. Marston and Hyre also apply the Kalina cycle as a bottoming cycle. They simulate single-stage and multistage Kalina cycles based on 566 °C heat [47]; these cycles produce 2.1% and 11.7% more output power, respectively, than the baseline triple-pressure Rankine cycle. Park and Sonntag analyze exergy losses in the various unit operations of the Kalina and Rankine cycles [48]. They find that the Kalina cycle conserves much more exergy inside the boiler and that this gives rise to its increased efficiency.

Jonsson et al. simulate several Kalina cycle configurations of increasing complexity driven by 410 °C – 418 °C spark ignition engine exhaust and secondary heat [49]. These configurations produce 17.5% to 54.3% more output power than the baseline. It is of note that in this study, the Rankine cycle heat source leaves the boiler at least 93 °C hotter than in the Kalina cycles. This means the Kalina cycles absorb much more of the exhaust heat, which improves their performance margin. In a related study, Jonsson and Yan compare Jonnson et al.’s results to those of Kalina cycles using heat from diesel engines (321 °C – 330 °C) [50]. Despite Jonsson and Yan's expectation that the Kalina cycle's performance margin over the Rankine cycle would increase with decreasing heat source temperature, performance margins actually increase with increasing source inlet temperature. Olsson et al. examine Kalina cycles at six different heat source boundary conditions [51] (source inlet temperatures tested are 300 °C and 400 °C, and outlet temperatures are 175 °C, 130 °C, and 80 °C). Like in the two preceding studies, the Kalina cycle's performance margin increases with heat source temperature drop inside the boiler ($\Delta T_s$).
4.1.2 Kalina Cycle Optimization Studies

Two additional papers provide background for the optimization of the Kalina cycle. In the first of these papers, Marston examines the influence of turbine stream composition and separator temperature on a Kalina cycle using 550 °C waste heat and a boiler pressure of 10 MPa [8]. His results suggest that the cycle conserves maximum exergy in the boiler at turbine stream compositions of 0.55 – 0.60 (mol frac) ammonia, which compositions are lower than the more widely-used value of 0.70. In the second paper, El-Sayed and Tribus, with "an objective…to determine under what circumstances one cycle [either the Kalina or Rankine] has the advantage over the other," seek to quantify the influence of $T_{S,in}$ and $T_{S,out}$ on the Kalina cycle optimum turbine stream composition [52]. These authors show that for a constant boiler pressure of 8.3 MPa:

1. Increasing $T_{S,in}$ from 316 °C to 816 °C decreases the optimum composition from 1.0 to 0.1 (mol frac) ammonia.
2. Increasing $T_{S,out}$ from 38 °C to 177 °C at constant $T_{S,in}$ decreases the optimum composition from 0.5 to 0.25.

As will be shown, the results of this work confirms only the second of El-Sayed and Tribus' trends.

4.1.3 Objectives of this Work

To sum up, much literature compares efficiencies and/or power outputs of the Kalina and Rankine cycles. The consensus is that the Kalina cycle's performance margin increases with $T_{S,in}$ and $\Delta T_S$. Of the papers reviewed, none fully optimize the Kalina cycle and report its performance over a large range of source inlet and outlet temperatures. This work seeks to build on the existing knowledge base by doing the following:
1. Optimizing the Kalina cycle over a range of source inlet and outlet temperatures.
2. Quantifying the relationship between $T_{S,in}$, $\Delta T_S$, and Kalina cycle efficiency.
3. Quantify the conditions under which the Kalina cycle produces more power than the Rankine cycle.

Regarding the cycle comparisons required by the third objective, there are two separate cases of interest. The first case is that in which heat source outlet temperature is constrained, as it would be if the heat source was going be later used for district heating, for example. The second case is that in which source outlet temperature is unconstrained. This would be the case if there were no further use for the heat source once it left the boiler. Since it has been shown that the Kalina cycle's performance margin is highest when this cycle is allowed to capture low temperature heat, these two cases produce different results.

4.2 Method Overview

Simulating both the Rankine and Kalina cycles over a range of heat source inlet/outlet temperature combinations provides performance data for both cases. Source inlet and outlet temperature ranges are 375 K – 525 K and 350 K – 500 K, respectively. The upper limit on source inlet temperature helps to avoid computational problems. Above 525 K, mixtures with high ammonia fractions ($\approx 0.85$ mol frac) cannot exist in two phases, making it impossible for the thermodynamics simulator to identify the state of mixtures at these conditions. The lower outlet limit (350 K) is chosen to avoid a temperature cross in the distiller. The heat source stream for all simulations is pure water, which enters the boiler as a saturated liquid at the designated inlet temperature and remains a liquid throughout heat exchange. The rationale behind this choice is that the nearly linear $TQ$ profile of the liquid heat source approximates the profiles of other single-phase heating media. This means the results of this work should apply quite well to
cycles using single-phase liquid, vapor or gas heating media. Note that all of the following cycle simulations that follow—both Rankine and Kalina—use nonlinear $TQ$ profiles during heat exchange. These nonlinear profiles used in this chapter make its simulations more rigorous than those of Chapter 3, which assumes linear profiles.

The Rankine and Kalina cycle configurations used to generate performance data are the same as those described in Chapter 3. This analysis also uses many of the same assumptions as in that chapter (for example, the minimum pinch temperature in all heat exchangers is 10 °C). The parameters held constant in this analysis appear in Table 4-1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>$\chi_s$</td>
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</tr>
<tr>
<td>$\dot{m}_s$</td>
<td>100 kg/s</td>
</tr>
<tr>
<td>$T_{CW}$</td>
<td>25 °C</td>
</tr>
<tr>
<td>$\Delta T_{min}$</td>
<td>10 °C</td>
</tr>
<tr>
<td>$\chi_{condensate}$</td>
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</tr>
<tr>
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<td>0.85</td>
</tr>
<tr>
<td>$\eta_T$</td>
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</tbody>
</table>

Both the Kalina and Rankine cycles must be optimized at each heat source inlet/outlet temperature combination. Optimization allows each cycle to operate at maximum possible efficiency for each set of conditions, which ensures apples-to-apples comparisons of the results later on.

### 4.3 Rankine Cycle Optimization

Optimizing the Rankine cycle to produce maximum output power is straightforward. The boiler pressure, $P_1$, is the only optimizable parameter, though it is limited by certain constraints. For each heat source temperature combination, $P_1$ should be as high as possible to maximize the
pressure drop in the turbine and, by extension, the cycle work output. $P_1$ must also be low enough to maintain at least a 10 K approach temperature difference during boiling. Both of these objectives are met by optimizing $P_1$ so that $\Delta T_{\text{min}}$ is exactly 10 K. This optimization is accomplished by using a bracketed Newton-Raphson root-finding solver, which iteratively varies pressure until $\Delta T_{\text{min}} = 10$ K. For this cycle, the turbine outlet pressure is always 0.0086 MPa. Adding the turbine output and pump input power values gives the cycle's net power output. The Rankine cycle layout is the same as in Figure 3-1.

### 4.4 Kalina Cycle Optimization

Full optimization of the Kalina cycle (refer to Figure 1-1) is more complicated than that of the Rankine cycle since turbine stream composition ($z_3$), boiler pressure ($P_3$), and separator temperature ($T_{11}$) are all optimizable parameters. This analysis assumes that for a given $z_3$, the Kalina cycle output power ($W_{\text{net}}$) is maximized by operating at the:

1. Maximum allowable $P_3$.
2. Minimum allowable $T_{11}$.

In these assumptions, the maximum and minimum "allowable" values are those that do not cause minimum temperature differences of less than 10 °C in the heat exchangers.

Another way to state the above assumptions is to say that increasing $P_3$ always increases output power, regardless of the value of $T_{11}$, and vice versa. Operating at the maximum allowable $P_3$ is thermodynamically intuitive. Raising boiler pressure enables a larger pressure drop through the turbine, which corresponds to a larger change in enthalpy and thus more output power. Figure 3-2 from Section 3.3 shows that cycle efficiency (and by extension power output) always increases with decreasing $T_{11}$. This trend is expected, since decreasing separator
temperature lowers the ammonia fraction of Streams 6-11, which translates to lower turbine outlet pressure and higher power output.

These assumptions allow a stepwise, rather than simultaneous, optimization of $P_3$ and $z_{11}$. The optimization steps are given below, and Figure 4-1 shows example results for steps 2 and 3. The convergence criteria for optimized $P_3$ and $T_{11}$ values is that $\Delta T = 10 \pm 0.1 \, ^\circ\text{C}$ at the pinch point.

![Figure 4-1: Optimized boiler (left) and distiller (right) TQ profiles have a minimum approach temperature of 10 K.](image)

**Optimization Steps**

1. Choose a value of $z_3$.

2. Find the value of $P_3$ so that $\Delta T_{\text{min}} = 10 \, \text{K}$ in the boiler. This is the maximum allowable boiler pressure. Use this value to simulate Streams 1-3, Pump 1, and the PHX.

3. Find the value of $T_{11}$ so that $\Delta T_{\text{min}} = 10 \, \text{K}$ in the distiller. This is the minimum allowable separator temperature. Use this value to simulate the rest of the cycle, then record the values of all optimizable parameters and $\dot{W}_{\text{net}}$. Note: Sometimes optimization produces an obvious pinch point like the one in Figure 4-1. At other times the pinch is noticeable...
by a marked change in slope of the cold stream as it begins to vaporize; in this case, the
point at which its slope's rate of change has become minimal is used as the pinch point.

4. Repeat steps 1-3, choosing a new value of $z_3$ each time. Continue iterating until the
optimization converges on a single value for $z_3$.

4.4.1 Predicting Optimum Turbine Stream Compositions

Turbine stream composition, $z_3$, is basically optimized by hand. At the beginning of each
optimization choosing values of $z_3$ is done by trial and error, but once a wide enough spectrum
of $(z_3, \dot{W}_{\text{net}})$ pairs are available it is possible to see a trend. Fitting a quadratic polynomial to
these data and differentiating to find the minimum predicts the $z_3$ value that approximately
maximizes cycle work output. This $z_3$ value is the logical choice for the next trial. With each
successive trial, the $z_3$ prediction improves until finally, the predicted value is the same as one
already tested to within ±0.005 (mol frac). At that point, the optimization has converged. See
Figure 4-2 for a visual of this process.

![Figure 4-2: Fitting a quadratic to initial data (left) helps predict the optimal $z_3$ (right).](image)

Because the quadratic fit is an imperfect approximation of the $(z_3, \dot{W}_{\text{net}})$ data, this
optimization method sometimes converges to a value of $z_3$ that produces slightly less $\dot{W}_{\text{net}}$ than
one of the other $z_3$ values tested. In these cases, the $z_3$ value that produces maximum $\dot{W}_{\text{net}}$ is recorded as the optimum whether or not it was the convergence value. For example, the left-hand plot of Figure 4-2 shows $(z_3, W_{\text{net}})$ data gathered by simulating the same cycle at three different values of $z_3$. Fitting a quadratic to these data predicts that this cycle will produce maximum (i.e., most negative) power output at $z_3 = 0.49$, the point indicated by a red cross. Simulating this cycle again at $z_3 = 0.49$ produces a fourth data point, as shown in the right-hand plot. The quadratic fit is modified to include this fourth data point. The fit now predicts a minimum at the same composition as before. Thus the optimization for this cycle has converged, with the optimization predicting maximum work output at $z_3 = 0.49$. However, it is apparent from the plot that the simulation using a composition of $z_3 = 0.50$ actually produces more output power than the simulation at $z_3 = 0.49$. In light of this, $z_3 = 0.5$ is recorded as the composition that produces maximum work output, even though it was not the convergence value predicted by the optimization.

4.4.2 Bracketing

Because the cycle simulator computations fail with unreasonable inputs, it is sometimes helpful to use a bracketing root-finding technique to find $P_3$ and $T_{11}$ in steps 2 and 3 of the optimization process described above. Bracketing prevents the root-finder from choosing out-of-bounds values as it iterates to a solution. The root-finder used to optimize $P_3$ and $T_{11}$ is Scipy's implementation of Brent's method, which is dependable and fast [53]. Fast convergence is especially important while optimizing $T_{11}$ because each of the Brent's method iteration contains a nested set of iterations required to find $z_{11}$ (see Section 3.2.2).

Identifying brackets is where the stepwise nature of the optimization is important. The stepwise approach allows one to first bracket and converge $P_3$ then use its optimized value to
bracket $T_{11}$. In general, brackets for $P_3$ and $T_{11}$ are identified through trial and error. However, the optimal values of $P_3$ and $T_{11}$ tend to vary predictably with $z_3$. This lets one fit a curve to previously optimized values of $P_3$ and $T_{11}$ to help choose appropriate brackets at new $z_3$ values (see Figure 4-3).

![Figure 4-3: The optimum values of $P_3$ (left) and $T_{11}$ (right) vary predictably with $z_3$, which helps locate their approximate values at untested points.](image)

4.4.3 Measuring Efficiency: Energy versus Exergy

While net power output is completely acceptable for comparing cycle performances, the power values themselves are in this case arbitrary because of the assumed heat source flow rate of 100 kg/s. Normalizing each cycle's output power against a common value produces an efficiency it can be easily compared to others. This work uses both energy and exergy efficiencies to make comparisons.

Thermodynamic efficiency, also called energy efficiency, is helpful when comparing cycles with the same heat source inlet and outlet temperatures—that is, comparisons in which the outlet temperature is constrained. If outlet temperature were not constrained, the amount of heat absorbed in the boiler ($\dot{Q}$) would be different for the cycles being compared, invalidating the
comparison. Equation (4-1) gives the equation for thermodynamic efficiency, $\eta_I$, which is a cycle's net power normalized against its heat input.

$$\eta_I = -\frac{\dot{W}_{\text{net}}}{Q}$$  (4-1)

When determining which cycle is superior based solely on source inlet temperature, exergy efficiency should be used instead. Exergy efficiency normalizes $\dot{W}_{\text{net}}$ against the maximum power the heat source could generate by flowing from its inlet temperature to the surroundings temperature (see Equation (4-2)). This value, $\dot{W}_{\text{ideal}}$, is calculated by Equation (4-3). This work assumes a surroundings temperature ($T_\sigma$) of 298.15 K.

$$\eta_{II} = \frac{\dot{W}_{\text{net}}}{\dot{W}_{\text{ideal}}}$$  (4-2)

$$\dot{W}_{\text{ideal}} = \dot{m}(\Delta h - T_\sigma \Delta s)$$  (4-3)

### 4.5 Results/Discussion

#### 4.5.1 Optimal Turbine Stream Compositions

The optimization of $z_3$ provides insight into the Kalina cycle's region of applicability. For some cases when the source temperature drop is small, the quadratic fit used to predict the value of $z_3$ corresponding to maximum net power identifies a $z_3$ value near or below zero—the composition of pure water. It is difficult or impossible to converge cycles in which $z_3 \leq 0.05$, so there is no data for these cases. Figure 4-4 shows the quadratic fit for one such case. The quadratic in this figure predicts maximum output power at $z_3 \approx -0.25$, a nonphysical result. The best "realistic" composition would be that of pure water, $z_3 = 0.0$. The Kalina cycle cannot operate with pure water due to its separation process. Even if this were possible, the resulting power output would be inferior to that of the Rankine cycle. Using pure water would eliminate the Kalina cycle's ability to match the heat source temperature profile. Also, the Kalina cycle's
additional pump would make the Kalina cycle power output lower than that of a Rankine cycle at the same conditions. These facts suggest that for cases in which optimization predicts $z_3 \leq 0.0$, the single-stage Rankine cycle produces more net power, despite the lack of optimized Kalina cycle data. This result is supported by the comparison of first law efficiencies presented below.

![Graph](image)

**Figure 4-4:** The predicted optimum $z_3$ is negative for this case, in which $\Delta T_S = 50$ K.

For each heat source temperature combination, the optimal value of $z_3$ depends strongly on $\Delta T_S$ and weakly on $T_{S,in}$. Figure 4-5 shows the optimal $z_3$ values on a grid of source inlet and outlet temperatures. The grayed portion of this figure represents nonphysical temperature combinations (e.g. the source fluid cannot enter the boiler at 450 K and leave it at 500 K). The plot exhibits the following relationships between $T_{S,in}/T_{S,out}$ and $z_3$:

1. White squares represent points at which no data is available for the Kalina cycle. As stated above, this occurs when optimization suggests operating with pure or nearly pure water.

2. At constant $\Delta T_S$ (up and to the right on a diagonal) $z_3$ slightly decreases.

3. For a given $T_{S,in}$, $z_3$ increases with $\Delta T_S$ (from top to bottom on the plot).
4. For a given $T_{S,\text{out}}$, $z_3$ generally increases with $\Delta T$ (from left to right). However, the bottom two lines of data ($T_{S,\text{in}} = 350$ K and $T_{S,\text{in}} = 375$ K) exhibit maximum $z_3$ values at intermediate $\Delta T$ values. More data are needed to determine whether this is a general trend.

![Figure 4-5: The optimal Kalina cycle working fluid composition ($z_3$) depends on heat source inlet/outlet temperatures.](image)

4.5.2 Energy Efficiency Comparisons

When $T_{S,\text{out}}$ is constrained, the Kalina cycle output power and efficiency generally increase with $\Delta T_S$. This trend is apparent in Figure 4-6, in which each colored square indicates the margin by which the Kalina cycle's thermodynamic efficiency surpasses that of the Rankine cycle for the given heat source inlet/outlet temperature combination. On this plot, lighter colors correspond to larger margins. Dark purple squares denote cases in which the Kalina cycle's
efficiency is only slightly higher; for example, the square at $T_{S,in}/T_{S,out} = 525 \text{ K}/450 \text{ K}$ corresponds to a margin of only $\Delta \eta_I = 1.45 \cdot 10^{-4}$.

![Figure 4-6: First law efficiency margins; the region below the red dotted line approximately marks the conditions at which the Kalina cycle operates with higher efficiency than the Rankine cycle.](image)

Figure 4-6 generally shows the Kalina cycle's advantage decreasing with $\Delta T_S$, both from bottom to top and right to left. For example, at $T_{S,in} = 525 \text{ K}$, the margin decreases from $\Delta \eta_I = 0.065$ at $\Delta T_S = 175 \text{ K}$ to $\Delta \eta_I = 1.45 \cdot 10^{-4}$ at $\Delta T_S = 75 \text{ K}$. Extrapolating the data only slightly further suggests that the Kalina cycle loses any advantage at some $\Delta T_S$ between 75 K and 50 K. Not coincidentally, this is also the point below which the optimization of $z_3$ suggests using pure water. One can conclude that both Figure 4-5 and Figure 4-6 show the same thing: the Kalina cycle loses its advantage at low $\Delta T_S$ (where the squares become white).

The $\Delta T_S$ required for superior Kalina thermodynamic efficiency appears to grow with increasing $T_{S,in}$. For example, for $T_{S,in} = 525 \text{ K}$, a $\Delta T_S$ of 75 K is necessary, but at $T_{S,in} = 425 \text{ K}$
a $\Delta T_s$ of only 50 K is required. The red dotted line on the plot marks the Kalina cycle's approximate region of effectiveness. Below the line, the Kalina cycle produces higher power output than the Rankine cycle. The dotted line is only an approximation since no data is available for cases in which optimization predicts $z_3 \leq 0.05$.

4.5.3 Exergy Efficiency Comparisons

When $T_{S,\text{out}}$ is unconstrained—that is, when there is no lower limit to how cool the source can be when it leaves the boiler—the data show that the Kalina cycle produces higher $W_{\text{net}}/\eta_{\text{II}}$ for all $T_{S,\text{in}}$ considered in this study except 375 K. Exergetic efficiencies for the Kalina and Rankine cycles are given in Figure 4-7.

![Figure 4-7: Cycle exergetic efficiencies for the Rankine (left) and Kalina (right) cycles; comparing the maximum efficiency of each cycle in a given column indicates which cycle to use if source outlet temperature is unconstrained.](image)

Testing a range of $T_{S,\text{out}}$ values for a single $T_{S,\text{in}}$ identifies the condition at which the each cycle produces the maximum exergetic efficiency. This is essentially the same process as searching each vertical line in Figure 4-7 for the point of maximum efficiency. Figure 4-8 illustrates this process, plotting $\eta_{\text{II}}$ versus $T_{S,\text{out}}$ for a source inlet temperature of 525 K.
In Figure 4-8, both the Rankine and Kalina efficiency curves exhibit maxima. As mentioned previously, the Rankine cycle boiler pressure must be optimized for a given source inlet temperature, balancing 1) average heat absorption temperature against 2) the amount of heat absorbed. At $T_{S,\text{in}} = 525$ K, the Rankine cycle maximum efficiency occurs at $T_{S,\text{out}} = 400$ K. At source outlet temperatures below this, the Rankine cycle absorbs more heat but must do so at low temperature. At higher outlet temperatures, this cycle absorbs little heat but does so at high temperature (i.e. the cycle's thermodynamic efficiency is high, but its net power output and exergy efficiency is low).

The exergetic efficiency data suggest that the Kalina cycle may experience a similar tradeoff—that its efficiency reaches a maximum at some intermediate $T_{S,\text{out}}$, rather than the lowest possible one. In Figure 4-8, the Kalina cycle's optimum $T_{S,\text{out}}$ is roughly 375 K, about 25 K lower than that of the Rankine cycle. This same trend is apparent at all other source inlet temperatures with more than one data point: the Kalina's maximum efficiency always occurs at a lower $T_{S,\text{out}}$ than that of the Rankine cycle. The Kalina cycle maximum efficiency is also
significantly higher than that of the Rankine. These facts support the assertion in the literature that the Kalina cycle achieves better efficiencies by absorbing heat over large temperature ranges at relatively high pressures.

The Kalina cycle produces higher exergetic efficiencies than the Rankine cycle for all inlet temperatures except $T_{S,in} = 375$ K. Figure 4-9 shows this by plotting the maximum exergetic efficiency produced by each cycle for each $T_{S,in}$ temperature. In the case in which $T_{S,in} = 375$ K, the restriction placed on $T_{S,out}$ requires a source temperature drop too small ($\Delta T_S = 25$ K) to give the Kalina cycle any advantage, so the Rankine cycle is favored. In every other case, the Kalina cycle produces exergetic efficiencies 0.04 − 0.10 higher than the Rankine cycle, corresponding to net power increases of 13.9% − 25.4%. The maximum power increase occurs at $T_{S,in} = 500$ K. Data at higher temperatures are needed to ascertain if the Kalina cycle continues to achieve power improvements at even higher source inlet temperatures.

![Figure 4-9: For heat source inlet temperatures at or above 400 K, the Kalina cycle produces exergetic efficiencies that are 13.9% - 25.4% higher than those of the Rankine cycle.](image)
4.6 Conclusions

The inlet and outlet temperatures of the heat source strongly influence the performance of the Kalina cycle relative to that of the Rankine cycle. Comparing these cycles' efficiencies for different inlet/outlet source temperature combinations gives insight as to where the Kalina cycle is best applied. Thermodynamic efficiency is an appropriate performance metric only for comparisons in which both cycles operate with the same source inlet and outlet temperatures—i.e., when $T_{S, out}$ is constrained. The metrics of exergy efficiency or net power output should be used when comparing cycles with a common $T_{S, in}$ but different $T_{S, out}$ values because the cycles absorb different amounts of heat. When $T_{S, out}$ is constrained, the Kalina cycle outperforms the Rankine cycle only if the source temperature drop inside the boiler, $\Delta T_S$, is large enough. The required $\Delta T_S$ grows with source inlet temperature: at $T_{S, in} = 400$ K, the required $\Delta T_S$ is between 25 K and 50 K; at $T_{S, in} = 525$ K, the required $\Delta T_S$ has grown to about 75 K. When there is no constraint on $T_{S, out}$, the Kalina cycle produces more power than the Rankine cycle for all $T_{S, in}$ considered in this work except 375 K. Power increases range between 13.9% and 25.4%.
5 CONCLUSION

Prerequisite to ammonia/water power cycle analysis is the identification of a program capable of simulating the thermodynamics of this mixture. Instead of adapting a currently available program, this work first develops and validates a new ammonia/water thermodynamics simulation tool called Clearwater. This tool is written in Python and is packaged with the prebuilt unit operations needed for power and refrigeration cycle simulation. The tool will be provided free online as open-source code via Github so other researchers interested in ammonia/water cycles can easily download and use it. Accompanying descriptions of Clearwater's VLE calculation and phase identification algorithms are presented here to aid users as they adapt it for their own needs.

The motivating purpose of this work was to determine if the Kalina cycle can convert power from pressurized-water reactors (PWR) more efficiently than the Rankine cycle. Comparing single-stage versions of these cycles reveals that the Kalina cycle a poor choice for PWR power conversion. Analysis shows that a working fluid ammonia fraction of 0.125 (mol frac) produces nearly parallel $TQ$ profiles in the Kalina cycle steam generator, but the efficiency of the Kalina cycle in this scenario is still 0.4 percentage points below that of the Rankine cycle. Furthermore, a parametric analysis of the Kalina cycle shows that its thermodynamic efficiency always increases with decreasing ammonia fraction. It is concluded that the Kalina cycle achieves more parallel temperature profiles in the boiling portion of the
steam generator but that this cycle also has negative aspects, namely its 1) higher turbine exhaust pressure and 2) slower liquid temperature rise before the onset of boiling. For PWR power conversion, the efficiency gain from the Kalina cycle's sloped boiling curve are not sufficient to overcome the efficiency losses due to the negative effects outlined above, so the Rankine cycle is a better choice.

Having concluded this, a comprehensive summary was developed to describe when the Kalina cycle is a better alternative than the Rankine cycle. The performances of the two cycles were compared over a large range of heat source inlet/outlet temperatures to identify the conditions under which the Kalina cycle produces higher efficiency. The heat source inlet and outlet temperatures ranges for the comparison are $375 \text{ K} < T_{S,\text{in}} < 525 \text{ K}$ and $350 \text{ K} < T_{S,\text{out}} < 500 \text{ K}$, respectively. The results depend on whether or not the two cycles are forced to use the same $T_{S,\text{out}}$ (i.e., if they absorb the same amount of heat in the boiler). If this condition is applied, the efficiency of the Kalina cycle is higher when the heat source temperature drop, $\Delta T_S$, is above a certain threshold. This threshold increases with $T_{S,\text{in}}$. For example, at a $T_{S,\text{in}}$ of 400 K, the minimum required $\Delta T_S$ is between 25 K and 50 K; however, for $T_{S,\text{in}} = 525 \text{ K}$ the $\Delta T_S$ threshold is $\sim 75$ K. If the Kalina cycle is allowed to absorb more heat in the boiler, it can produce higher work output/exergetic efficiency for every $T_{S,\text{in}}$ tested except for 375 K, with efficiency increases ranging from 13.9% and 25.4%. This quantification of the Kalina cycle's region of applicability is an important contribution to the existing body of Kalina cycle research.

5.1 Recommendations for Future Work

This work concludes that the single-stage Kalina cycle is a poor choice for PWR power conversion, but the effects of multiple expansion stages and reheating on this cycle's efficiency are not investigated, and the effect of feedwater heating is not fully explored. Adding these
operations will likely increase the Kalina cycle's efficiency. However, added complexity also increases the Rankine cycle's efficiency, so additional research is needed to determine whether a more complex Kalina cycle would have any advantage over a Rankine cycle of similar complexity.

As stated previously, the continuous boundary comparison could be extended by simulating the Kalina and Rankine cycles over larger source temperature ranges. Extending the comparison would clarify whether every source inlet temperature has a corresponding outlet temperature for which the Kalina cycle produces maximum exergetic efficiency. It would also help to better characterize relationships between the source temperatures and the Kalina cycle optimum working fluid composition and cycle efficiencies. One challenge to high temperature simulations is the Gibbs equation of state's inability to accurately predict mixture critical points. This inability makes it difficult to identify the composition above which a given mixture becomes a supercritical fluid inside the boiler. To fix this problem, the equation of state should be modified and re-correlated to predict critical points or else a different equation of state should be used instead.
REFERENCES


APPENDIX A.

A.1 Gibbs Free Energy Correlation

Table A-1: Pure-component Gibbs Equation Coefficients

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Table A-2: Gibbs Excess Energy Coefficients

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</tr>
<tr>
<td>$E_{16}$</td>
<td>$-2.07 \cdot 10^1$</td>
</tr>
</tbody>
</table>
A.2  *Clearwater* State Functions

**Figure A-1:** The State\((T, P, z_1)\) phase identification algorithm compares system and equilibrium compositions.

In: \(T, P, z_1\)

Try calculation: \(T, P \rightarrow x_{1,eq}, y_{1,eq}\)

- **P > \(P_{1}^{sat}(T)\)?**
  - Yes: \(x_1 = z_1\)
  - No: \(\chi = 0\)

- Solution for \(x_{1,eq}, y_{1,eq}\)?
  - Yes: \(z_1 \leq x_{1,eq}\)?
    - Yes: \(x_1 = x_{1,eq}\), \(y_1 = y_{1,eq}\), \(\chi = \frac{z_1 - x_{1,eq}}{y_{1,eq} - x_{1,eq}}\)
    - No: \(z_1 \geq y_{1,eq}\)?
      - Yes: \(y_1 = z_1\), \(\chi = 1\)
      - No: Error

- **P < \(P_{2}^{sat}(T)\)?**
  - Yes: \(x_1 = x_{1,eq}\), \(y_1 = y_{1,eq}\)
  - No: \(P > P_{c,mix}(T)\)
Figure A-2: The State($P, h, z_1$) algorithm compares enthalpies to identify phase.
A.3 Clearwater Package Structure

![Diagram of Clearwater package structure]

Figure A-3: The Clearwater package is organized into three modules.

A.4 Clearwater Unit Operation Validation

<table>
<thead>
<tr>
<th>Stream</th>
<th>$P$ (MPa)</th>
<th>$T$ (K)</th>
<th>$z$ (mol)</th>
<th>$h$ (J/mol)</th>
<th>$s$ (J/mol/K)</th>
<th>$\dot{n}/\dot{n}_{13}$</th>
</tr>
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<tbody>
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<td>0.4676</td>
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Table A-3 Continued

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<th>$h$ (J/mol)</th>
<th>$s$ (J/mol/K)</th>
<th>$\dot{n}/\dot{n}_{13}$</th>
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<td>2.6678 · $10^0$</td>
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<td>5.4084 · $10^3$</td>
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A.5 Multistage Rankine Cycles

Two- and three-stage Rankine cycle configurations provide efficiency values for future Kalina/Rankine comparisons at PWR conditions. Both configurations use intermediate moisture separation, reheating, and feedwater heating to increase the efficiency of the base case. These configurations are essentially the same as those presented by Memmott et al. in [5]. Diagrams of the cycles appear in Figure A-4 and Figure A-5, respectively.

For both multistage configurations, reheating occurs outside of the steam generator to allow the cycle to generate maximum output power. This reheating setup also has other benefits. For one, it requires only one heat exchanger to contact the reactor coolant, which minimizes the possibility of radioactive leakage from the primary to the secondary loop. It is also easy to control the feedwater temperature and flow rate to the secondary loop to ensure that the core coolant reenters the core at its design temperature. This would be more difficult if, for example, the core coolant directly reheated a turbine outlet stream inside an additional exchanger; if the reheated stream inlet temperature were not properly controlled, it could shift away from its
design specification, thereby changing the reactor inlet coolant temperature and causing unexpected core transients.

Figure A-4: The two-stage Rankine cycle increases the efficiency of the single-stage case.

The simulation converges the two-and three-stage cycles by bisecting a mass flow rate such that the same cold leg temperature is computed at the steam generator inlet both forwards (through the cycle) and backwards (through the steam generator). Although the Babcock and Wilcox data provides some parameters for these cycles, others—like the intermediate pressures—remain unknown, so Wilding's program also uses a multi objective genetic algorithm to find their optimal values. This algorithm seeks to transform an initially random population of cycles into one in which each cycle has high efficiency and low cost. The algorithm follows the following series of steps to produce a Pareto front that balances efficiency against cost.

1. It creates a population of cycles called "options," each with its own randomly-selected set of values for the optimizable parameters called "attributes."
2. The options compete for the chance to pass on the values of their optimizable parameters; competitions are won or lost based on each option's efficiency and cost.

3. It creates offspring from the winners first by pairing them up, then randomly swapping some of their attribute values. These values can then "mutate" up or down slightly.

4. It eliminates the more unfit half of the population based on efficiency and cost, then repeats the process from step 1.

*Aspen Plus* simulations of the same cycles provide verification to the in-house analysis. They use *Aspen's* built-in optimizer to find the highest-efficiency option and do not provide any cost information. Results of these optimizations appear in Table A-4. In this table, only the highest efficiency option of each genetic optimization is compared with the corresponding *Aspen* value, instead of the entire Pareto front. The table does not show the converged values for the optimizable parameters, but it should be noted that these differ significantly between the two types of optimization. The discrepancies may be anomalous. However, in the case that they are not, careful standardization of the simulation specifications may fix the problem.

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<th>Table A-4: Multistage Rankine Optimization Results</th>
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<td>Optimization Type</td>
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<td>Genetic</td>
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<tr>
<td>Aspen Plus</td>
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Figure A-5: The three-stage Rankine cycle yields the best efficiency of the three considered in this work.
A.6 Comparison of Cycles Using Pressurized-Water Reactor Heat

Table A-5: Rankine Cycle Stream Information

<table>
<thead>
<tr>
<th>Stream</th>
<th>$P$ (MPa)</th>
<th>$T$ (°C)</th>
<th>$\chi$</th>
<th>$h$ (J/mol)</th>
<th>$s$ (J/mol/K)</th>
<th>$\dot{n}$ (mol/s)</th>
</tr>
</thead>
<tbody>
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<td>0.00</td>
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<tr>
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<td>7.6790</td>
<td>43.5</td>
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<td>3399.5</td>
<td>11.1</td>
<td>$2.688 \cdot 10^4$</td>
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<tr>
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<td>35139.4</td>
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Table A-6: Kalina Cycle Stream Information

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<th>$T$ (°C)</th>
<th>$z_1$</th>
<th>$\chi$</th>
<th>$h$ (J/mol)</th>
<th>$s$ (J/mol/K)</th>
<th>$\dot{n}$ (mol/s)</th>
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<td>0.125</td>
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### A.7 Continuous Boundary Comparison

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<th>$T_{S, \text{out}}$ (K)</th>
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<th>$\eta_{\text{II}}$</th>
<th>$z_3$ (mol)</th>
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**Table A-7: Optimization Parameters and Cycle Efficiencies**
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<th>$\eta_\text{II}$</th>
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